04 University of Plymouth Research Theses

01 Research Theses Main Collection

1989

## PLASMA SPECTROCHEMICAL ANALYSIS OF SLURRIES

## FOULKES, MICHAEL EDWARD

http://hdl.handle.net/10026.1/1928

http://dx.doi.org/10.24382/4978 University of Plymouth

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

# PLASMA SPECTROCHEMICAL ANALYSIS OF SLURRIES

M. E. FOULKES

Ph.D. 1989

#### A thesis entitled

#### PLASMA SPECTROCHEMICAL ANALYSIS

#### **OF SLURRIES**

presented by

## MICHAEL EDWARD FOULKES, GRIC, CChem, MRSC

In part fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY of the COUNCIL FOR NATIONAL ACADEMIC AWARDS

Department of Environmental Sciences Polytechnic South West Drake Circus Plymouth PL4 8AA

Collaborating Establishment: British Petroleum Research Centre Chertsey Road Sunbury-on-Thames Middlesex TW16 7LN



#### ABSTRACT

#### MICHAEL EDWARD FOULKES

#### PLASMA SPECTROCHEMICAL ANALYSIS OF SLURRIES

The analysis of ores, minerals and refractory materials by slurry atomisation has been investigated using inductively coupled plasma and direct current plasma-atomic emission spectrometry (ICP-AES, DCP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Aqueous calibrants were used. Fundamental aspects were modelled.

The particle size and dispersion of samples are the most important criteria in slurry nebulisation. The particle size should be below 5  $\mu$ m, preferably below 3  $\mu$ m for refractories. Comminution techniques were used to reduce samples to this size range; the comminution time depended upon sample hardness. Suitable disperants were identified.

Laser diffraction measurements showed the modification of aerosol distributions, for solutions and slurries, by the spray chamber and injector. Few aerosol particles over 18  $\mu$ m, and solid particles over 6 to 8  $\mu$ m, size reached the ICP. Fine slurries (<6  $\mu$ m solid size) produced aerosols which modelled those from solutions in size and mass transport efficiency. Representative solid transport of starting slurries was particle size dependent.

Analysis of finely powdered (<6  $\mu$ m) ores, minerals and refractories by the slurry technique showed good agreement with certificate and known values. Ultrafine slurries (<2.5  $\mu$ m) yielded full recoveries. Reduced recoveries were found to be due to segregation of large particles and possibly atomisation effects. There were suggestions of reduced atomisation efficiency (60-70%) for refractory particles (>5  $\mu$ m). Enhancements from easily ionisable elements were also observed.

Rotational temperature measurements showed equivalent values for solutions and slurries (up to 1% m/v loading) in the ICP. The temperature range covered (2000-3600 K) was dependent upon the plasma conditions and torch used; tangential flow (TFT) or laminar flow (LFT). A Greenfield size LFT offered the advantage of reduced gas consumption compared with the TFT.

Semi-quantitative slurry atomisation ICP-MS produced rapid elemental values, generally within a factor of 3, of certified values. Grinding contamination was also measured on a semi- quantitative basis.

#### ACKNOWLEDGEMENTS

I wish to express my sincerest gratitude to my supervisor, Professor L Ebdon, for his invaluable guidance, support, encouragement and patience throughout this work and for his willingness to take a chance on a late academic runner. I also wish to express my thanks to Dr S Hill for his help and advice in his role as second supervisor.

I owe a debt of gratitude to my industrial supervisor, Dr J Crighton of British Petroleum, for his advice, support and enthusiasm in this study and also to Mr J Muriss and Dr J Hendry of the Analytical Support Group, BP Sunbury.

I would like to thank the Science and Engineering Research Council and British Petroleum under the CASE award scheme which has made this work possible. I would also like to thank Dr C Tye and Dr J Dean for their help and VG Elemental for the use of their equipment.

I extend my thanks to all those at the BP Research Laboratories, Sunbury-on-Thames who have also made their time and resources available for this work. In particular Mr G Bullen, Mr I Shrubb, Dr D Campbell, and those of the University Liaison Group.

I would like to thank my colleagues at Plymouth for the many stimulating and helpful discussions throughout the duration of this work. I am grateful to Mr D Regan and all those from New Horizon and to Heather Lock who have helped in the presentation of this thesis.

Finally I should like to thank my parents, for all their help on this long road and my wife, Rosemary, for her support and encouragement, patience, and for tea and sympathy during the writing of this thesis. "This is the Universe. Big isn't it?" (Michael Powell and Emeric Pressburger 1946)

#### CONTENTS

| ABSTRACT                        |  |     |
|---------------------------------|--|-----|
| ACKNOWLEDGEMENT                 | 5  |     |
| CHAPTERS 1-9 CO                 | NTENTS   | i   |
| LIST OF FIGURES                 |  | vi  |
| LIST OF TABLES                  |  | xvi |
| CHAPTER 1                       | INTRODUCTION   | 1   |
| CHAPTER 2                       | THE PREPARATION OF SLURRIES FOR ANALYSIS   | 19  |
| CHAPTER 3                       | TRANSPORTATION PHENOMENA   | 50  |
| CHAPTER 4                       | ELEMENTAL ANALYSIS OF SOLIDS BY SLURRY<br>ATOMISATION PLASMA EMISSION SPECTROMETRY             | 157 |
| CHAPTER 5                       | ROTATIONAL TEMPERATURE MEASUREMENTS IN<br>THE INDUCTIVELY COUPLED PLASMA                       | 253 |
| CHAPTER 6                       | THE LAMINAR FLOW TORCH   | 281 |
| CHAPTER 7                       | SLURRY ATOMISATION PLASMA SOURCE MASS<br>SPECTROMETRY  | 309 |
| CHAPTER 8                       | CONCLUSION AND SUGGESTIONS FOR FUTURE WORK.  | 329 |
| REFERENCES                      |  | 341 |
| APPENDIX I                      | COMPUTER PROGRAM TO CALCULATE PERCENTAGE<br>VOLUME SIZE DISTRIBUTIONS FROM POPULATION<br>DATA. | la  |
| MEETINGS OF THE                 | ROYAL SOCIETY OF CHEMISTRY   | lb  |
| LECTURES AND ASSOCIATED STUDIES |  |     |
| PRESENTATIONS A                 | ND PUBLICATIONS  | ld  |

.

.

.

Page No.

.

•

|             | - · · · ·  | Page<br>No.          |
|-------------|--|----------------------|
| <u>CHAP</u> | TER 1 INTRODUCTION   | 1                    |
| 1.1         | INTRODUCTION   | 1                    |
|             | 1.1.1 The Analysis of Refractory Materials and   | 1                    |
|             | 1.1.2 Sample Preparation   | 1                    |
| 1.2         | SOLID SAMPLE ANALYSIS  | 2                    |
|             | 1.2.1 Instrumental Techniques available for the<br>Analysis of Solid Samples.  | 2                    |
| 1.3         | SLURRY ATOMISATION   | 7                    |
|             | 1.3.1 The Inductively Coupled Plasma and Slurry<br>Atomisation.  | 11                   |
| 1.4         | THE OBJECTIVES OF THIS WORK.   | 16                   |
|             |  |                      |
| <u>CHAP</u> | TER 2 THE PREPARATION OF SLURRIES FOR ANALYSIS   | 19                   |
| 2.1         | INTRODUCTION   | 19                   |
|             | 2.1.1 The Dispersion of Powders 2.1.2 The Measurement of Dispersion  | 20<br>21             |
| 2.2         | THE DIRECT PREPARATION OF SLURRIES WITHOUT SAMPLE<br>PRE-TREATMENT   | 22                   |
| 2.3         | THE PRE-TREATMENT OF SAMPLES FOR ANALYSIS  | 24                   |
|             | 2.3.1 Experimental and Results   | 26                   |
|             | <ul> <li>2.3.1.1 First stage grinding process</li> <li>2.3.1.2 Second stage grinding process</li> <li>2.3.1.3 The bottle and bead method</li> <li>2.3.1.4 The microniser method</li> </ul> | 29<br>29<br>33<br>42 |
| 2.4         | DISCUSSION AND CONCLUSION S.   | 42                   |
| CHAP        | TER 3 TRANSPORTATION PHENOMENA   | 50                   |
| 3.1         | INTRODUCTION   | 50                   |
| 3.2         | THE SAMPLE INTRODUCTION SYSTEM   | 51                   |
|             | 3.2.1 The Physical Processes within the Sample   | 53                   |
| ·           | Introduction System<br>3.2.2 Primary Aerosol Formation<br>3.2.3 Aerosol Modification and Loss Processes in<br>the Spray Chamber  | 55<br>55             |

•

.

.

|      |                    |   | Page<br>No. |
|------|--------------------|---|-------------|
| 3.3  | THE ME/            | ASUREMENT OF SOLUTION AND SLURRY AEROSOLS   | 58          |
|      | 3.3.1<br>3.3.2     | <br>Non-Intrusive Laser Measuring Methods<br>Intrusive Measuring Methods                      | 59<br>60    |
| 3.4  | THE ME/<br>INTRUS  | ASUREMENT OF AEROSOL DROPLET SIZE USING NON-<br>IVE LASER TECHNIQUES                          | 63          |
|      | 3.4.1              | Aerosol Distributions Measured by a Malvern 2600/3600 VA2                                     | 64          |
|      |                    | 3.4.1.1 Experimental  | 64          |
|      | 343                | 3.4.1.2 Results and Discussion  | 64<br>70    |
|      | 5.4.2              | Aerometrics phase/Doppler Sprav Analyser  | /0          |
|      |                    | 3.4.2.1 Experimental and Results  | 70          |
|      |                    | 3.4.2.2 Discussion  | 110         |
|      |                    | 3.4.2.3 Conclusions   | 130         |
| 3.5  | THE ME<br>AEROSOI  | ASUREMENT OF SLURRY SOLID PARTICLE SIZE IN<br>LS USING INTRUSIVE IMPACTOR TECHNIQUES          | 133         |
|      | 3.5.1              | Introduction  | 133         |
|      | 3.5.2              | Experimental  | 133         |
|      | 3.5.3              | Results and Discussion  | 135         |
|      | 3.5.4              | Conclusions   | 148         |
| 3.6  | THE ME             | ASUREMENT OF SLURRY SOLID PARTICLE SIZE IN<br>LS USING THE INTRUSIVE BOTTLE COLLECTION METHOD | 148         |
|      | 3.6.1              | Introduction  | 148         |
|      | 3.6.2              | Experimental  | 149         |
|      | 3.6.3              | Results and Discussion  | 149         |
|      | 3.6.4              | Conclusions   | 156         |
| CHAP | <u>IER 4 1</u>     | ELEMENTAL ANALYSIS OF SOLIDS BY SLURRY  | 157         |
|      | <u>/</u>           | ATOMISATION PLASMA EMISSION SPECTROMETRY  |             |
| 4.1  | INTROD             | UCTION  | 157         |
| 4.2  | INSTRU             | MENTATION   | 158         |
|      | 4.2.1              | The Plasmakon S-35 IC Plasma .  | 160         |
|      | 4.2.2              | The ARL 35000 IC Plasma   | 161         |
|      | 4.2.3              | The Spectraspan IIIA dc Plasma  | 164         |
| 4.3  | MINERAL<br>EMISSI( | L ANALYSIS BY SLURRY ATOMISATION PLASMA   | 165         |
|      | 4,3,1              | In-House Sulphide Ores  | 165         |
|      |                    | 4.3.1.1 Standardisation and Preliminary<br>Slurry Atomisation Experiments                     | 165         |
|      |                    | 4.3.1.2 Results and Discussion  | 166         |
|      |                    | 4.3.1.3 Slurry Analysis by direct current   | 174         |
|      |                    | Plasma Emission Spectrometry  |             |
|      |                    | 4.3.1.4 Results and Discussion  | 175         |

.

.

.

.

.

.

Page No.

| IJ | 5 |  |
|----|---|--|
|    |   |  |

|         | 4.3.1.5 Slurry Analysis and Matrix Effects     | 177   |
|---------|--|-------|
|         | 4.3.1.6 Results and Discussion                 | 178   |
|         | 4.3.1.7 Segregation Phenomena in Multi-        | 187   |
| •       | ( 3 ) P Populta and Discussion                 | 197   |
|         | 4.3.1.9 The Effect of Injector Bore on         | 188   |
|         | 4.5.1.9 The Effect of Injector Bore on         | 100   |
|         | 4.2.1.10 Populto and Discussion                | 189   |
|         | 4.3.1.10 Results and Discussion                | 191   |
|         | for Ore Slurry Analysis                        | 1/1   |
|         | 4 3 1 12 Results and Discussion                | 193   |
| 432     | Canadian Certified Reference Ores              | 196   |
| 7       | 4.3.2.1 Slurry Atomisation Experiments with    | 197   |
|         | KCla and MPla Using the Plasmakon              |       |
|         | S-35 ICP                                       |       |
|         | 4.3.2.2 Results and Discussion                 | 197   |
|         | 4.3.2.3 Slurry Atomisation Experiments with    | 205   |
|         | KCla and MPla Using the ARL 35000              |       |
|         | ICP  |       |
|         | 4.3.2.4 Results and Discussion                 | 205   |
| 4.3.3   | Dolomite and Feldspar Certified Reference      | 209   |
|         | Materials                                      |       |
|         | 4.3.3.1 The Analysis of Dolomite and           | 210   |
|         | Feldspar by Slurry Atomisation                 | ~ ~ ~ |
|         | 4.3.3.2 Results and Discussion                 | 210   |
|         |  | 212   |
|         | CC AND ATOMISATION PHENOMENA FROM ALOMINA      | 215   |
| SLOKKI  | L) ·   |       |
| 4 4 1   | The Determination of Aluminium in Alumina      | 214   |
| 4.4.2   | Results and Discussion                         | 216   |
| 4.4.3   | The Measurement of AlO Emission in a Plasma    | 222   |
| 1.1.1.2 | From Solutions and Slurries                    |       |
| 4.4.4   | Results and Discussion                         | 223   |
| 4.4.5   | Atomisation Phenomena from Alumina Slurries    | 227   |
| 4.4.6   | Results and Discussion                         | 227   |
|         |  |       |
| THE DE  | TERMINATION OF MAJOR ELEMENTS IN CERAMIC       | 235   |
| MATERI  | ALS BY SLURRY ATOMISATION                      |       |
|         |  |       |
| 4.5.1   | The Recoveries of Zirconium from Fine          | 235   |
|         | Zirconia Powders                               |       |
| 4.5.2   | Results and Discussion                         | 236   |
| 4.5.3   | The Determination of Boron and Iron in         | 239   |
|         | Polyboron Nitride                              |       |
| 4.5.4   | Results and Discussion                         | 239   |
| 4.5.5   | The Determination of Boron in Ceramic          | 242   |
|         | starting Materials                             | 24.2  |
| 4.5.6   | Results and Discussion                         | 242   |
| TRANCO  | OPT AND ATOMICATION EFFICIENCIES FROM EMISSION | 247   |
|         | ANT AND ATOMIZATION EFFICIENCIES FROM EMISSION | 271   |
|         |  |       |
| 4.6.1   | Experimental                                   | 247   |
| 4.6.2   | Results and Discussion                         | 248   |
|         |  |       |

4.4

4.5

4.6

|             |                         |   | Page<br>No.                            |
|-------------|-------------------------|---|--|
| 4.7         | CONCLU                  | SIONS   | 251                                    |
|             |                         |   |  |
| <u>CHAP</u> | <u>TER 5</u>            | ROTATIONAL TEMPERATURE MEASUREMENTS IN THE<br>INDUCTIVELY COUPLED PLASMA  | 253                                    |
| 5.1         | INTROD                  | UCTION  | 253                                    |
| 5.2         | TEMPER                  | ATURE AND THE INDUCTIVELY COUPLED PLASMA  | 254                                    |
|             | 5.2.1                   | The Gas Kinetic/Rotational Temperature  | 255                                    |
| 5.3         | EXPERI                  | MENTAL AND RESULTS  | 258                                    |
|             | 5.3.1                   | The Measurement of the Rotational Temperature of the OH Radical   | 258                                    |
| 5.4         | DISCUS                  | SION  | 259                                    |
| 5.5         | THE TEN<br>POINT S      | MPERATURE RANGE AND ATOMISATION OF HIGH BOILING SOLIDS  | 274                                    |
| 5.6         | EXPERI                  | MENTAL AND RESULTS  | 275                                    |
|             | 5.6.1                   | Slurry Atomisation of High Boiling Point<br>Solids  | 275                                    |
| 5.7         | DISCUS                  | SION  | 276                                    |
| 5.8         | CONCLUS                 | SIONS   | 277                                    |
| CHAP        | <u>TER 6</u>            | THE LAMINAR FLOW TORCH  | 281                                    |
| 6.1         | INTRODU                 | UCTION  | 281                                    |
|             | 6.1.1                   | Plasma Torches  | 281                                    |
| 6.2         | EXPERIN                 | MENTAL  | 282                                    |
|             | 6.2.1<br>6.2.2<br>6.2.3 | Laminar Flow Torches<br>The Brass-Base LFT<br>The PTFE/GF-Base LFT<br>6.2.3.1 Simplex Optimisation Experiments<br>6.2.3.2 Rotational Temperature Measurements<br>Using the PTFE/GF-Base LFT | 282<br>289<br>289<br>289<br>289<br>290 |
| 6.3         | RESULTS                 | S AND DISCUSSION  | 292                                    |
|             | 6.3.1<br>6.3.2          | Brass-Base Laminar Flow Torch<br>The PTFE/GF-Base Laminar Flow Torch<br>6.3.2.1 Simplex Optimisation Experiments<br>6.3.2.2 Rotational Temperature Measurements<br>in the LFT               | 292<br>298<br>298<br>301               |

|   |               |  | Page<br>No. |
|---|---------------|--|-------------|
|   | 6.4           | CONCLUSIONS  | 308         |
|   |               |  |             |
|   | <u>CHAP T</u> | ER 7 SLURRY ATOMISATION-PLASMA SOURCE MASS<br>SPECTROMETRY | 309         |
|   | 7.1           | INTRODUCTION   | 309         |
|   |               | 7.1.1 Semi-Quantitative Analysis using ICP-MS              | 310         |
|   | 7.2           | EXPERIMENTAL   | 311         |
|   | 7.3           | RESULTS AND DISCUSSION                                     | 317         |
|   | 7.4           | CONCLUSION   | 328         |
|   |               | - · · · ·  |             |
|   | <u>CHAPT</u>  | ER 8 CONCLUSION AND SUGGESTIONS FOR FUTURE WORK            | 329         |
|   | 8.1           | CONCLUSION   | 329         |
| • | 8.2           | FUTURE WORK  | 337         |

.

. .

· · ·

.

. .

•

#### LIST OF FIGURES

.

.

|            |   | Page<br>No. |
|------------|---|-------------|
| FIGURE 2.1 | Potential energy curve against distance from a particle.  | 23          |
| FIGURE 2.2 | By volume particle size distribution of BP<br>sulphide ore, J+L4 after 10 minutes<br>grinding in a TEMA disk mill.  | 30          |
| FIGURE 2.3 | By volume particle size distribution of BP<br>sulphide ore, SA1/Cl2O, after 10 minutes<br>grinding in a TEMA disk mill.   | 31          |
| FIGURE 2.4 | By weight particle size distributions of a<br>Polyboron nitride ceramic after grinding<br>(a) 2 minutes in a TEMA disk mill and<br>(b) 3 hours by the bottle and bead method.   | 32          |
| FIGURE 2.5 | By volume particle size distributions of BP sulphide ore, J+L4, with grinding time by the bottle and bead method.   | 41          |
| FIGURE 3.1 | Diagram of the Ebdon V-groove nebuliser.  | 52          |
| FIGURE 3.2 | Schematic representation of the possible<br>aerosol motion and loss mechanisms in spray<br>chambers.  | 54          |
| FIGURE 3.3 | Diagram of the Andersen Cascade impactor.   | 61          |
| FIGURE 3.4 | By volume particle size distribution of the<br>BP sulphide ore, J+L4, used in the Malvern<br>laser aerosol measurement experiments.   | · 65        |
| FIGURE 3.5 | By weight aerosol distribution (Malvern) of<br>a 0.1% m/V sodium hexametaphosphate<br>solution produced by an Ebdon nebuliser at<br>1.5 l min <sup>-1</sup> argon gas flow rate measured<br>20mm from gas orifice.                    | 66          |
| FIGURE 3.6 | Diagram of Scott-type double pass spray chamber.  | 67          |
| FIGURE 3.7 | By weight aerosol size distributions<br>(Malvern) of a 0.1% m/V sodium hexameta-<br>phosphate solution and a 1% m/V ore slurry<br>measured at the exit from the double pass<br>spray chamber. Gas flow rate 1.5 l min <sup>-1</sup> . | 69          |
| FIGURE 3.8 | By volume particle size distribution of the<br>BP sulphide ore, SAl/Cl2O, used in the<br>Aerometrics laser aerosol measurement<br>experiments.  | 72          |

|            |  | No.  |
|------------|--|--|
| <b>3.9</b> | Diagram of single pass spray chamber.<br>ARL design without impact bead.   | 73   |
| 3.10       | Population size distributions of aerosols<br>produced by a high solids nebuliser at a<br>carrier gas flow rate of 0.75 (a, b, d, e,<br>g) and 1.5 (c, f, h) 1 min <sup>-1</sup> from water<br>(a), 0.1% m/V SHMP solution (b, c, d, f, g,<br>h) and 1% m/V slurry (e) measured at 5mm<br>(a, b, c), 20mm (d, e, f) and 132mm (g, h)<br>from the nebuliser face.        | 84   |
| 3.11       | Population size distributions of aerosols<br>measured from a single pass conical spray<br>chamber (a) and above a 2mm injector (b to<br>g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f)<br>and 0.5 (g) 1 min <sup>-1</sup> carrier gas flow rate<br>using 0.1% m/V SHMP solution (a, b, d, e,<br>g) and 1% slurry (c, f).  | 85   |
| 3.12       | Population size distributions of aerosols<br>measured from a single pass conical spray<br>chamber (a) and above a 3mm injector (b to<br>g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f)<br>and 0.5 (g) 1 min <sup>-1</sup> carrier gas flow rate<br>using 0.1% m/V SHMP solution (a, b, d, e,<br>g) and 1% slurry (c, f).  | 86   |
| 3.13       | Population size distributions of aerosols<br>measured from an inner pass chamber (a, b)<br>and double pass spray chamber (c to f) at<br>0.75 (a, c, d) and 1.5 (b, e, f) 1 min <sup>-1</sup><br>carrier gas flow rate using 0.1% m/V SHMP<br>solution (a, b, c, e) and 1% m/V slurry<br>(d, f).  | 87   |
| 3.14       | Population size distributions of aerosols<br>measured from a double pass spray chamber<br>with 2mm injector at 1.5 (a, b), 1.1 (c,<br>d), 0.75 (e, f) and 0.5 (g) 1 min <sup>-1</sup> carrier<br>gas flow rate using 0.1% m/V SHMP solution<br>(a, c, e, g) and 1% m/V slurry (b, d, f).   | 88   |
| 3.15       | Population size distributions of aerosols<br>measured from a double pass spray chamber<br>with 3mm injector at 1.5 (a, b, h), 1.1<br>(c), 0.75 (d, f, g) and 0.5 (e) 1 min <sup>-1</sup><br>carrier gas flow rate using 0.1% m/V SHMP<br>solution (a, c, d, e, g, h) and 1% m/V<br>slurry (b, f). Aerosol distribution (h)<br>measured at edge of 3mm injector stream. | 89   |
|            | <ul> <li>3.9</li> <li>3.10</li> <li>3.11</li> <li>3.12</li> <li>3.13</li> <li>3.14</li> <li>3.15</li> </ul>  | <ul> <li>3.9 Diagram of single pass spray chamber.<br/>ARL design without impact bead.</li> <li>3.10 Population size distributions of aerosols produced by a high solids nebuliser at a carrier gas flow rate of 0.75 (a, b, d, e, g) and 1.5 (c, f, h) 1 min<sup>-1</sup> from water (a), 0.1% m/V SHMP solution (b, c, d, f, g, h) and 1% m/V SILUrry (e) measured at 5mm (a, b, c), 20mm (d, e, f) and 132mm (g, h) from the nebuliser face.</li> <li>3.11 Population size distributions of aerosols measured from a single pass conical spray chamber (a) and above a 2mm injector (b to g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f) and 0.5 (g) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, b, d, e, g) and 1% slurry (c, f).</li> <li>3.12 Population size distributions of aerosols measured from a single pass conical spray chamber (a) and above a 3mm injector (b to g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f) and 0.5 (g) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, b, d, e, g) and 1% slurry (c, f).</li> <li>3.13 Population size distributions of aerosols measured from an inner pass chamber (a, b) and double pass spray chamber (c to f) at 0.75 (a, c, d) and 1.5 (b, e, f) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, b, c, e) and 1% m/V SHMP solution (a, b, c, e) and 1% m/V SHMP solution (a, c, e, g) and 1% m/V Slurry (d, f).</li> <li>3.14 Population size distributions of aerosols measured from a double pass spray chamber with 2mm injector at 1.5 (a, b), 1.1 (c), 0.75 (e, f) and 0.5 (g) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, c, e, g) and 1% m/V Slurry (b, d, f).</li> <li>3.15 Population size distributions of aerosols measured from a double pass spray chamber with 3mm injector at 1.5 (a, b, h), 1.1 (c), 0.75 (d, f, g) and 0.5 (g) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, c, d, e, g, h) and 1% m/V slurry (b, f). Aerosol distribution (h) measured at edge of 3mm injector stream.</li> </ul> |

-vii-

Page

.

|             |  | Page<br>No. |
|-------------|--|-------------|
| FICURE 3.16 | Population size distributions of organic<br>liquid aerosols measured from a double pass<br>spray chamber with 2mm injector at a gas<br>flow rate of 0.8 l min <sup>-1</sup> (a) white spirit,<br>(b) white spirit-xylene mixture (1:1),<br>(c) white spirit-xylene mixture containing<br>l00µg ml <sup>-1</sup> of surfactant, (d) 1/250<br>dilution of (c), (e) aqueous aerosol (0.1%<br>SHMP) produced under similar conditions for<br>comparison. | 90          |
| FICURE 3.17 | % volume size distributions of aerosols<br>produced by high solids nebuliser at 0.75<br>(a, b) and 1.5 (c) 1 min <sup>-1</sup> carrier gas flow<br>rate using water (a), 0.1% m/V SHMP<br>solution (b, c), and measured 5mm from<br>nebuliser face.  | 91          |
| FIGURE 3.18 | % volume size distributions of aerosols<br>produced by high solids nebuliser at 0.75<br>(a, b) and 1.5 (c) 1 min <sup>-1</sup> carrier gas flow<br>rate using 0.1% m/V SHMP solution (a, c)<br>and 1% m/V slurry (b) measured 20mm from<br>nebuliser face.   | 92          |
| FIGURE 3.19 | % volume size distributions of aerosols<br>produced by a high solids nebuliser (a, b),<br>measured 132mm from nebuliser face, and<br>single pass conical spray chamber (c) at<br>0.75 (a, c) and 1.5 (b) 1 min <sup>-1</sup> carrier gas<br>flow rate using 0.1% m/V SHMP solution.  | 93          |
| FIGURE 3.20 | % volume size distributions of aerosols<br>measured from a single pass conical spray<br>chamber with 2mm injector at a carrier gas<br>flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and<br>0.5 (d) 1 min <sup>-1</sup> using 0.1% m/V SHMP<br>solution.  | 94          |
| FIGURE 3.21 | % volume size distributions of aerosols<br>measured from single pass conical spray<br>chamber with 2mm injector at a carrier gas<br>flow rate of 1.5 (a, b) and 0.75 (c, d)<br>l min <sup>-1</sup> using 0.1% m/V SHMP solution (a, c)<br>and 1% m/V slurry (b, d).  | 95          |
| FIGURE 3.22 | % volume size distributions of aerosols<br>measured from single pass spray chamber<br>with 3mm injector at a carrier gas flow<br>rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5<br>(d) 1 min <sup>-1</sup> using 0.1% m/V SHMP solution.   | 96          |

|             |  | Page<br>No. |
|-------------|--|-------------|
| FIGURE 3.23 | % volume size distributions of aerosols<br>measured from single pass conical spray<br>chamber with 3mm injector at a carrier gas<br>flow rate of 1.5 (a, b) and 0.75 (c, d)<br>1 min <sup>-1</sup> using 0.1% m/V SHMP solution (a, c)<br>and 1% m/V slurry (b, d).              | 97          |
| FIGURE 3.24 | % volume size distributions of aerosols<br>measured from a single pass conical spray<br>chamber alone (a), with 2mm injector (b)<br>and 3mm injector (c) at a carrier gas flow<br>rate of 0.75 l min <sup>-1</sup> using 0.1% m/V SHMP<br>solution.                              | 98          |
| FIGURE 3.25 | % volume size distributions of aerosols<br>measured from a high solids nebuliser (a,<br>b) and the inner pass from a double pass<br>spray chamber (c, d) at a carrier gas flow<br>rate of 0.75 (a, c) and 1.5 (b, d) 1 min <sup>-1</sup><br>using 0.1% SHMP solution.            | 99          |
| FIGURE 3.26 | % volume size distributions of aerosols<br>measured from the inner pass of a double<br>pass spray chamber (a, b) and from a double<br>pass spray chamber (c, d) at a carrier gas<br>flow rate of 0.75 (a, c) and 1.5 (b, d)<br>l min <sup>-1</sup> using 0.1% m/V SHMP solution. | 100         |
| FIGURE 3.27 | % volume size distributions of aerosols<br>measured from a double pass spray chamber<br>at a carrier gas flow rate of 0.75 (a, b)<br>and 1.5 (c, d) 1 min <sup>-1</sup> using 0.1% m/V SHMP<br>solution (a, c) and 1% m/V slurry (b, d).   | 101         |
| FIGURE 3.28 | % volume size distributions of aerosols<br>measured from a double pass spray chamber<br>with 2mm injector at a carrier gas flow<br>rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5<br>(d) 1 min <sup>-1</sup> using 0.1 m/V SHMP solution.  | 102         |
| FIGURE 3.29 | % volume size distributions of aerosols<br>measured from a double pass spray chamber<br>(a, c) and double pass spray chamber with<br>2mm injector (b, d) at a carrier gas flow<br>rate of 0.75 (a, b) and 1.5 (c, d) 1 min <sup>-1</sup><br>using 0.1% m/V SHMP solution.        | 103         |
| FIGURE 3.30 | % volume size distributions of aerosols<br>measured from a double pass spray chamber<br>with 2mm injector at a carrier gas flow<br>rate of 1.5 (a, b) and 0.75 (c, d) 1 min <sup>-1</sup><br>using 0.1% m/V SHMP solution (a, c) and 1%<br>m/V slurry (b, d).                    | 104         |

Page

No.

105

106

- FIGURE 3.31 % volume size distributions of aerosols ... measured from double pass spray chamber with 3mm injector at a carrier gas flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5 (d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.
- FIGURE 3.32 % volume size distributions of aerosols measured from a double pass spray chamber with 3mm injector at a carrier gas flow rate of 1.5 (a, b) and 0.75 (c, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).
- FIGURE 3.33 % volume size distributions of aerosols measured from a double pass spray chamber with 3mm injector (a, b) and from a double pass spray chamber alone (c, d) at a carrier gas flow rate of 1.5 (a, c) and 0.75 (b, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.
- FIGURE 3.34 % volume size distributions of organic liquid aerosols measured from a double pass spray chamber with 2mm injector at a gas flow rate of 0.8 1 min<sup>-1</sup>. (a) white spirit, (b) white spirit-xylene mixture (1:1), (c) white spirit-xylene mixture containing 100µg ml<sup>-1</sup> of surfactant, (d) 1/250 dilution of (c) with mixture.
- FIGURE 3.35 % volume size distributions of organic aerosols (a) white spirit, (b) white spirit-xylene mixture (1:1), and aqueous aerosols (c, d) 0.1% m/V SHMP solution, measured from a double pass spray chamber with 2mm injector at a gas flow rate of 0.8 1 min<sup>-1</sup> (a, b, c) and a 3mm injector at 1.5 1 min<sup>-1</sup> (d). Aerosol (d) measured at edge of stream from injector.
- FIGURE 3.36 Diagram of the Andersen stack sampler and 134 double pass spray chamber arrangement used for the cascade impactor experiments.
- FIGURE 3.37 By volume particle size distribution of the 137 starting ore slurry, 5% m/V SA1/Cl20, used in Cascade impactor study (i).
- FIGURE 3.38 By volume particle size distributions of 138 ore fractions collected by Cascade impactor (study(i)) from aerosol exiting a double pass spray chamber with 3mm injector at 1.6 1 min<sup>-1</sup> gas flow rate.

107

108

Page No.

139

140

141

142

143

144

- FIGURE 3.39 By weight aerosol size distribution of 5% m/V ore slurry, SAl/Cl2O, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 1.6 l min<sup>-1</sup> gas flow rate.
- FIGURE 3.40 By weight aerosol size distribution of 5% m/V ore slurry SAl/Cl20, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 0.85 1 min<sup>-1</sup> gas flow rate.
- FIGURE 3.41 By weight aerosol size distribution of 2.5% m/V ore slurry SAl/Cl2O, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 1.6 l min<sup>-1</sup> gas flow rate.
- FIGURE 3.42 By weight aerosol size distribution of 2.5% m/V ore slurry SAl/Cl20, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 0.85 1 min<sup>-1</sup> gas flow rate.
- FIGURE 3.43 By volume particle size distribution of the starting ore slurry, 2.5% m/V SA1/Cl20, used in Cascade impactor study (ii).
- FIGURE 3.44 By volume particle size distributions of ore fractions collected by Cascade impactor (study (ii)) from aerosol exiting a double pass spray chamber with 3mm injector at 0.75 1 min<sup>-1</sup> gas flow rate.
- FIGURE 3.45 By weight aerosol size distributions of 145 (a) 2.5% m/V ore slurry SA1/Cl20, collected by Cascade impactor (study (ii)) and (b) 1% m/V sodium chloride solution from aerosol exiting a double pass spray chamber with 3mm injector at 0.75 1 min<sup>-1</sup> gas flow rate.
- FIGURE 3.46 By volume particle size distributions of 5% 151 ore slurry, J + L4, acquired by the bottle collection method from aerosols exiting a double pass spray chamber with 1.1mm injector at gas flow rates (b) 0.66, (c) 1.73, (d) 3.4 1 min<sup>-1</sup> together with starting slurry distribution (a).
- FIGURE 3.47 By volume particle size distributions of 5% m/V ore slurry, J + L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 2.2 mm injector at gas flow rates (b) 1.73, (c) 3.4 l min<sup>-1</sup> together with starting slurry distribution (a).

Page

No.

FIGURE 3.48 By volume particle size distributions of 153 .. 5% m/V ore slurry, J + L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 3.2mm injector at gas flow rates (b) 0.66, (c) 1.73, (d) 3.4 1 min<sup>-1</sup> together with starting slurry distribution (a). FIGURE 3.49 By volume particle size distributions of 154 5% m/V ore slurry, J + L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 3.6mm injector at gas flow rates of (b) 0.66, (c) 1.73, (d) 3.4  $1 \text{ min}^{-1}$  together with starting slurry distribution (a). FIGURE 4.1 Schematic diagram of Kontron S-35 ICP-AES 159 instrumentation. FIGURE 4.2 Diagram of Greenfield-type inductively 163 coupled plasma torch. FIGURE 4.3 Calibration plots for zinc, copper and lead 181 (a, b, c) showing the deviation from linearity of the bottom standard solution emission (no iron present) compared with the two top standards (iron present). Plot (d) shows lead top standard emission without iron present. FIGURE 4.4 Graph showing the matrix effect of iron and 182 surfactant (SHMP) concentration upon the net emission intensity of scandium (a) and lead (b) at 1150W and 1800W forward power. Concentrations in  $\mu g m l^{-1}$ . FIGURE 4.5 By volume particle size distribution of 183 slurry ore, SA1/C120. FIGURE 4.6 By volume particle size distributions of 186 (a) starting ore slurry, SA1/C120, and (b) the solid fraction collected by Cascade impactor after passing through a double pass spray chamber with 3mm injector at gas flow rate 1.5 1 min<sup>-1</sup>. FIGURE 4.7 200 Graph showing the correlation between the elemental heat of atomisation and the percentage recovery (E) obtained from the analysis of the CANMET ores KCla and MPla. FIGURE 4.8 Viewing height emission profiles for 203 equivalent concentrations of elements in solution and slurry (KCla) under plasma conditions which produce a cross over (a) silver, (b) copper.

|             |  | Page<br>No. |
|-------------|--|-------------|
| FIGURE 4.9  | Viewing height emission profiles from iron<br>in BCS 368 Dolomite slurry using the iron<br>ion line 259.94nm and iron atom line<br>371.993nm at low gas flow rate (1.3 1 min <sup>-1</sup> )<br>and high gas flow rate (2.3 1 min <sup>-1</sup> ).       | 212         |
| FIGURE 4.10 | By volume particle size distribution of<br>ground alumina slurry before and after<br>transportation through a double pass spray<br>chamber with 3mm injector at a gas flow<br>rate of 2 l min <sup>-1</sup> .  | 219         |
| FICURE 4.11 | By weight particle size distribution of<br>aerosol exiting a double pass spray chamber<br>and theoretical maximum alumina particle<br>size produced by decomposition of 500µg ml <sup>-1</sup><br>aluminium nitrate aerosol of the same<br>distribution. | 220         |
| FIGURE 4.12 | Wavelength emission scan across the 484.2nm<br>AlO emission band head obtained from<br>aspirating a 1% m/V aluminium solution into<br>the plasma and viewed at 40mm above load<br>coil.  | 224         |
| FIGURE 4.13 | Graph showing the net intensity of the AlO<br>emission band head, from a 2% m/V ultrafine<br>alumina slurry and a solution of equivalent<br>aluminium concentration, against viewing<br>height in plasma.  | 225         |
| FIGURE 4.14 | Graph showing the net intensity of the AlO<br>emission band head 484.2nm, from a 2% m/V<br>coarse alumina slurry and a solution of<br>equivalent aluminium concentration, against<br>viewing height in plasma.   | 226         |
| FIGURE 4.15 | Viewing height emission profiles of the<br>aluminium atom line, 396.152nm, from (a) an<br>ultrafine alumina slurry and solution and<br>(b) a coarse alumina slurry and solution of<br>equivalent aluminium content.                                      | 231         |
| FIGURE 4.16 | Viewing height emission profiles of the<br>aluminium atom line, 308.215nm, from a<br>ground alumina slurry and from a solution<br>of equivalent aluminium content at gas flow<br>rates of (a) 1.1, (b) 1.2 and (c) 1.3 1<br>min <sup>-1</sup> .          | 232         |
| FIGURE 4.17 | Viewing height emission profiles of the<br>aluminium atom line, 396.152nm, from a<br>ground alumina slurry and from a solution<br>of equivalent aluminium content produced at<br>high gas flow rates with increase in<br>forward power.                  | 234         |

.

.

.

.

•

• •

|            |   | Page<br>No. |
|------------|---|-------------|
| FIGURE 5.1 | Spectral scan of the (0-0) band emission from OH showing Q and R branches.  | 264         |
| FIGURE 5.2 | Plot of Q <sub>1</sub> branch line emission intensities<br>against energy level from the OH (0-0) band<br>measured at 2.3 l min <sup>-1</sup> injector gas flow<br>rate and 19mm viewing height from a 1500W<br>plasma.   | 265         |
| FIGURE 5.3 | Plot of Q <sub>1</sub> branch line emission intensities<br>against energy level from the OH (O-O) band<br>measured at 1.4 l min <sup>-1</sup> injector gas flow<br>rate and 19mm viewing height from a 1500W<br>plasma.   | 266         |
| FIGURE 5.4 | Graph showing the change in rotational<br>temperature, K, with injector gas flow rate<br>for a constant viewing height of 19mm in a<br>1500W plasma.  | 268         |
| FIGURE 5.5 | Graph showing the change in rotational<br>temperature, K, with viewing height for a<br>constant injector gas flow rate 1.4 l min <sup>-1</sup><br>in a 1500W plasma.  | 270         |
| FIGURE 5.6 | Plot of R <sub>2</sub> branch line emission intensities<br>against energy level from the OH (0-0) band<br>measured at 1.4 l min <sup>-1</sup> injector gas flow<br>rate and 30mm viewing height from a 1500W<br>plasma.   | 272         |
| FICURE 5.7 | Plot of Q <sub>1</sub> branch line emission intensities<br>against energy level from the OH (0-0) band<br>measured at 1.4 l min <sup>-1</sup> injector gas flow<br>rate and 30mm viewing height while<br>aspirating a 500µg ml <sup>-1</sup> boron solution and<br>slurries containing 0.1 and 1% m/V<br>polyboron nitride. | 273         |
| FIGURE 6.1 | Diagram of brass body Greenfield-size<br>laminar flow torch.  | 283         |
| FIGURE 6.2 | Diagram of PTFE/Glass fibre body<br>Greenfield-size laminar flow torch.   | 284         |
| FIGURE 6.3 | Plot of Q <sub>1</sub> branch line emission intensities<br>against energy level from the OH (0-0) band<br>measured at 1.7 l min <sup>-1</sup> injector gas flow<br>rate and 19mm viewing height from a 1500W<br>laminar flow plasma.  | 302         |
| FIGURE 6.4 | Graph showing the change in rotational<br>temperature, K, with injector gas flow rate<br>for a constant viewing height of 19mm in a<br>1500W laminar flow plasma.   | 304         |

· ..

.

.

•

.

•

-xiv-

.

`

|            |  | Page<br>No. |
|------------|--|-------------|
| FIGURE 6.5 | Graph showing the change in rotational<br>temperature, K, with viewing height for<br>a constant injector gas flow rate of<br>1.4 l min <sup>-1</sup> in a 1500W laminar flow plasma. | 306         |
| FIGURE 7.1 | Schematic diagram of inductively coupled plasma mass spectrometer instrumentation.   | 312         |
| FIGURE 7.2 | Diagram illustrating the plasma sampling interface.  | 313         |

#### LIST OF TABLES

|       |      |  | Page<br>No. |
|-------|------|--|-------------|
| TABLE | 2.1  | Major components of the samples J+L4,<br>SA1/C120, KCla, MPla and polyboron nitride<br>together with their measure of hardness<br>(MOH)  | 27          |
| TABLE | 2.2  | Materials commonly used as grinding media<br>together with their major and minor<br>elemental components and measure of<br>hardness.   | 28          |
| TABLE | 2.3  | Particle size distribution (% volume) of<br>ore J+L4 against grinding time. No<br>dispersant (bottle and bead method).   | 34          |
| TABLE | 2.4  | Particle size distribution (% volume) of<br>ore J+L4 against grinding time. 0.1% m/v<br>sodium hexametaphoshate dispersant (bottle<br>and bead method).  | 35          |
| TABLE | 2.5  | Particle size distribution (% volume) of<br>ore J+L4 after 3 hours grinding against<br>concentration of dispersant (bottle and<br>bead method).  | 36          |
| TABLE | 2.6  | Particle size distribution (% volume) of<br>ore SAl/Cl20 with grinding time. No<br>dispersant (bottle and bead method).  | 37          |
| TABLE | 2.7  | Particle size distribution (% volume) of<br>ore SA1/C120 against grinding time.<br>0.1% m/v sodium hexametaphosphate<br>dispersant (bottle and bead method).   | 38          |
| TABLE | 2.8  | Particle size distribution (% volume) of<br>ore SA1/Cl20 with grinding time. 1% m/v<br>sodium hexametaphosphate dispersant (bottle<br>and bead method).  | 39          |
| TABLE | 2.9  | Particle size distribution (% volume) of<br>ore SA1/C120 after 1 hour grind against<br>concentration of various dispersants<br>(bottle and bead method).   | 40          |
| TABLE | 2.10 | Particle size distribution (% volume) of ore<br>SA1/C120 against grinding time. 0.1% m/v<br>sodium hexametaphosphate dispersant<br>(microniser grinding method with results<br>from bottle and bead method for comparison).  | 43          |
| TABLE | 2.11 | Particle size distributions (% volume) of<br>mineralised ores KCla and MPla as received,<br>after 30 minutes grinding using the<br>microniser method and after 4 hours using<br>the bottle and bead method (B+B). 0.1% m/v<br>sodium hexametaphosphate dispersant. | 44          |

٠

|       |      |   | Page '<br>No. |
|-------|------|---|---------------|
| TABLE | 2.12 | Particle size distributions (% volume) of<br>ore SAL/Cl20 and soil SO-1 in water (no<br>dispersant) after being ground using the<br>bottle and bead method and when redispersed<br>after stated time period (stability tests).                              | 48            |
| TABLE | 2.13 | Particle size distributions (% volume) of<br>ores SA1/Cl2O and J+L4 (dispersed in O.1 %<br>m/v SHMP solution) after being ground using<br>the bottle and bead and microniser methods<br>and when redispersed after stated time<br>period (stability tests). | 49            |
| TABLE | 3.1  | A summary of the possible aerosol formation<br>and loss processes occuring in the spray<br>chamber (SC)   | 57            |
| TABLE | 3.2  | Table of experiments used in the<br>measurement of aerosols from various<br>sample introduction systems. (1) Nebuliser<br>and single pass spray chamber (SPSC), 2mm<br>and 3mm injectors.   | 75            |
| TABLE | 3.3  | Table of experiments used in the<br>measurement of aerosols from various<br>sample introduction systems (II) Double<br>pass spray chamber (DPSC), 2 and 3mm<br>injectors.   | 76            |
| TABLE | 3.4  | Table of experiments used in the<br>measurement of organic liquid aerosols<br>from various sample introduction systems<br>(III) Double pass spray chamber, 2mm<br>injector.   | 77            |
| TABLE | 3.5  | Population count data for aerosols measured from nebuliser and single pass spray chamber (SPSC).  | 78            |
| TABLE | 3.6  | % volume and velocity data for aerosols<br>measured from nebuliser and single pass<br>spray chamber (SPSC)  | 79            |
| TABLE | 3.7  | Population count data for aerosols measured<br>from inner and outer passes of double pass<br>spray chamber (DPSC)   | 80            |
| TABLE | 3.8  | % volume and velocity data for aerosols<br>measured from inner and outer passes of<br>double pass spray chamber (DPSC).   | 81            |
| TABLE | 3.9  | Population count data for organic liquid<br>aerosols measured from 2mm injector/double<br>pass spray chamber (DPSC).  | 82            |

| Page |  |
|------|--|
| No.  |  |

NU .

| TABLE | 3.10  | % volume and velocity data for organic<br>liquid aerosols measured from 2mm<br>injector/double pass spray chamber (DPSC).   | 83               |
|-------|-------|---|------------------|
| TABLE | •3.11 | Aerosol volume and population data from the<br>nebuliser and the single pass spray<br>chamber (SPSC) with and without 2 and 3mm<br>bore injectors at a gas flow rate of<br>0.75 l min- <sup>1</sup> .       | 114              |
| TABLE | 3.12  | Volume data measured from aerosols at the<br>nebuliser, inner pass exit, DPSC exit and<br>top of the 2 and 3mm bore injectors at gas<br>flow rates of 0.75 and 1.5 l min-l                                  | 122              |
| TABLE | 3.13  | Settling diameters $d_{TV}$ and $d_{c50}$ calculated for the outer pass at four flow rates.   | 127              |
| TABLE | 3.14  | Mass transport efficiencies (MTE)<br>calculated from cascade impactor studies.  | 147              |
| TABLE | 3.15  | Table of cross-referenced figures to the aerosol bottle collection experiments performed.   | 150 <sub>.</sub> |
| TABLE | 4.1   | Plasma conditions used for the determin-<br>ation of iron, copper, zinc and silver in<br>sulphide ore fusion solutions of J+L4 and<br>SA1/C120 using the ARL 35000 ICP<br>spectrometer.                     | 167              |
| TABLE | 4.2   | Plasma conditions used for the determin-<br>ation of iron, copper, zinc and silver in<br>sulphide ore slurries J+L4 and SA1/C120<br>using the Kontron S-35 ICP spectrometer.                                | 168              |
| TABLE | 4.3   | The determination of iron, zinc, copper and<br>silver in the minerals J+L4 and SA1/C120<br>(designated J and S ) after a fusion/<br>dissolution stage had been performed.<br>Instrument used ARL 35000 ICP. | 169              |
| TABLE | 4.4   | The determination of zirconium in 100 ml<br>solutions of J+L4 and SA1/C120 after<br>performing a sodium peroxide fusion in<br>zirconium crucibles.  | 171              |
| TABLE | 4.5   | The determination of iron, zinc, copper and<br>silver in the minerals J+L4 and SA1/C120<br>(designated J and S) by slurry atomisation<br>using the Plasmakon S-35 ICP.                                      | 172              |

.

.

.

.

-

.

,

|       |      |  | Page<br>No. |
|-------|------|--|-------------|
| TABLE | 4.6  | The determination of silver in the ores<br>J+L4 and SAI/Cl20 by slurry atomisation<br>ICP-AES. Slurries prepared by grinding<br>with zirconia beads over 2 hour period.<br>Wavelength monitored 328.068 nm.  | 173         |
| TABLE | 4.7  | Operating conditions used on the<br>Spectraspan III dc plasma for analysis of<br>solutions and slurries of in-house ores.  | 173         |
| TABLE | 4.8  | The determination of iron, zinc and copper<br>in the minerals J+L4 and SA1/C120<br>(designated J and S) by slurry atomisation<br>and in solution using the Spectraspan III<br>dc plasma.   | 176         |
| TABLE | 4.9  | Operating conditions used on the ARL 35000<br>ICP for the analysis of in-house ores (J<br>and S) by slurry atomisation.  | 176         |
| TABLE | 4.10 | Standards table used in the calibration of<br>the ARL 35000 for the determination of Zn,<br>Cu, Fe, Pb, Zr and Ag in micronised slurry<br>sample SA1/Cl20.   | 180         |
| TABLE | 4.11 | The determination of copper, zinc, iron,<br>lead, zirconium and silver in the ore<br>SA1/C120 by slurry atomisation using the<br>ARL 35000 ICP.  | 184         |
| TABLE | 4.12 | Results from the determination of elements<br>of known concentration in solution<br>containing sodium hexametaphosphate (SHMP)<br>buffer.  | 185         |
| TABLE | 4.13 | A comparison of the iron, zinc, copper and<br>lead contents of the ore SA1/C120 as<br>received and collected after transportation<br>through a Scott-type double pass spray<br>chamber and 3mm injector at a gas flow rate<br>of 1.5 l min <sup>-1</sup> . | 185         |
| TABLE | 4.14 | The recovery of iron from a fine slurry of<br>the ore SA1/Cl20 with variation in carrier<br>gas flow rate, viewing height and injector<br>bore. Analysis performed using the Kontron<br>S-35 ICP at 1500 W   | <b>190</b>  |
| TABLE | 4.15 | Multi-element simplex optimisation (I) of<br>slurry SA1/Cl20 for maximum recovery using<br>the ARL 35000 ICP.  | 194         |
| TABLE | 4.16 | Multi-element simplex optimisation (II) of<br>slurry SAl/Cl20 for maximum recovery using<br>the ARL 35000 ICP.   | 195         |

.

. .

|       |             |   | Page<br>No. |
|-------|-------------|---|-------------|
| TABLE | <b>4.17</b> | Operating conditions used on the Kontron S-<br>35 ICP for the analysis of CRM ores KCla<br>and MPla by the slurry technique.  | 198         |
| TABLE | 4.18        | The determination of eight elements in the<br>CANMET CRM ores MPla and KCla by slurry<br>atomisation using the Kontron S-35 ICP   | 199         |
| TABLE | 4.19        | Heats of vaporisation $\Delta H_{(vap)}$ and total enthalpy change (TEC) data for some of the minerals in KCla and MPla over the temperature range 2000 to 3500 K.  | 201         |
| TABLE | 4.20        | New plasma operating conditions used for<br>the determination of copper and silver in<br>the ore slurries KCla and MPla.  | 204         |
| TABLE | 4.21        | The determination of copper and silver in<br>ores KCla and MPla by slurry atomisation<br>using the conditions shown in Table 4.20   | 204         |
| TABLE | 4.22        | Plasma running conditions used for the<br>determination of six analytes in the ores<br>KCla and MPla using the ARL 35000 ICP.   | 206         |
| TABLE | 4.23        | The analysis of KCla and MPla CRM ores by slurry atomisation using the ARL 35000 ICP.   | 207         |
| TABLE | 4.24        | Results from the determination of copper,<br>iron, zinc and lead in the bottle and bead<br>ground slurries KCla and MPla together with<br>the copper and iron values from the ore<br>SA1/C120. Analysis on ARL 35000 ICP. | 208         |
| TABLE | 4.25        | The analysis of Dolomite and Feldspar<br>certified reference materials by slurry<br>atomisation ICP AES.  | 211         |
| TABLE | 4.26        | Plasma running conditions used on the<br>Plasmakon S-35 ICP for the determination of<br>aluminium in coarse, medium and fine<br>alumina slurries and fusion solutions.  | 215         |
| TABLE | 4.27        | Variation, with particle size, of the<br>aluminium recovery (R%) from coarse, medium<br>and fine alumina slurries.  | 221         |
| TABLE | 4.28        | Plasma running conditions used on the<br>Plasmakon S-35 ICP for the measurement of<br>the AlO emission band head (0-0) as a<br>function of viewing height.  | 221         |
| TABLE | 4.29        | Plasma running conditions (Plasmakon S-35)<br>used to produce the viewing height emission<br>profiles shown in Figures 4.17 (a) to (d).   | 233         |

|       |        |  | No. |
|-------|--------|--|-----|
| TABLE | 4.30 . | The effect of plasma running conditions<br>upon the recovery of zirconium from 'Sample<br>l' of zirconia powder by slurry atomisation<br>together with the recoveries from samples<br>2, 3 and 4.                                  | 237 |
| TABLE | 4.31   | The particle size distributions of the zirconia powder samples 1, 2, 3 and 4.  | 238 |
| TABLE | 4.32   | Plasma conditions used on the Plasmakon S-<br>35 ICP for the determination of boron and<br>iron in 0.1 to 2% m/v slurries of polyboron<br>nitride.   | 240 |
| TABLE | 4.33   | The determination of boron in ceramic starting materials by slurry atomisation using the Plasmakon S-35 ICP.   | 243 |
| TABLE | 4.34   | Particle size distributions of some ceramic<br>starting materials ground for 3 hours by<br>the bottle and bead method.   | 244 |
| TABLE | 4.35   | The effect of carrier gas flow rate and<br>forward power upon the peak emission signal<br>for boron from the slurry 2LFC (42.6 µg ml <sup>-1</sup><br>boron) and a standard 40 µg ml <sup>-1</sup> boron<br>solution .             | 245 |
| TABLE | 4.36   | The effect of carrier gas flow rate and<br>forward power upon the VHEP coincidence<br>points from a boron containing slurry and<br>solution.   | 246 |
| TABLE | 4.37   | The recovery for magnesium adsorbed onto silica-based cation exchange slurries of 5 and 10 $\mu$ m sizes, at various carrier gas flow rates compared with solutions of equal magnesium concentration.                              | 250 |
| TABLE | 4.38   | Ratio of the magnesium signal for the SCX<br>particles to that of an aqueous solution of<br>the same magnesium concentration (recovery<br>values) and also for silicon (recovery) and<br>silicon corrected for magnesium recovery. | 250 |
| TABLÉ | 5.1    | s<br>Assignment, wavelength <sup>y</sup> , energies and<br>transition probabilities for the Q <sub>1</sub> and R <sub>2</sub><br>branches of the OH (0-0) band.  | 263 |
| TABLE | 5.2    | Plasma running conditions used for the recording of OH spectra.  | 267 |

•

Page

|            |        |     |  | Page<br>No. |
|------------|--------|-----|--|-------------|
| т          | ABLE   | 5.3 | OH rotational temperatures (T <sub>rot</sub> )<br>determined at a constant viewing height of<br>1.9 cm for carrier gas flow rates of 1.4 to<br>2.6 l min <sup>-1</sup> .   | 267         |
| T.         | ABLE   | 5.4 | OH rotational temperatures T <sub>rot</sub> determined<br>at a constant gas flow rate of 1.4 l min <sup>-1</sup><br>for viewing heights of 1.0 to 3.7 cm (above<br>load coil).   | 269         |
| T.         | ABLE   | 5.5 | Table of experiments performed to determine<br>the effect of various solutions and<br>slurries on the rotational temperature.  | 271         |
| . т.       | ABLE   | 5.6 | Some refractory materials likely to be<br>encounted for analysis in a plasma with<br>melting or boiling/decomposition points<br>comparable to T <sub>rot</sub> .   | 278         |
| T,         | ABLE   | 5.7 | Running conditions used on the Plasmakon S-35 ICP for the determination of Cr and Mg recoveries in $Cr_2O_3$ and MgO slurries (0.1% m/v).  | 279         |
| . т.       | ABLE   | 5.8 | Recoveries for Cr and Mg from 0.1% m/v slurries of $Cr_2O_3$ and MgO.  | 280         |
| . T/       | ABLE   | 6.1 | Gas flow rates for the laminar flow torch<br>annuli based on a Reynolds number 2000.   | 287         |
| T          | ABLE   | 6.2 | Gas flow rates for axial holes of laminar flow torches based on a Reynolds number of 2000.   | 288         |
| Т <i>і</i> | ABLE   | 6.3 | Conditions used for the measurement of the<br>OH (0-0) band spectra with the PTFE/GF-base<br>extended laminar flow torch (LFT) on the<br>Kontron S-35 ICP.   | 291         |
| ۲۸         | ABLE . | 6.4 | Operating conditions for stable laminar<br>flow plasma with injector flow using the<br>brass laminar flow torch.   | 293         |
| T/         | ABLE   | 6.5 | Operating conditions for the best signal to noise ratio obtained from $100 \ \mu g \ ml^{-1}$ iron solution (Fe II 259.939 nm) using the brass-base laminar flow torch together with the conditions necessary to produce an equivalent signal to noise ratio using the turbulent flow torch. | 294         |

|       |             |   | Page<br>No. |
|-------|-------------|---|-------------|
| TABLE | <b>6.6</b>  | Low laminar flow, low power operating<br>— conditions for comparable signal to noise<br>ratio from 100 µg ml <sup>-1</sup> Fe solution<br>(Fe II 259.939 nm) using conditions from<br>Table 6.5.  | 296         |
| TABLE | 6.7         | Operating conditions for the brass-base LFT<br>optimised on signal to background ratio<br>using simplex program.  | 297         |
| TABLE | 6.8         | Conditions found for maximum signal to<br>background ratio from a simplex program<br>(5 parameters) for the Fe II 259.939 nm<br>line from a 0.1% m/v slurry of SA1/C120<br>using the PTFE/GF-base laminar flow torch<br>on the Kontron S-35 ICP.                    | <b>299</b>  |
| TABLE | 6.9         | Conditions found for maximum signal to<br>background ratio from a simplex program (3<br>parameters) for the FeII 259.939 nm line<br>from a 0.1% m/v slurry of SA1/C120 using<br>the PTFE/GF-base laminar flow torch on the<br>Kontron S-35 ICP.                     | 300         |
| TABLE | <b>6.10</b> | The change in rotational temperature (T <sub>rot</sub> )<br>with carrier gas flow rate at a constant<br>viewing height (19 mm) using the PTFE/CF-<br>base laminar flow torch calculated from the<br>OH(0-0) band spectrum, Q <sub>1</sub> series.                   | 303         |
| TABLE | 6.11        | The change in rotational temperature (T <sub>rot</sub> )<br>with viewing height at a constant carrier<br>gas flow rate (1.4 1 min <sup>-1</sup> ) using the<br>PTFE/GF-base laminar flow torch calculated<br>from the OH(0-0) band spectrum, Q <sub>1</sub> series. | . 305       |
| TABLE | 7.1         | Instrumental details for the VG Elemental<br>Plasmaquad ICP-MS plasma system.   | 314         |
| TABLE | 7.2         | Instrument running conditions for the VG<br>Plasmaquad ICP-MS.  | 315         |
| TABLE | 7.3         | % volume particle size distributions for<br>the CRM coals (SARM 18, 20; NBS 1632b), fly<br>ash (NBS 1633a) and soils (SO-1 and SO-2)<br>determined using the Coulter Counter TAII.  | 318         |
| TABLE | 7.4         | Results for rapid semi-quantitative (S-Q)<br>analysis of seven CRM coals using slurry<br>atomisation.   | 321         |
| TABLE | 7.5         | Results for rapid semi-quantitative (S-Q)<br>analysis of three CRM soils using slurry<br>atomisation.   | 323         |

-xxiii-

|       |     |  | Page<br>No. |
|-------|-----|--|-------------|
| TABLE | 7.6 | Semi-quantitative analysis of blank<br>elements in 100 ml of solution after<br>zirconia grinding.  | 325         |
| TABLE | 7.7 | A comparison of the lanthanide group<br>elemental concentrations (μg g <sup>-1</sup> ) in the<br>soils SO-1 and SO-2 determined by semi-<br>quantitative slurry atomisation ICP-MS and<br>by a quantitative dissolution technique. | 327         |

•

#### CHAPTER 1

#### INTRODUCTION

1.1. INTRODUCTION.

1.1.1. The Analysis of Refractory Materials and Minerals.

Refractory materials and minerals serve as the source for many products in industry and for research (1). The quality of such products has to be strictly controlled, thus the analysis of refractories is of considerable importance. Interest in these materials has grown over the past 30 years which has resulted in an increased demand for rapid elemental characterisation. However the elucidation of mineral and refractory composition is not an easy task, given physical and chemical variations, and no single analysis route will completely characterise these materials. When the major interest in a material is the quantification of metal constituents the task is simplified and many instrumental techniques are available to the chemist to accomplish the analysis. Given the diversity of refractory and mineral types it would be a distinct advantage to be able to determine the major, minor and trace elemental components in a single preparative step and to this end the analyst is restricted to a narrower range of techniques.

1.1.2. Sample Preparation

For many techniques the determination of the elemental constituents in minerals and refractories involves a solubilisation stage. Materials of this type are generally resistant to simple acid attack, not only because of their chemical behaviour but also due to crystal hardening; a result of their age and the pressure and thermal histories involved in their formation. Materials which contain silica and/or siliceous-

based compounds often require hazardous acid mixtures, including hydrofluoric acid, to bring about dissolution. However, the presence of other species, not soluble in hydrofluoric acid, is often a problem. Also a component necessary to the dissolution stage may not be compatible with the favoured analytical technique. Hence extreme or exotic measures are frequently required to overcome this resistance or compatibility. The use of an alkali fusion technique, e.g. sodium peroxide, where the sample is fired at 600-700°C followed by acidification, is one route often employed in mineral and refractory dissolution. Such a technique results in high salt content in the final solution together with the possibility of introducing contaminants. A dissolution procedure always includes dilution of the sample thereby degrading the detection limit for any trace elements under review. This is a deleterious step when considering the analysis of, for example, the noble or platinum group metals at low levels in a sample. Direct analysis of the solid sample would negate many of the problems stated and in many cases reduce the time taken for analysis.

#### 1.2. SOLID SAMPLE ANALYSIS

## 1.2.1. Instrumental Techniques Available for the Analysis of Solid Samples

A number of instrumental techniques are available for the direct analysis of solids, each with its own advantages and disadvantages. Arc and Spark emission spectrometry have for many years been an important solid analysis technique (2,3). While probably unsurpassed for rapid qualitative analysis of samples some limitations of its use in quantitative analysis do exist. Poor precision is often obtained with non-conducting samples due to matrix effects. Stability of the arc must be high and the requirement for closely matched standards

dictates the necessity of some prior compositional knowledge. Greater precision is obtained with conducting samples, such as metals, but matrix matching is still required.

Spark source mass spectrometry (SSMS) is a sensitive solids technique (4) which allows the determination of most elements down to the sub  $\mu g$  $g^{-1}$  level. Detection limits can be as low as 10 ng  $g^{-1}$  (5). Like arc and spark emission spectrometers, the limitations of instrument stability and poor precision are inherent, with the added disadvantage of long analysis time. These problems together with the cost and complexity of the instrument have resulted in a decline, in recent years, in its popularity. The technique has been reviewed by Bacon and Ure (5) and a comprehensive list of applications includes the analysis of geological and related materials (Table 9 of reference 5).

X-ray fluorescence (XRF) is now a routine technique in most laboratories for solids analysis (6). Its response at trace level is very elemental and matrix dependent and while it may cover a detection range from percentage level down to  $\mu$ g g<sup>-1</sup> the need for closely matched standards is important. In many cases some sample pretreatment, by a grinding, mixing and pelletising or fusion technique is also required to overcome particle size and inhomogeneity effects. The relatively new sister technique of total reflectance X-ray fluorescence (T-XRF; 7,8) is more sensitive, ng g<sup>-1</sup> and below detection limits, and is reported to be less matrix dependent but this technique is not yet widely available.

The introduction of solids into atomisers for atomic absorption spectrometry (AAS) has been reviewed by Van Loon (2) and Langmyhr (9). The former covers not only flame and electrothermal systems but also
atomic emission and fluorescence spectrometry. Certainly a number of workers (10-14) have employed various methods for solids analysis using flame and electrothermal AAS with varying degrees of success. Lack of precision, low recoveries and high detection limits hamper flame systems while poor precision, small sample sizes and matrix interferences are limitations of the electrothermal atomisation technique. Automation of the sampling will, to a certain extent, improve the precision of the latter but by far the greatest advantage to using the furnace atomisation technique is its sensitivity down to the picogram level in absolute terms (15).

Neutron activation analysis can be a very sensitive solids analysis technique but its applicability is dependent upon a number of factors; (i) not all elements produce appropriate radioactivity decay curves; (ii) large quantities of sample are often required; (iii) a 'cool-down' period to stabilise the decay is required prior to the statistical counting procedure and hence results may not be available for many days; (iv) a strong neutron flux source is required to irradiate the sample (small reactor or accelerator) and this expensive source is not readily available to most laboratories. While this technique has the advantages of direct solid analysis, with no volatile analyte loss or contamination, together with representative sampling, the problems outlined above and occasional 'matrix effects' tend to outweigh these except for rather specialised applications.

Both glow discharge atomic emission spectrometry (GDAES) (16) and glow discharge mass spectrometry (GDMS) (4,17) are used for the analysis of solid samples. The Grimm (18) glow discharge lamp has been extensively employed for emission analysis since 1968 and various modifications and improvements upon this design have been produced (19). Although GDMS

has only recently been exploited commercially it is in fact one of the oldest ion-mass spectrometer systems, dating back to Aston (20) from the 1920's and 1930's. Both techniques have been reviewed (GDAES(21); GDHS (22)) and recently an assessment of GDMS has appeared in the literature (23) which also references several alternative techniques for elemental solids analysis by mass spectrometry (4). Use of these techniques for the analysis of refractories and minerals is reported in the literature (4, 23, 24). Detection limits are slightly matrix dependent but generally fall in the region 40 to 100 ng g $^{-1}$  for a sample such as shale (23). While matrix effects are stated to be acceptable for metal samples, complex powder mixes are dependent upon the sample preparation. Other limitations include spectral interferences from the discharge gas and other background gases, polyatomic interferences from sputtered matrix atoms in combination with other plasma species and increased cost and complexity compared with alternative emission techniques.

Since its inception as an emission spectroscopic source in the early 1960's the inductively coupled plasma (ICP) (25) has grown in popularity and a review by Greenfield <u>et al</u>. (26) traces the history and uses of plasma emission sources over a 15 year period. Solid samples have been introduced into the ICP for as long as solutions. The advantages of low detection limits (ng  $g^{-1}$ ), long linear working ranges  $(10^4 - 10^5)$ , multielement capability and the high temperature environment of the plasma offers an ideal spectroscopic technique for solids analysis. The ability to determine trace elemental components in solids without employing a solubilisation step has been the driving force for many groups and as a result numerous introduction techniques have been tried.

In powdered form samples of fine (less than 66µm size) CaCO3 SiO2,  $Al_2O_3$  and MgO powders have been analysed using such introduction techniques as fluidised beds and swirl cups (27) while a vibrating cup (28) has been used for lithium salt and alumina analysis. More recently, direct argon elutriation of certified reference (CR) coal fly ash into the ICP has been performed (29). In a similar manner certified reference fire brick was analysed (30) using a CR coal ash for calibration. Air elutriation was used to analyse fine (below 40  $\mu$ m size) CaCO<sub>3</sub> powders directly conveyed to an air-ICP (31). Problems associated with segregation, agglomeration and calibration were noted. Thermal vaporisation systems, where the sample is swept in vapour form into the ICP, have been reviewed by Kantor (32) and, more recently, Matusiewicz (33). The comprehensive review by Matusiewicz also includes laser ablation (LA) and direct sample insertion techniques (DSIT), where the sample, solid or liquid, is inserted into the plasma in a graphite cup or wire loop. The importance of direct solid sampling for minerals and technical products is displayed in the applications list shown in reference 33.

Of the solids introduction techniques mentioned for the ICP all may suffer from matrix effects to some degree and matching standards are important for calibration. Probe devices, due to the reduced thermal environment experienced by the sample, compared with swept vapour systems, create conditions where selective volatility of species is evident (34). Laser ablation ICPAES also shows interferences due to selective volatility from a matrix (35). However, acceptable results were reported with small quantities of powdered minerals using continuous laser ablation to bring about complete vaporisation of the sample (36).

Inductively coupled plasma-mass spectrometry (ICP-MS)(4,37) is a sensitive and selective technique that, by solution analysis, has shown detection limits down to 70 to 80 pg ml<sup>-1</sup> for the elements tungsten and molybdenum in geological materials (38). The technique has been extended to include the analysis of solids by laser ablation (39) and more recently by slurry atomisation (40,41). Chapter 7 of this thesis describes the semi-quantitative determination of concomitant elements in coal minerals by slurry atomisation which has now been published (41).

The direct current plasma (DCP) atomic emission spectrometer in its commercially available three electrode form has been described by Decker (42). While the DCP is a cooler source compared to the ICP detection limits from solution are noted to be in the range 0.2 to 20 ng ml<sup>-1</sup> for elements such as magnesium, iron, nickel and lead. Matrix effects, particularly those from easily ionised elements (EIE) are a characteristic of the DCP but are suitably 'buffered out' by use of an EIE, such as lithium or sodium, in excess. Solids analysis may be performed by the slurry technique to which the sample introduction system of the DCP is well suited. Minerals and soils have been analysed by this method (43,44).

1.3. SLURRY ATOMISATION

The slurry atomisation technique can be defined as the introduction of a fine material, dispersed in an aqueous or non-aqueous medium, to an atom-forming environment. For powder samples of small particle size or particularly friable materials a slurry is produced by simple stirring or grinding in the required medium and, if necessary in the presence of a suitable wetting agent. While this is a heterogeneous system, in macroscopic terms a homogeneous dispersion may be maintained by

agitation. When the solids loading is low (<2%m/v) many of the rheological properties of the slurry system model those of a solution of similar matrix (at atmospheric pressure). Hence, in analytical terms, solids which are transported to an atomising environment and vaporised in this state may be calibrated using simple solutions, to determine a particular analyte present.

The slurry technique has been used to analyse a wide variety of samples by a number of spectroscopic techniques. Gilbert (45) introduced soil slurries into a flame, of a total consumption burner, and noted the emission lines, from major elements present, on a qualitative basis. Since this pioneering investigation (see Van Loon (2), Langmyhr (9) and Schrenk (46)) a number of workers have employed the slurry technique with flames. Willis (47) suspended mineral samples (<44 µm size) in water and aspirated the slurry into three different flame systems. Quantitative measurements showed the response to be particle size dependent and he concluded that for acceptable recoveries samples should be ground to less than 10  $\mu$ m size. Fuller (12) analysed suspended titanium dioxide pigments in a liquid medium and in a comparison between the techniques of flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) concluded that the latter technique was more tolerant of particle size. Fry and Denton (11) analysed milk concentrates and tomato sauce directly by flame AAS using a standard addition technique to calibrate. A Babington-type nebuliser was used and the results suggest that internal calibration overcame matrix transport problems. Since then the modified Babington design nebuliser has been generally used and other slurried samples analysed by flame systems include animal tissue (10), minerals (48), soils (49) and more recently prepared meats for consumption (50). Mohamed et al. (51) analysed coal

slurries after grinding and sieving to below 45  $\mu$ m and attributed the low signal recoveries to aerosol mass transport loss and incomplete vaporisation of the larger particles.

Electrothermal atomic absorption spectrometry has been used to analyse a number of different materials by slurry atomisation. Particle size effects are not so prevalent with this system because of the method of direct sample transport to the atomising cell. However, limitations due to the maximum temperature attainable by the furnace with resistive heating (just over 3000°C), may result in some refractory materials suffering incomplete atomisation. Fuller et al. (48) investigated the effect of particle size upon recovery for chromium and vanadium from ilmenite and rutile slurries. A sampling error due to the reduced number of particles pipetted ( $20\mu$ l, 20  $\mu$ g of sample) when the particle size was increased was evident from the standard deviations obtained in the experiments. However near to full mean recoveries were observed from particles up to 100  $\mu m$  in size. Both arsenic (13,14) and selenium (52) have been determined in coal slurries and complete recoveries were achieved, together with good precision, when the particle size was reduced to 30 µm. Environmental samples have also been analysed by slurry ET-AAS for both lead (53) and cadmium (54).

The direct current plasma (DCP) has been used, successfully, to analyse slurried samples for a number of years. Mohamed <u>et al</u>. (55) investigated the aqueous aerosol size produced by a Babington-type nebuliser, single pass spray chamber and 7 mm internal diameter injector tube prior to the introduction of homogenised beef liver in slurry form (13% m/v). A maximum aerosol size of 62  $\mu$ m was observed with the mode of the distribution at 6 to 7  $\mu$ m size. The study was essentially semiquantitative for the elements copper, zinc, calcium and phosphorus.

Certified reference coal has been analysed using slurry atomisation (10% m/v) by McCurdy et al. (56). Simple aqueous standards were used to calibrate for Cr, Cu, Mg, Mn, Ni and Pb in the samples. Slurries were prepared by an aqueous grinding technique which reduced the particle size to below 22  $\mu$ m; the median size being 5 to 6  $\mu$ m. The recoveries reported were between 80 and 100% of the known value. More recently Sparkes and Ebdon (43,44) have shown that the properties of CRM soil, milk, plant and kaolin, as slurries, are similar to those of the solution used for calibration. The recoveries from the determination of major, minor and trace elements in these materials were generally of the order 80 to 100%. This may be attributed to the fine particle size of the solids in the slurries and to the transport properties of the single pass spray chamber with 10 mm injector used in the analysis. Plant tissues have also been analysed by slurry atomisation DCP-AES by Vien and Fry (57).

Of the instrumental techniques previously mentioned matrix effects were evident in several analyses using the slurry technique. These phenomena were successfully taken into account as shown in the results from a few workers using DCP-AES and ET-AAS. It is of note that an instrumental technique which is less matrix dependent, suffers less chemical interference and offers good precision, and in some cases greater sensitivity, than alternative techniques is that of inductively coupled plasma atomic emission spectrometry (ICP-AES). With only the replacement of the concentric glass nebuliser by one of a high solids design (58) the conventional sample introduction system may be retained for slurry work.

On a theoretical basis plasmas in general have been described by Bittencourt (59) and Griem (60) and with particular reference to the ICP by Sharp (61) and Blades (62).

1.3.1. The Inductively Coupled Plasma and Slurry Atomisation.

From 1961 to 1962 Reed described in a series of three papers (63,64,65) the construction of a concentric tube ICP torch and some of the physical properties of the argon and mixed gas-argon plasma. This plasma was sustained by a radio-frequency (RF) induction system which was used for growing crystals. Only passing mention was made as to its possible use as a spectroscopic source for solids. This potential was fully realised by Greenfield, and in a paper in 1964 Greenfield and coworkers (66) described the construction and use of a three concentric tube torch, with a 2.5 kW, 36 MHz RF induction generator, for the production of an annular argon plasma. In this design the sample was introduced as an aerosol through the hole punched in the plasma body with the argon gas flow from an injector tube. The narrow tail flame which resulted, above the tunnel in the plasma, was used as the spectroscopic source. Since this pioneering work numerous ICP systems have been developed (25,26). While today the most popular torch design used is that known as the 'Fassel torch', the difference to that of the 'Greenfield torch' is mainly in size (Fassel coolant tube 20 mm outside diameter, Greenfield coolant tube 29 mm outside diameter). Use of the smaller torch is widespread because of its lower power and argon requirements.

Greenfield <u>et al</u>. were the first to report (66) the introduction of slurries into the ICP although no quantitative measurements were made.

Using a high solids nebuliser of similar design to that of Wolcott and Sobel (67), Fuller et al. (48) investigated the effect of particle size upon the recovery of vanadium and zirconium from ilmenite and rutile slurried ores. Ground samples with a particle size, said to be, below 6 µm gave the greatest recoveries which were some 20 to 50% of known values. Transport efficiency was suggested to be responsible for the low recoveries. Saba et al. (68) studied the efficiencies of different sample introduction systems (nebulisers/spray chambers) for the transportation of metallic iron particles in oil to the ICP. They concluded that the ceramic DCP nebuliser/single pass glass (horn-like) spray chamber was the most efficient. After correcting for transport effects they calculated that for iron particles of 7  $\mu$ m size and less an atomisation efficiency of 77% occurred in the ICP. No comparison with solution transport was made and no mass distributions were determined. Wilkinson et al. introduced coal slurries (69) into the ICP using a Babington-type nebuliser (70). The effects of particle size, pumping rate and slurry concentration on the observed manganese emission were investigated. The solids particle size was found to be a critical factor and inefficient atomisation was suggested as the cause for reduced recoveries of manganese from particles of 70 µm size and above. A linear increase in the manganese emission signal was noted with increasing slurry concentration up to 20% m/v. A variable step size simplex method (71) was used to optimise the signal to background ratio of the manganese atom line employed in the experiments with an all argon and nitrogen-cooled argon plasma. Sugimae and Mizoguchi (72) suspended airborne collected particles in xylene and determined nine elements of interest in the filter samples. Calibration was performed using CRM slurries ground to a similar particle size range as the collected particles (0.1 to 100  $\mu$ m size). While Spiers et al. (73) analysed clay suspensions for their elemental constituents Watson and

Moore (74) determined noble metals adsorbed from dissolved ores onto ion-exchange resins. These resins were ground to below 75 µm size and introduced as slurries (4 to 17% m/v) into a single pass spray chamber and a 10 kW plasma at high gas flow rates (2.6 l min<sup>-1</sup>). Calibration was performed using ground resin slurries with known quantities of noble metals adsorbed onto them. Mackey and Murphy (75) used both aqueous and organic (xylene) media to suspend synthetic zeolites for the direct determination of their Si/Al, Na/Al and K/Al ratios. These ratios allowed simple characterisation of the minerals without the need for absolute values. The direct determination of wear metals in lubricating oils was performed by Algeo et al. (76) using a heated Babington-type nebuliser to reduce viscosity effects, as an alternative to dilution. Both normal geometry and inverted (like Reed (63)) plasmas were used, with modified spray chambers, to investigate transport properties of the metallic contaminants. While normal geometry plasma values showed loses (50 to 70% recovery) for the slurry method compared with the ashed sample the inverted plasma/spray chamber arrangement showed full recoveries.

Watson (77) used standard slurry suspensions to calibrate in the determination of various elements in slurries of ferro-alloys, ores and slags (2% m/v). A scandium internal standard was employed. Optimum plasma running conditions for the slurries were determined by a simplex method (71,78). Introduction of these slurries into a 7 kW plasma at 2.8 1 min<sup>-1</sup> through a single pass spray chamber (SPSC) gave near to full recoveries for eight elements of interest. McCurdy and Fry (79) determined sulphur in ground coal slurries (mean size 6  $\mu$ m) using a SPSC with no baffles or obstructions. Aqueous standards were used for calibration. Aqueous aerosol sizes were determined by a laser

technique and the data was used to consider transport properties on a simple theoretical basis.

Ebdon and Wilkinson (80,81) analysed coal slurries after dry grinding the samples (particle size 30  $\mu m$  and less). They concluded that the particle size of the slurry sample was important when considering recoveries, which under simplexed (71) conditions for manganese gave between 90 and 100% recovery. Concentrated slurries (10% m/v) produced recoveries of between 25 and 200% depending upon the element of interest and the plasma conditions used. The effect of particle size upon the transportation of kaolin slurries and the recovery for various elements was investigated by Ebdon and Collier (82). This fundamental study showed that the distribution of solid particles reaching the plasma was significantly influenced by the spray chamber design and bore of the injector. The largest particles being transported by a direct vertical injection nebuliser and 4 mm injector. As this sample introduction system led to instability of the plasma a straight through SPSC with 3 mm injector was recommended for practical analysis of slurries. The recoveries for iron, magnesium, titanium, aluminium and silicon were found to increase with a decrease in mean particle size of the solids in the slurries. Equivalent atomisation efficiency to that of the simple calibration solutions was obtained for these elements, with the exception of aluminium, when the mean particle size of the slurry was 0.5 μm. When a DPSC with 2.2 mm bore injector was used recoveries of 55 to 73% were observed. In a subsequent paper Ebdon and Collier (83) used the known silicon content of a kaolin slurry as an internal standard to correct for variable atomisation efficiencies associated with different particle sizes. When a lanthanum salt was added to a series of concentrated slurries and monitored, deviations from linearity, for an analyte emission versus the slurry concen-

tration, were able to be corrected. While the lanthanum internal standard corrected for viscosity effects and extended the linear range to 20% m/v solids it is of note that the solution standards which contained an equivalent concentration of analyte produced linear graphs with a greater slope. Differences in transportation and atomisation efficiencies between solutions and slurries were therefore not corrected by the lanthanum internal standard.

Rock and mineral slurries were used by Halicz and Brenner (84) and Verbeek and Brenner (85) to investigate the effect of particle size upon emission intensity of an analyte as a ratio to a scandium internal standard.Transport problems are evident due to particle size (up to 10  $\mu$ m) and possibly dispersion/flocculation effects. Signal to background emission profiling with viewing height showed irregularities for slurries compared with solutions and were attributed to differences in the atomisation of solid particles of varying grain size. Mixed gas plasmas were also investigated.

Foulkes <u>et al</u>. (86) studied the effect of grinding time upon the particle size of ores and minerals, the direct preparation and stabilisation of slurries and the recoveries of various elements with change in particle size under different plasma running conditions. Aerosol particle size distributions (PSD) of solutions and slurries were measured exiting from a DPSC using a laser analyser and no significant difference was observed under the conditions employed. The solid PSD of slurries reaching the plasma under various flow conditions using different injector/spray chamber systems was also studied. Evidence for differing kinetic and thermodynamic atomisation processes between slurries and solutions was presented in the paper.

Broekaert et al. (87) studied the emission of various elements from titania and alumina slurries. Magnesium, iron and aluminium were determined in the titania samples (particle size range 2 µm to 18 µm) using aqueous calibration standards and ratioing each analyte's intensity to that from a titanium emission line. This was performed in order to reduce any effects from transportation or atomisation in the slurry calculations. Alumina slurries of mean particle size 0.6 µm (93% by volume below 1 µm size) at low carrier flow rates showed over 95% of the response from solutions of equivalent aluminium concentration. Raeymaekers et al. (88) investigated aqueous and slurry (alumina) aerosol size distributions using a cascade impactor. No solid distributions for post-nebulised slurries were shown, and severe limitations in their experimental methodology casts doubts upon their results and some of the theoretical calculations presented e.g. assumed transport efficiency and distribution of solids reaching the plasma, that alumina particles act like coal particles, that spray chambers produce identical aerosol distributions, that injectors do not affect aerosol size reaching the plasma and that analyte recovery is dependent only upon degree of atomisation.

1.4. THE OBJECTIVES OF THIS WORK.

Browner and Boorn (89) have described the sample introduction system as the 'Achilles heel' of atomic spectroscopy, and stated that major advances will come only when a sound framework of fundamental knowledge is in place. This statement can also be considered to apply to the slurry technique when simple aqueous solutions are used for calibration. A greater understanding of the mechanisms involved, from slurry preparation through to plasma atomisation was one of the major objectives of this work.

While light, friable matrices will generally form slurries quite easily, efficient grinding techniques which reduce the particle size of a hard or refractory material to the region of 5  $\mu$ m in as short a time period as possible required investigation. The minimum of contamination being a necessary criterion. The stability of a slurry dispersion, in both the short and long term, and any effects from working the slurry <u>e.g.</u> pumping, nebulising, charging etc., was also an area for study.

For full recoveries to be realised from an ideal slurry the transportation and atomisation processes should, in magnitude, model those of the solutions used in the calibration. It was therefore necessary to ascertain the degree to which a slurry models a solution and to this end the major slurry transportation processes were studied i.e. efficiency, particle size distribution of aerosol and solids transported to plasma. A comparison with simple solutions was then performed under the same conditions. While plasma atomisation effects, if present, are difficult to isolate, the use of various plasma running conditions to vaporise high boiling point and refractory minerals was undertaken to exaggerate, if possible, any differences between a solution and slurry. The monitoring of viewing height emission profiles of atomic and molecular species allowed such differences to be observed. The effect of slurry particle size upon the efficiencies of transportation and atomisation was investigated for a variety of minerals, ores and ceramics.

The hardware and software of the modern ICP is continually changing. Developments in torch design have resulted in the extended and laminar flow torches being offered as improvements upon existing hardware. The

performances of the large 'Greenfield', smaller 'Fassel' and large 'laminar flow' torches were studied using solutions and slurries together with a simplex program to optimise the running conditions.

The ability of a plasma to vaporise a sample completely will depend upon a number of factors, the particle size and residence time in the plasma, the matrix energy demand of the material and the thermal temperature of the atomising cell. It is therefore necessary to ascertain the value of the 'breakdown' temperature of the plasma if atomisation mechanisms are to be considered in the slurry/solution model. The value of the rotational temperature ( $T_{rot}$ ) in the analyte channel of the plasma was determined as a diagnostic indicator of the 'thermal' temperature that may be experienced by a slurry or solution aerosol. The change in  $T_{rot}$  as a function of height in the plasma, carrier gas flow and matrix loading (solution and slurry) was also studied.

The work was extended to evaluate the use of slurry atomisation with the technique of ICP-MS. Samples of certified reference coals and soils were analysed on a semi-quantitative basis in order to assess, rapidly, threshold values for concomitant elements of interest.

#### CHAPTER 2

## THE PREPARATION OF SLURRIES FOR ANALYSIS

#### 2.1 INTRODUCTION

As previously stated a slurry is a heterogeneous (two phase) system which comprises a dispersed particulate solid in a liquid medium. For particles larger than 0.5  $\mu$ m and media of low viscosity a homogeneous dispersion, in macroscopic terms, may be maintained by agitation <u>i.e.</u> shaking, stirring, ultrasonication, sparging etc., which results in a suspension. Dispersed particles of 0.2  $\mu$ m size and less are often considered colloidal and are not subject to gravitational settling forces; being held in suspension by Brownian motion, (the continual random displacement of very small particles caused by molecular bombardment from the dispersion medium). For a greater appreciation of the relationship that exists between suspensions, sols and solutions the reader is directed to references 90, 91 and 92.

When a powder is added to a dispersion medium a number of inter-related factors need to be considered. If the powder surface is lyophobic, (solvent - hating) it is difficult to disperse. If it is lyophilic, (solvent - liking) the powder disperses easily. In aqueous systems the terms are hydrophobic and hydrophilic respectively. In order to make a powder surface lyophilic a dispersing agent is added. The correct choice of dispersing agent also has the effect of stabilising the dispersion for long time periods and of reducing Ostwald ripening (slow dissolution of very fine crystalline particles with subsequent precipitation onto the larger particle fraction, the driving force being the reduction of the high surface free energy contribution from the finer

fraction). Hence dispersing agents are frequently added to lyophilic powders.

2.1.1. The Dispersion of Powders (93,94)

When a dry powder is added to a liquid medium three stages in the dispersion process may be distinguished.

(i) The process of wetting which is defined as the replacement of the solid-air interface by a solid-liquid interface.

(ii) The process of disaggregation of clusters of particles.

(iii) The process of dispersion stabilisation (93).

The wetting process is quantified by the interfacial tensions between solid and liquid  $\mathcal{V}_{SL}$ , solid and air  $\mathcal{V}_{SA}$  and liquid and air  $\mathcal{V}_{LA}$  (all in Nm<sup>-1</sup>) in the expression:

$$\mathbf{S}_{LS} = \mathbf{\mathcal{V}}_{SA} - \mathbf{\mathcal{V}}_{SL} - \mathbf{\mathcal{V}}_{LA} \tag{2.1}$$

where  $S_{LS}$  is the spreading coefficient (in Nm<sup>-1</sup>) which when positive indicates the liquid will spread. The addition of a surface active agent usually decreases the value of  $\mathcal{V}_{LA}$  and, if adsorbed, decreases  $\mathcal{V}_{SL}$ . Both of which lead to greater wetting. As the change in  $\mathcal{V}_{SA}$  is small for most cases the dominating factor is  $\mathcal{V}_{LA}$ , the surface tension of the liquid phase.

The second stage in the dispersion process involves the breakdown of aggregates and agglomerates after wetting. Penetration by the liquid

into the voids between particles may bring about disintegration for easily wetted powders. Normally however, the use of mechanical energy (stirring, grinding etc.) is required.

The third stage involves the stability of the wetted dispersed system and depends upon the forces between particles. Particles can be brought into close contact by random motion which may cause them to flocculate, (the collision frequency depends upon the concentration, viscosity and temperature of the system). The potential barrier which exists between particles governs whether they combine or not. The potential energy can be considered to consist of two terms, the attractive (London - van der Waals) force, and the repulsive (electrical double layer) force. The interaction curve (Figure 2.1, (94)) follows an exponential decay pattern; the sum of the forces 'A' (attraction) and 'R' (repulsion) gives the total energy curve 'B'. If the maximum has an energy of more than 15kT (or 36.5 KJ mol<sup>-1</sup> at room temperature) the system is stable. This concept cannot account for the action shown by many non-ionic surface active agents and those nonaqueous systems of low dielectric constant. In such cases stabilisation depends upon steric and/or entropic repulsion.

2.1.2. The Measurement of Dispersion.

On a more practical basis the efficiency of a surface active agent in aiding dispersion was gauged by comparative particle sizing, with time. Two techniques were used in this study.

 (i) Optical microscopy. The use of a calibrated graticule allowed visible recognition of maximum particle sizes together with the broad range and narrow peak range distributions of a

dispersed sample. The presence or formation of flocs could be monitored as could the degree of agglomeration. Cross-pole analysis and filters for phase contrasting were also used to distinguish between flocs, aggregates and agglomerates.

(ii) Electrical sensing - zone particle analysis. Particle size distributions of powders and slurries were measured using a Coulter Counter TA II multi-channel particle analyser (Coulter Counter Ltd, Luton, Beds, UK). The Coulter Counter principle (94,95) is based upon the change in electrical conductivity that occurs when a particle, suspended in an electrolyte, is drawn through a small aperture, on either side of which is an electrode for monitoring the impedance. The change in detector voltage is proportional to the volume of electrolyte displaced by the particle as it passes through the aperture. Proprietory Coulter electrolyte (ISOTON II) was used for all particle size determinations and both 30 µm and 140 µm orifice tubes were employed in the determinations.

2.2. THE DIRECT PREPARATION OF SLURRIES WITHOUT SAMPLE PRETREATMENT.

Industrial and naturally occurring powder samples which are of very fine particle size (less than 10  $\mu$ m) can be considered suitable for analysis by the slurry technique without any pre-treatment. Dispersion is brought about by using a suitable medium, and where necessary a surface active agent. A number of examples are cited in the literature where ICP-AES and flame atomic absorption were used for the elemental analysis of fine slurries. Mackey and Murphy (75) analysed zeolites in both xylene and water using the known aluminium content of the samples as an intrinsic internal standard to obtain full recoveries. A similar



. . .



;

procedure was adopted by Ebdon and Collier (83) using the known silicon content of aqueous kaolin slurries. Air-borne particulates dispersed in xylene were analysed by Sugimae and Mizoguchi (72) while Fry and Denton (11) analysed milk, blood and food sauce by flame AAS. Other examples include ultrafine alumina ((86); Chapter 4, Section 4.4 of this thesis), ion-exchange resins (74), wear metals in oil (76), kaolin (43,82), titanium dioxide, river water and PTFE (96) and zirconia (Chapter 4; Section 4.5 of this thesis). In all but those samples which can be considered ultrafine problems associated with particle size were encounted. While using an intrinsic internal standard does negate many of these problems the use of standard suspensions of similar matrix (72) is dependent upon close matching of the particle size distributions.

2.3. THE PRETREATMENT OF SAMPLES FOR ANALYSIS.

For the excitation systems that employ the slurry technique (48) the particle size of the analyte is a major consideration. The time taken for a solid matrix to form atoms is dependent not only upon the temperature of the atomising cell but also on the size of the matrix particle. When nebulisation is used to introduce the slurry to the atom cell the particle size effect is compounded by the efficiency of the transport system (82).

It is reported (48) that, for atomisation to be efficient in a plasma, a maximum particle size of 10  $\mu$ m (8  $\mu$ m from reference 82) is required. Unless the material to be analysed is naturally of this size range a suitable comminution process (97) is necessary. Hence for most samples to be analysed by slurry atomisation using the conventional nebulisation technique size reduction is a necessary preparative step.

For size reduction to be an efficient stage in the analysis route the following criteria are considered important:

- (i) the process should be rapid;
- (ii) the process should allow a representative sample to be taken;
- (iii) no contamination, of the elements of interest, should result from the grinding process;
- (iv) the slurry to be analysed should contain a maximum particle size of 10  $\mu$ m, preferably less than 8  $\mu$ m.

For those samples which have a very wide particle size distribution, e.g. coarse ores and minerals, sintered ceramic powders, or those that need to be reduced to powder form e.g. granular feeds, ceramic sheets and formers, catalyst shells, glassed pellets, criterion (ii) becomes very important. A sufficiently large sample should be taken and broken down in order to furnish a representative sub-sample of the bulk. Laboratory grinding instruments capable of reducing material to the sub 10 µm range are generally designed to handle only small quantities. Hence certain samples dictate that size reduction be carried out in two stages. A number of grinding techniques have been attempted to overcome the two step process but to date the routes described below have proved optimal. While many different samples have been ground, using the three milling methods to be described, the following examples serve to show the capabilities of the comminution techniques and the applicabilty of certain dispersion systems. The grinding technique used for specific samples together with their dispersion system and subsequent size distribution are to be found in Chapter 4 of this thesis under the relevant heading.

#### 2.3.1. Experimental and Results

The samples chosen for the slurry preparation experiments were (i) two sulphide-bearing ores (J+L4 and SA1/Cl20, BP Research Centre, Sunburyon-Thames, Middlesex, UK) with a particle size ranging from 100 µm up to 4 mm, (ii) two standard reference mineralised rocks (MPla and KCla, Canadian Centre for Mineral and Energy Technology, CANMET 555 Booth Street, Ottawa, Ontario, Canada) sieved to below 74 µm and (iii) a polyboron nitride ceramic in sheet form (vapour deposition, Ringsdorff-Werke GmbH, Bad Godesburg,5300 BONN 2,West Germany). Taking into consideration the need to avoid contamination and the hardness of the samples it was necessary that the grinding media be composed of a material higher on a 'measure of hardness' (MOH) scale. While an alternative is to use grinding media lower on the scale that do not contaminate the slurry with the elements of interest, it is of note that brittle or friable grinding media will contribute solid to the slurry. If this solid is of a large particle size it may modify the transport efficiency of the sample and in some cases spectrally interfere (e.g. zirconia grinding media give Zr interference on the primary silver emission line). The major components of each of the samples together with their 'measure of hardness' (MOH) are shown in Table 2.1 (1). Table 2.2 shows a list of commonly used grinding media together with their MOH and composition (98,99).

.

Major components of the samples J+L4, SAl/Cl20, KCla, MPla and polyboron nitride together with their 'Measure of Hardness' (MOH)

| Mineral              | Formula   | мон     | J+L4 | SA1/<br>C120 | KCla       | MP1a         | poly-<br>boron<br>nitride |
|----------------------|---|---------|------|--------------|------------|--------------|---------------------------|
| Sphalerite           | Zn(Fe)S   | 3.5-4.0 | v    | v            | v          | v            |                           |
| Pyrite               | FeS2  | 6.0-6.5 | v    | v            | v          | · <b>v</b> . |                           |
| Chalcopyrite         | CuFeS2  | 3.5-4.0 | v    | v            | v          | v            |                           |
| Galena               | PbS   | 2.5-2.8 | v    | v            | v          | v            |                           |
| Arsenopyrite         | FeAsS   | 5.5-6.0 | v    |              |            | v            |                           |
| Friebergite          | (AgCu)(SbAs)S   | 3.0-4.5 | v    |              |            |              |                           |
| Native silver        | Ag  | 2.5-3.0 |      |              | v          |              |                           |
| Quartz               | SiO2  | 7       | v    | v            | . <b>`</b> | v            |                           |
| Chlorite (Fe,        | Mn)(Al,SiO,OH)  | 6.5     |      |              |            | v            |                           |
| Chalcocite           | Cu <sub>2</sub> S   | 3.5-4.0 |      | v            |            |              |                           |
| Topaz Al             | 2SiO <sub>4</sub> (F,OH) <sub>2</sub>                           | 8       |      |              |            | v            |                           |
| Fluorite             | Ca F <sub>2</sub>   | 4       |      |              |            | v            |                           |
| Cassiterite          | Sn0 <sub>2</sub>  | 6.0-7.0 |      |              | v          | v            |                           |
| Kaolinite A          | 1 <sub>2</sub> Si <sub>2</sub> 0 <sub>5</sub> (0H) <sub>4</sub> | 2.0-2.5 |      |              |            | v            |                           |
| Stannite             |   |         |      |              |            | v            |                           |
| Rutile               | Ti0 <sub>2</sub>  | 6.0-7.0 |      |              |            | v            |                           |
| Carbon               | С   | 1.0-2.0 |      |              | v          |              |                           |
| Polyboron<br>Nitride | (BN) <sub>x</sub>   | 9       |      |              |            |              | v                         |

Materials commonly used as grinding media together with their major and minor elemental components and measure of hardness.

Grinding Major elements Minor elements Measure of Material Hardness

| Plastics <sup>(3)</sup> | с      | -  | 1.5 - 2.0 |
|-------------------------|--------|--|-----------|
| Hardened steel          | Fe     | Cr, Si, Mn, C                            | 5.5 - 6.0 |
| Stainless steel         | Fe,Cr  | Ni, Mn <sup>(1)</sup> , S <sup>(1)</sup> | 5.0 - 5.5 |
| Agate                   | Si     | Al,Na,Fe,K,Ca,Mg <sup>(2)</sup>          | 6.0 - 7.0 |
| Fused zirconia          | Zr     | Si, Hf                                   | 7.0 - 8.0 |
| Alumina ceramic         | Al     | Si, Ca, Mg                               | 8.0 - 9.0 |
| Silicon ceramic         | Si, C  | -  | 8.0 - 9.0 |
| Tungsten carbide        | W,C,Co | Ta, Ti, Nb                               | 8.5 - 9.0 |
| Boron carbide           | B,C    | -  | 9.0 - 9.5 |

- 1. Possibly present
- 2. Usually less than 0.02%
- 3. Polystyrene and Methacrylate

2.3.1.1 First stage grinding process.

A Tema disc mill (51,80) (Tema Machinery Ltd, Oxon, UK) with a tungsten carbide lined chamber and solid tungsten carbide ring and plug grinding elements (Campbell Ltd, Stoke-on-Trent, UK) was used for the initial grinding step. A dry grinding process was used to facilitate representative sub-sampling for the second stage slurry process. Experiments where 100g of ores J+L4 and SA1/Cl20 were ground showed under microscopical examination that after three minutes the maximum particle size had been reduced from 4 mm to  $100 \ \mu\text{m}$  and after 10 minutes most of the material was less than 50  $\mu$ m. Wet sieving analysis of the 10 minute ground ore showed that greater than 90% by mass passed through a 38 µm mesh (J+L4, 8.9% and SA1/Cl20, 3.5% greater than 38 µm). Particle size distributions (Coulter Counter) of the 10 minute ground ores are shown in Figures 2.2. and 2.3. For comparison the particle size distribution of a polyboron nitride sample which had been dry ground for two minutes using the Tema mill is shown in Figure 2.4. The low density of polyboron nitride together with its physical form (thin sheets) restricted the amount ground in one batch to about 20 g.

2.3.1.2. Second stage grinding process.

Two different techniques were used for the combined grinding and slurry preparation stage, (i) the bottle and bead method (40,44,86) and (ii) the microniser method.





<u></u>









2.3.1.3. The bottle and bead method.

A suitable quantity of sample (0.1 to 2 g) is placed in a 30 ml polythene bottle which contains a minimum 10 times weight ratio of 2.5 mm zirconia beads (not less than 10 g used) to sample (fused zirconia beads, Glen Creston, Stanmore, Middx, UK). An aqueous solution of a dispersing agent (<u>e.g.</u> 0.1% m/v sodium hexametaphosphate) is added until the beads are just covered.

The bottle is sealed and shaken using a laboratory flask shaker (Gallenkamp) for the period of time necessary to bring the particle size down to that required (1 to 3 hours). The slurry is washed into a volumetric flask, through a coarse sieve which retains the grinding media, and made up to the mark (e.q. with surfactant solution, 0.1% m/v). The conditions employed in the bottle and bead method were determined from grinding trials on the two ores J+L4 and SA1/C120. The effect on the particle size distribution by varying the grinding time (0 to 3 hours) and concentration (0.1 to 5% m/v) of different surfactants (SHMP, TSPP, TX100) was measured using a Coutler Counter. The results of the trials are shown in Tables 2.3 to 2.9. A graphical representation of the variation in particle size distribution with grinding time for the ore J+L4 is shown in Figure 2.5. Variations of up to +4% by volume in a size range were found between subsequent determinations under the same conditions. Duplicate runs were closer in value.

Figure 2.4 shows the particle size distribution of the polyboron nitride sample before (post 2 minutes grinding on Tema mill) and after a 3 hour grinding period using the bottle and bead method.

Particle size distribution (% volume) of ore J+L4 against grinding time. No dispersant (bottle and bead method)

Grinding time (hours)

| Size range (µm) | 0      | • 0.5 | 1    | 3    |
|-----------------|--------|-------|------|------|
|                 |        |       |      |      |
| up to 2.52      | 17.5   | 26.4  | 34.2 | 48.4 |
| 2.52 - 3.17     | 15.3   | 22.2  | 25.1 | 28.9 |
| 3.17 - 4.0      | 16.3   | 21.1  | 20.0 | 14.5 |
| 4.0 - 5.04      | . 14.0 | 15.6  | 11.9 | 4.2  |
| 5.04 - 6.35     | 12.3   | 9.2   | 5.9  | 1.1  |
| 6.35 - 8.0      | 9.5    | 3.7   | 1.5  | 0.3  |
| 8.0 - 10.08     | 7.4    | 1.1   | 0.3  | 0    |
| 10.08 - 12.7    | 4.0    | 0.4   | 0.2  | 0    |
| 12.7 - 16.0     | 2.4    | 0.4   | 0    | 0    |
| 16.0 - 20.16    | 0.9    | 0     | 0.3  | 0    |
| 20.16 - 25.4    | 0.3    | 0     | 0    | 0    |

Particle size distribution (% volume) of ore J+L4 against grinding time. 0.1% (m/v) sodium hexametaphosphate dispersant (bottle and bead method)

Grinding time (hours)

| Size range (µm) | 0    | 0.5  | 1    | 2    | 3     |
|-----------------|------|------|------|------|-------|
| up to 2.52      | 16.7 | 23.0 | 33.3 | 35.0 | 44.2  |
| 2.52 - 3.17     | 17.2 | 21.9 | 27.0 | 29.2 | 29.3  |
| 3.17 - 4.0      | 19.8 | 23.4 | 22.8 | 21.2 | 17.2  |
| 4.0 - 5.04      | 17.3 | 16.8 | 11.3 | 9.7  | 6.5   |
| 5.04 - 6.35     | 13.4 | 8.6  | 3.6  | 3.1  | 1.5   |
| 6.35 - 8.0      | 8.1  | 3.3  | 0.9  | 0.8  | 0.3   |
| 8.0 - 10.08     | 5.2  | 1.3  | 0.3  | 0.3  | 0.3   |
| 10.08 - 12.7    | 2.6  | 0.6  | 0.3  | 0.3  | 0     |
| 12.7 - 16.0     | 0.9  | 0.8  | 0.3  | 0.5  | (0.6) |
| 16.0 - 20.16    | 0    | 0.3  | 0.2  | 0    | 0     |
| 20.16 - 25.4    | 0    | 0.1  | 0    | 0    | 0     |

Particle size distribution (% volume) of ore J+L4 after 3 hour grind against concentration of dispersant (bottle and bead method)

% m/v sodium hexametaphosphate dispersant

.

| Size range (µm) | 0    | 0.1  | 5    |
|-----------------|------|------|------|
| up to 2.52      | 48.4 | 44.2 | 50.2 |
| 2.52 - 3.17     | 28.9 | 29.3 | 29.4 |
| 3.17 - 4.0      | 14.5 | 17.2 | 13.2 |
| 4.0 - 5.04      | 4.2  | 6.5  | 3.0  |
| 5.04 - 6.35     | 1.1  | 1.5  | 0.6  |
| 6.35 - 8.0      | 0.3  | 0.3  | 0.2  |
| 8.0 - 10.08     | 0    | 0.3  | 0    |

.

Particle-size distribution (% volume) of ore SA1/C120 with grinding time. No dispersant (bottle and bead method)

Grinding time (hours)

| Size range (µm) | 0    | 0.5   | 1    |
|-----------------|------|-------|------|
| up to 2.52      | 8.9  | 15.8  | 19.9 |
| 2.52 - 3.17     | 9.0  | 16.0  | 20.7 |
| 3.17 - 4.0      | 12.7 | 19.3  | 23.3 |
| 4.0 - 5.04      | 11.7 | 18.0  | 18.5 |
| 5.04 - 6.35     | 11.0 | 15.1  | 11.4 |
| 6.35 - 8.0      | 10.3 | 9.1   | 4.7  |
| 8.0 - 10.08     | 11.7 | . 5.2 | 1.3  |
| 10.08 - 12.7    | 10.1 | 1.3   | 0.3  |
| 12.7 - 16.0     | 7.0  | 0.2   | 0    |
| 16.0 - 20.16    | 5.2  | 0     | 0    |
| 20.16 - 25.4    | 2.0  | 0     | 0    |
| 25.4 - 32.0     | 0.3  | 0     | 0    |

Particle size distribution (% volume) of ore SAl/Cl2O against grinding time. 0.1% (m/v) sodium hexametaphosphate dispersant (bottle and bead method)

# Grinding time (hours)

| Size range (µm) | 0    | 0.5  | 1    | 2     | 3     |
|-----------------|------|------|------|-------|-------|
| up to 2.52      | 11.0 | 13.0 | 18.8 | 28.6  | 37.0  |
| 2.52 - 3.17     | 12.8 | 14.8 | 20.3 | 27.6  | 30.8  |
| 3.17 - 4.0      | 17.5 | 20.2 | 24.0 | 23.7  | 23.2  |
| 4.0 - 5.04      | 17.2 | 19.9 | 19.6 | 13.3  | 8.2   |
| 5.04 - 6.35     | 15.8 | 16.0 | 11.5 | 5.3   | 1.8   |
| 6.35 - 8.0      | 12.0 | 9.5  | 4.3  | 1.2   | 0.2   |
| 8.0 - 10.08     | 9.4  | 4.9  | 1.3  | 0     | 0     |
| 10.08 - 12.7    | 3.5  | 1.3  | 0.1  | 0     | 0     |
| 12.7 - 16.0     | 0.7  | 0.4  | 0.2  | (0.4) | (0.4) |
| 16.0 - 20.16    | 0    | 0    | 0    | 0     | 0     |

.

Particle size distribution (% volume) of ore SA1/C120 with grinding time. 1% m/v sodium hexametaphosphate dispersant (bottle and bead method).

Grinding time (hours)

| Size range (µm) | 0     | 1    | 3     |
|-----------------|-------|------|-------|
|                 |       |      |       |
| up to 2.52      | 7.5   | 19.1 | 32.2  |
| 2.52 - 3.17     | 8.6   | 21.3 | 30.2  |
| 3.17 - 4.0      | 12.5  | 23.7 | 23.5  |
| 4.0 - 5.04      | 12.3  | 18.9 | 10.4  |
| 5.04 - 6.35     | 11.7  | 10.9 | 2.7   |
| 6.35 - 8.0      | 10.6  | 4.0  | 0.39  |
| 8.0 - 10.08     | 10.8  | 1.1  | 0     |
| 10.08 - 12.7    | 8.5   | 0.2  | • 0   |
| 12.7 - 16.0     | 7.0   | 0.3  | (0.5) |
| 16.0 - 20.16    | 4.7   | 0.2  | 0     |
| 20.16 - 25.4    | . 3.9 | 0.2  | 0     |
| 25.4 - 32.0     | 1.3   | 0    | 0     |
TABLE 2.9

Particle size distribution (% volume) of ore SAl/Cl20 after 1 hour grind against concentration of various dispersants (bottle and bead method)

| Dispersant*                      | NONE           | SHMP | SHMP | SHMP | TX100 | TX100 | TSPP | TSPP |
|----------------------------------|----------------|------|------|------|-------|-------|------|------|
| % m∕v Dispersa                   | nt O           | 0.1  | 1    | 5    | 0.1   | 1     | 0.1  | 1    |
| Size range (µm                   | )              |      |      |      |       |       |      |      |
|                                  |                |      |      |      |       |       |      |      |
| up to 2.52                       | 19.9           | 18.8 | 19.1 | 15.6 | 20.3  | 13.5  | 19.8 | 19.4 |
| 2.52 - 3.17                      | 20.7           | 20.3 | 21.3 | 21.0 | 22.9  | 17.1  | 23.5 | 22.9 |
| 3 <b>.</b> 17 <sup>′</sup> - 4.0 | 23.3           | 24.0 | 23.7 | 24.3 | 21.5  | 21.6  | 23.8 | 23.6 |
| 4.0 - 5.04                       | 18.5           | 19.6 | 18.9 | 20.1 | 17.1  | 20.9  | 18.4 | 18.7 |
| 5.04 - 6.35                      | 11.4           | 11.5 | 10.9 | 12.4 | 11.1  | 15.6  | 10.0 | 10.7 |
| 6.35 - 8.0                       | 4.7            | 4.3  | 4.0  | 5.3  | 4.8   | 8.1   | 3.5  | 3.8  |
| 8.0 - 10.08                      | 1.3            | 1.3  | 1.1  | 1.4  | 1.9   | 2.8   | 0.7  | 0.7  |
| 10.08 - 12.7                     | 0.3            | 0.1  | 0.2  | 0    | 0.4   | 0.5   | 0.2  | 0.1  |
| 12.7 - 16.0                      | 0              | 0.2  | 0.3  | 0    | 0.1   | 0     | 0    | 0    |
| 16.0 - 20.16                     | 0              | 0    | 0.2  | 0    | 0     | 0     | 0    | 0    |
| 20.16 - 25.4                     | <sup>-</sup> 0 | 0    | 0.2  | 0    | 0     | 0     | 0    | 0    |

\*SHMP, sodium hexametaphosphate, anionic surfactant TX100, Triton X100, non-ionic surfactant TSPP, tetrasodium pyrophosphate, anionic surfactant





By volume particle size distributions of BP sulphide ore, J+L4,

Size reduction and slurry preparation, using the post Tema mill-ground ores has also been performed with a McCrone micronising mill (48,56,80, 81,86) (McCrone Research Associates Ltd, London, UK). The grinding vessel consists of a 125 ml capacity polypropylene jar fitted with a screw-capped polythene closure. The jar is packed with an ordered array of identical cylindrical grinding elements made of agate (chromium stabilised alumina are also available). A suitable quantity of ore (0.1 -2 g) is admitted to the jar which contains 15 ml of a solution of surfactant e.g. 0.1% m/v sodium hexametaphosphate. After sealing, the jar is clamped in the McCrone process timer and vibrated for a period necessary to bring the particle size down to the range required (10 to 30 minutes). The particle size distribution of the slurried ore SA1/C120 with grinding time (Microniser with agate elements) is shown in Table 2.10. For comparison the particle size distribution of the mineralised rocks KCla and MPla before and after grinding for 30 minutes using the microniser are shown in Table 2.11.

#### 2.4 DISCUSSION AND CONCLUSIONS

The grinding media used in all the comminution experiments were chosen for their properties of hardness, durability, grinding efficiency and chemical composition. Tungsten carbide has a measure of hardness (MOH) of over 8.5, a high resistance to abrasion, is long wearing and very efficient. The major elemental components are tungsten, carbon and cobalt (present as binder). Minor to trace impurities present are tantalum, titanium and niobium.Fused zirconia has a MOH of over 7.5, a resistance to abrasion not as high as tungsten carbide although still long wearing. The major constituents (100) are zirconium, silicon (as

Particle size distribution (% volume) of ore SA1/C120 against grinding time. 0.1% (m/v) sodium hexametaphosphate dispersant (microniser grinding method with results from bottle and bead method for comparison).

|                 | Microniser grinding |          |      | Bottle and bead method |                |  |  |
|-----------------|---------------------|----------|------|------------------------|----------------|--|--|
|                 | time (n             | ninutes) |      | grinding               | time (minutes) |  |  |
| Size range (µm) | 0                   | 10       | 30   | 30                     | 240            |  |  |
| 0.63 - 0.79     | 1.6                 | 4.6      | 12.8 |                        | 14.5           |  |  |
| 0.79 - 1.0      | 2.3                 | 6.5      | 14.2 |                        | 18.2           |  |  |
| 1.0 - 1.26      | 3.0                 | 9.9      | 20.5 |                        | 26.1           |  |  |
| 1.26 - 1.58     | 3.9                 | 10.7     | 21.1 |                        | 24.0           |  |  |
| 1.58 - 2.0      | 5.0                 | 11.2     | 16.3 |                        | 13.3           |  |  |
| 2.0 - 2.52      | 5.3                 | 10.2     | 8.3  | 13.0                   | 3.4            |  |  |
| 2.52 - 3.17     | 5.0                 | 11.7     | 5.0  | 14.8                   | 0.6            |  |  |
| 3.17 - 4.0      | 5.9                 | 11.6     | 1.8  | 20.2                   | • 0            |  |  |
| 4.0 - 5.04      | 6.0                 | 10.3     | 0.4  | 19.9                   |                |  |  |
| 5.04 - 6.35     | 6.1                 | 7.0      | 0    | 16.0                   |                |  |  |
| 6.35 - 8.0      | 6.7                 | 3.9      |      | 9.5                    |                |  |  |
| 8.0 - 10.08     | 6.8                 | 1.6      |      | 4.9                    |                |  |  |
| 10.08 - 12.7    | 7.2                 | 0.5      |      | 1.3                    |                |  |  |
| 12.7 - 16.0     | 7.7                 | 0.2      |      | 0.4                    |                |  |  |
| 16.0 - 20.16    | 7.3                 | 0.2      |      | 0                      |                |  |  |
| 20.16 - 25.4    | 7.6                 | 0.1      |      |                        | -              |  |  |
| 25.4 - 32.0     | 6.4                 | 0        |      |                        |                |  |  |
| 32.0 - 40.32    | 3.2                 |          |      |                        |                |  |  |
| 40.32 - 50.8    | 2.4                 | -        |      |                        |                |  |  |
| 50.8 - 64.0     | 0.6                 |          |      |                        |                |  |  |
| 64.0 - 80.6     | 0                   |          |      |                        |                |  |  |

Particle size distributions (% volume) of mineralised ores KCla and MPla as received, after 30 minutes grinding using the microniser method and after 4 hours using the bottle and bead method (B+B). 0.1% m/v sodium hexametaphosphate dispersant

## SAMPLE

|        |    | ·        |          | <u>KCla</u> |         | MPla     |            |         |  |  |
|--------|----|----------|----------|-------------|---------|----------|------------|---------|--|--|
|        |    |          | As       | 30 minutes  | 4 hours | As       | 30 minutes | 4 hours |  |  |
|        |    |          | received | microniser  | B+B     | received | microniser | B+B     |  |  |
| Size ı | ra | nge (µm) | )        |             |         |          |            |         |  |  |
| 0.63   | -  | 0.79     |          | 13.7        | 31.2    |          | 15.5       | 30.8    |  |  |
| 0.79   | -  | 1.0      |          | 13.7        | 21.3    |          | 15.5       | 22.3    |  |  |
| 1.0    | -  | 1.26     |          | 17.7        | 18.1    | ·        | 20.0       | 19.2    |  |  |
| 1.26   | -  | 1.58     |          | 17.2        | 10.7    |          | 18.5       | 12.1    |  |  |
| 1.58   | -  | 2.0      |          | 12.8        | 6.6     |          | 13.9       | 7.7     |  |  |
| 2.0    | -  | 2.52     | 6.3      | 7.3         | 3.0     | 5.5      | 7.8        | 4.0     |  |  |
| 2.52   | -  | 3.17     | 8.3      | 5.2         | 2.3     | 6.6      | 4.9        | 2.8     |  |  |
| 3.17   | -  | 4.0      | 12.8     | 2.4         | 1.5     | 10.1     | 2.8        | 1.1     |  |  |
| 4.0    | -  | 5.04     | 13.2     | 1.1         | 0.7     | 10.5     | 1.5        | 0.5     |  |  |
| 5.04   | -  | 6.35     | 13.4     | 1.0         | 0.6     | 11.3     | 0.1        | 0.3     |  |  |
| 6.35   | -  | 8.0      | 12.1     | 0.5         | 2.6     | 11.1     | 0          | 0       |  |  |
| 8.0    | -  | 10.08    | 12.3     | 1.8         | 2.1     | 12.8     |            |         |  |  |
| 10.08  | -  | 12.7     | 9.5      | 4.7         | 3.1     | 10.3     |            |         |  |  |
| 12.7   | -  | 16.0     | 5.6 ·    | 1.6         | 0       | 8.8      |            |         |  |  |
| 16.0   | -  | 20.16    | 3.9      |             |         | 5.7      |            |         |  |  |
| 20.16  | -  | 25.4     | 0.9      |             |         | 4.8      |            |         |  |  |
| 25.4   | -  | 32.0     | 1.6      |             |         | 2.0      |            |         |  |  |
| 32.0   | -  | 40.32    | 0.2      |             |         | 1.5      |            |         |  |  |
| 40.32  | -  | 50.16    | 0.9      |             |         | 0        |            |         |  |  |

silica) and nickel. Minor to trace levels of aluminium, iron, titanium, magnesium and boron are also present. Agate has a MOH of 7, a very high resistance to abrasion and is very long wearing. The major elemental component is silicon (as silica) with minor impurities of aluminium, sodium, iron, potassium, calcium and magnesium (all normally less than 0.02%).

It can be seen from Figures 2.2 to 2.4 that the tungsten carbide Tema disc mill is an efficient instrument to use where a sample requires a first stage dry grind to allow representative sub-sampling for subsequent slurry preparation. The size reduction of a starting sample from one of many millimetres in dimensions down to less than 40  $\mu$ m in a matter of minutes illustrates this efficiency (two minute period for the ceramic polyboron nitride, Figure 2.4, and 10 minutes for the siliceous sulphide ores, Figures 2.2 and 2.3) While contamination from the tungsten carbide chamber is minimal it is possible to utilise the coating of the walls and grinding elements, by the sample, as a sacrificial protective covering, <u>i.e.</u> the material adhering to the walls and elements is not used in the analysis. It is also of note that when good seals are present on the Tema chamber it is possible to wet grind samples.

The result from the 'bottle and bead' method grinding trials (Tables 2.3 to 2.9) show that:

- (i) the particle size of an ore decreases with increasing grinding time;
- (ii) the presence of a dispersing agent during grinding does not significantly change the particle size distribution;

(iii) a grinding period of two to three hours is necessary for the maximum particle size to be reduced to 8 µm.

The two ores J+L4 and SA1/C120 are hydrophylic and do not display the immediate effect of flocculation in the absence of a dispersing agent. The presence of a surfactant does, however, stabilize the suspension. With time the slurry particles settle 'hard' (agglomerate) which results in a shift of the distribution towards a larger particle size when redispersed (Table 2.12). The presence of 0.1% m/v sodium hexametaphosphate in a slurry hinders this effect and up to 5 day old slurries can be redispersed (using ultrasonics) to show little or no change from the original particle size distribution (Table 2.13).

It can be seen from the distribution of the three hour ground polyboron nitride sample (Figure 2.4) that this harder, smooth material was not as efficiently ground as the ores and rocks in the same time period. An appreciable amount of material above 8  $\mu$ m (24% by volume) still remained. It might be expected that a sufficiently high collision frequency between the sample of polyboron nitride and a suitable grinding medium given a high enough momentum will greatly improve the efficiency of grinding. Hence the use of tungsten carbide balls in a plastic container may overcome this problem in size reduction.

The results from the microniser method (Tables 2.10 and 2.11) show this technique to be not only efficient for the size reduction of ores and rocks (greater than 97% less than 8  $\mu$ m in a 10 minute grinding period for SA1/C120) but also more efficient, on a time basis, than the bottle and bead method (Tables 2.10 and 2.11). A four hour grinding period using the bottle and bead method is required in order to show a finer

distribution than a 30 minute grinding period using the microniser. For comparison McCurdy <u>et al.</u> (56) reduced a coal sample to a median particle diameter of 5.7  $\mu$ m in a 10 minute period using the McCrone microniser.

Table 2.13 also shows the particle size distribution of the month old micronised ore SA1/C120 after redispersion using ultrasonics as part of the stability testing programme. Little change has taken place in this time period.

It is of note that there is evidence to suggest the efficiency of the grinding technique is dependent upon the slurry load, <u>i.e.</u> as the solid load increases (0.1 up to 2 g) the efficiency of the grinding process decreases. Whilst this is not so marked in the microniser method it is obvious when using the bottle and bead method. This effect can be explained when the collision frequency for a particle being ground is considered. Knowing the ratio of grinding beads to sample and as not less than 10 g of beads is employed, when the sample weight is varied from 0.1 to 1 g the ratio changes from 100 down to 10, hence a 0.1 g sample is ground more efficiently than a 1 g sample. While contamination of a ground sample by the grinding elements can be gauged if prior compositional knowledge is available for both, the extent to which contamination has occured depends upon a number of factors and requires an analytical step for quantification. This topic is considered in Chapter 7 of this thesis.

47.

Particle size distributions (% volume) of ore SA1/C120 and soil SO-1 in water (no dispersant) after being ground using the bottle and bead method and when redispersed after stated time period (stability tests).

#### SLURRY SAMPLE

Size range (µm) SA1/C120

S0-1

|             | l hour old | 3 weeks old | l hour old | 3 weeks old |
|-------------|------------|-------------|------------|-------------|
|             | % ∨o       | olume       | % vol      | ume         |
| 0.63 - 0.79 | 1.9        | 0           | 30.6       | 29.0        |
| 0.79 - 1.0  | 3.6        | 0.3         | 21.5       | 19.0        |
| 1.0 - 1.26  | 11.2       | 3.1         | 19.4       | 17.0        |
| 1.26 - 1.58 | 24.8       | 8.6         | 13.7       | 10.2        |
| 1.58 - 2.0  | 32.4       | 17.1        | 8.5        | 5.6         |
| 2.0 - 2.52  | 18.8       | 23.3        | 3.2        | 3.0         |
| 2.52 - 3.17 | 5.1        | · 28.8      | 2.1        | 2.4         |
| 3.17 - 4.0  | 1.1        | 17.0        | 1.0        | 2.2         |
| 4.0 - 5.0   | 0          | 3.0         | 0          | 2.6         |
| 5.0 - 6.35  |            | 0.3         |            | 3.4         |
| 6.35 - 8.0  |            | 0           |            | 3.4         |
| 8.0 -10.08  |            |             |            | 2.0         |

TABLE 2.12

# TABLE 2.13

Particle size distributions(% volume) of ores SAl/Cl20 and J+L4 (dispersed in 0.1 % m/v SHMP solution) after being ground using the bottle and bead and microniser methods and when redispersed after stated time period (stability tests).

|                 | Bot    | tle and i | bead meth | od     | Microni | ser method |
|-----------------|--------|-----------|-----------|--------|---------|------------|
|                 | J      | +L4       | SA1       | /C120  | SA1     | /C120      |
| Size range (µm) | l hour | 3 days    | l hour    | 5 days | l hour  | l month    |
|                 | old    | old       | old       | old    | old     | old        |
| up to 2.52      | 37.0   | 36.9      | 25.9      | 24.6   | 21.0    | 18.9       |
| 2.52 - 3.17     | 29.1   | 28.7      | 26.1      | 27.4   | 21.9    | 23.1       |
| 3.17 - 4.0      | 19.4   | 19.6      | 23.5      | 23.9   | 21.9    | 25.1       |
| 4.0 - 5.04      | 8.5    | 8.7       | 14.5      | 14.7   | 21.9    | 18.6       |
| 5.04 - 6.35     | 2.9    | 2.7       | 6.0       | 6.0    | 7.0     | 9.3        |
| 6.35 - 8.0      | 0.6    | 0.9       | 1.5       | 1.6    | 3.9     | 3.0        |
| 8.0 - 10.08     | 0.5    | 0.4       | 0.7       | 0.4    | 1.6     | 0.9        |
| 10.08 - 12.7    | 0.5    | 0.6       | 0.4       | 0.3    | 0.5     | 0.6        |
| 12.7 - 16.0     | 0      | 0         | 0         | 0      | 0.2     | 0.5        |
|                 |        |           |           |        |         |            |

#### CHAPTER 3

#### TRANSPORTATION PHENOMENA

#### 3.1 INTRODUCTION

The most widely used method for transporting an analyte to a plasma is as a solution aerosol. This is formed by a nebuliser, carried through a spray chamber by an argon gas flow and directed to the central channel of the plasma by an injector tube (as part of the torch assembly). It has been stated that this sample introduction system is the "Achilles' heel" of atomic spectroscopy (89) and that without a sound framework of fundamental knowledge concerning the physical production and transfer processes involved with aerosols substantial improvements in accuracy, precision and detection limits are unlikely to be made.

Several workers have measured the aerosol droplet size having passed through the sample introduction system (SIS) (55,86,96,101,102,103,104) and distributions with maxima in the range 1 to 10 µm are found for a variety of combined nebuliser and spray chamber designs. It is evident from the literature that each SIS produces a different aerosol distribution which is also dependent upon the gas and liquid flow rates used. Fewer workers have studied the size range of slurry particles that exit from an injector tube of the SIS (55,68,82,83,86) but there is evidence that the bore size of the injector affects the solids distribution (82,86). Because simple solutions are used as standards for calibration in the slurry technique, it is obvious that a sound framework of fundamental knowledge concerning the physical production and transfer processes of slurry aerosols in the SIS is also necessary.

## 3.2 THE SAMPLE INTRODUCTION SYSTEM (SIS)

The sample introduction system for the production and transportation of liquid aerosols comprises a nebuliser, spray chamber and injector. A variety of nebulisers are available, e.g. concentric (105), cross flow (105), Babington (105), frit (106), Ultrasonic (107), and thermospray (108), and use of a particular design is primarily determined by sample compatibility (101). A review by Sharp (109) outlines the analytical properties of the above series of nebulisers as a guide for their use. The nebuliser credited with superior salt and particle tolerance, while maintaining comparable powers of detection to those of the concentric and cross flow designs is that of the Babington design (105). Most workers with slurries use a modified Babington-type nebuliser of the V-groove design (58, Figure 3.1) or modified cross flow nebuliser. As little or no venturi effect is present at the liquid exit orifice, solution and slurry samples are fed to the nebulisers by a peristaltic pump. Homogeneity of the slurry suspensions is maintained by a magnetic stirrer and bar (or, if paramagnetic materials are present or suspected, a top stirrer can be used).

While spray chamber designs are many and numerous (82), commercially available chambers are fewer in number. The most commonly used designs are the Scott-type double pass spray chamber (DPSC), Figure 3.6, the single pass spray chamber (a conical design without an impact bead is shown in Figure 3.9), and the cyclone or vortex spray chamber(58). The injector completes the sample introduction system and itself comes in a variety of designs, <u>e.g.</u> straight, taper and jet.



Diagram of the Ebdon V-groove nebuliser.



3.2.1. The Physical Processes within the Sample Introduction System

While the reviews by Sharp discuss the primary aerosol formation (105) and the transport process (109) in detail, it is also of interest to consider the approaches taken by Browner <u>et al.</u> (110) and Gustavsson (111). Although not as rigorous as Sharp, the equations used to describe the aerosol loss processes in the spray chamber allow order of magnitude calculations to be made with respect to particle size. Many of the processes can be described mathematically when the system is known to be in laminar or streamline flow (105).

A gas flowing through a pipe is said to be in laminar flow when the Reynolds number,  $R_e$ , is less than 2000 (105) and the flow is characterised by viscous or shear forces.

$$R_{e} = \frac{P_{g} V_{g} d_{p}}{\eta_{g}}$$
(3.1)

where  $P_g$  and  $M_g$  are the density and viscosity of the gas, dp is the pipe diameter and  $V_g$  the velocity of the gas. Particle Reynolds numbers  $R_{ep}$ should be less than one (preferably below 0.2) for non-turbulent laminar flow conditions to be considered at the gas/liquid drop interface. For  $R_{ep}$  calculations the terms become: dp the particle diameter and  $V_p$  the particle velocity (relative).

A schematic representation of the particle formation and loss processes for the sample introduction system is shown in Figure 3.2.

## FIGURE 3.2

Schematic representation of the possible aerosol motion and loss mechanisms in spray chambers.



#### **AEROSOL PROCESS**



The primary aerosol is produced by the nebuliser and in the case of the Babington design is a result of a liquid film being ruptured and accelerated as it spreads over a small (200 to 300  $\mu$ m) orifice through which gas is issuing at high velocity (200-300 m s<sup>-1</sup>). The aerosol as formed is in a turbulent gas flow region and the mechanisms of droplet formation are not well understood. An empirical approach to the estimation of the mean droplet diameter formed from a pneumatic nebuliser is given by the Nukiyama-Tanasawa equation (110) shown in equation 3.2.

$$d_{s} = \frac{585}{V} \left[ \frac{\sigma}{P} \right]^{0.5} + 597 \left[ \frac{\eta}{(\sigma P)^{0.5}} \right]^{0.45} \left[ \frac{10^{3} \varrho_{1}}{\varrho_{q}} \right]^{1.5}$$
(3.2)

Where  $d_s$  is the Sauter median (volume to surface area ratio) diameter ( $\mu$ m), V is the velocity difference between gas and liquid flows to the nebuliser ( $ms^{-1}$ ),  $\sigma$  is the surface tension of the liquid (dyn cm<sup>-1</sup>), P the liquid density (g cm<sup>-3</sup>),  $\eta$  the liquid viscosity (P) and  $Q_1$  and  $Q_g$  are the volume flow rates of liquid and gas (cm<sup>3</sup> s<sup>-1</sup>) respectively.

Equation 3.2 was developed for the concentric design nebuliser using subsonic gas velocities and liquids of surface tension 30 to 73 dyn cm<sup>-1</sup> and viscosity 1 to 30 cP. At high gas velocities (those encountered in analytical nebulisers) the first term in the equation predominates.

3.2.3 Aerosol Modification and Loss Processes in the Spray Chamber

Containment of the primary aerosol within a spray chamber results in a modification of the aerosol particle size distribution. The process of secondary fragmentation by the inclusion of an impact bead in the chamber is described by Sharp (109) but for slurry work the bead is

generally omitted as fragmentation is not preferred (unless a reduction of the solvent load is required).

A summary of the possible aerosol modification and loss processes occuring in a spray chamber is given in Table 3.1.

As previously stated, a lack of knowledge of the local field gas flows within a spray chamber means that the degree of turbulence and hence particle penetration factors are not known and calculations based on turbulent impaction/diffusion losses are extremely tentative <u>e.g.</u> particles above 5 to 6  $\mu$ m in size will be removed if a 60  $\mu$ m thick viscous sublayer exists next to the spray chamber wall assuming a transverse friction flow of 1 m s<sup>-1</sup> (109).

Under laminar flow conditions a centrifugal motion, which is present in reverse flow chambers, imparted to aerosol particles results in losses to a certain particle size (50% penetration), the relationship of which is given by equation 3.3 (112).

$$d_{c50} = \left[\frac{9 \text{ N} \text{W}_{i}}{2 \pi \text{ N} \text{V}_{i}(\text{P}_{i} - \text{P}_{g})}\right]^{1/2}$$
(3.3)

where  $d_{c50}$  is the particle diameter,  $\eta$  and  $\rho_{g}$  are the viscosity and density of the gas,  $\rho_{l}$  the density of the aerosol liquid,  $W_{i}$  the inlet width,  $V_{i}$  the inlet gas velocity and n the number of revolutions by the aerosol. For particles obeying Stokes law, <u>i.e.</u>  $R_{ep} < 1$  or if the particle number Kp < 3.3 (109,111), which is given by

$$Kp = d[g P_g (P_1 - P_g) / \eta^2]^{1/3}$$
(3.4)

where d is the particle diameter, g the gravitational acceleration,  $\rho_g$  and  $\rho_l$  the densities of the gas and liquid aerosol respectively and  $\eta$ 

# TABLE 3.1

A summary of the possible aerosol formation and loss processes occuring in a spray chamber (SC)

• •

| Particle Formation<br>Process                                | Particle Size Range<br>Involved  | Mechanism of Process  |
|--|--|---|
| Primary formation -<br>nebuliser                             | Large, medium and small particles formed                                   | Rupture of liquid<br>film. Shattering /<br>necking                                |
| Secondary formation -<br>impact bead                         | Large particles formed<br>Small particles formed<br>Small particles formed | Renebulisation<br>Particle bounce /<br>necking<br>Fragmentation                   |
| Coagulation  | Large and small particles<br>form larger particles                         | Diffusion, velocity<br>and accelerative<br>gradients. Bipolar<br>electrification. |
| Particle loss process  |  |   |
| Inertial deposition -<br>impact bead + SC end<br>wall        | Large ballistic and some<br>medium sized particles<br>lost                 | Flow line<br>interception   |
| SC side and end wall   | Medium and small sized<br>particles lost                                   | Turbulent and<br>recirculatory<br>diffusion                                       |
| SC side walls  | Large particles lost   | Centrifugation  |
| SC walls   | Large particles lost   | Gravitational<br>settling   |
| Evaporation  | Mainly small particles<br>decreasing contribution<br>as size increases     | Surface free energy<br>of small particles   |
| Note: Small particles<br>Medium particles<br>Large particles | l μm and less<br>l μm to 20 μm<br>above 20 <b>μ</b> m .                    |   |

is the gas viscosity, then the gravitational settling diameter  $d_{TV}$  for a particle travelling, in a gas, with a relative velocity  $V_{T}$  (terminal velocity) is given by equation 3.5 (110).

$$d_{TV} = \left[\frac{V_T \, 18 \, n}{(P_p - P_g)g}\right]^{1/2}$$
(3.5)

The 50% cut-off diameter,  $d_{c50}$  for a particle settling in a tube of diameter D is given by (110)

$$d_{c50} = 3 \left[ \frac{h D}{P_p g t} \right] \frac{1}{2}$$
(3.6)

where  $\eta$  is the viscosity of the gas,  $P_p$  is the density of the aerosol particle, g the acceleration due to gravity and t the residence time of the particle in the tube.

The particle stopping distance,  $l_s$ , under laminar flow conditions is Stokes dependent and respresents the distance required for a particle of diameter 2a travelling at velocity  $V_p$  to come to rest when directed into a static gas layer (viscous sublayer at spray chamber wall) (109).

$$l_{s} = \frac{2}{9} \frac{a^{2} P_{p} V_{p}}{h}$$
 (3.7)

where  $\mathbf{P}_{\mathbf{p}}$  is the aerosol particle density,  $\mathbf{n}$  the gas viscosity and  $\mathbf{a}$  the particle radius.

3.3 THE MEASUREMENT OF SOLUTION AND SLURRY AEROSOLS

Solution and slurry aerosols can be measured by two different approaches :

 Non-intrusive methods such as laser diffraction or scattering, and (ii) intrusive methods, such as cascade impaction, electrostatic precipitation, gel collection, salt collection and, in the case of slurries, filtration and bottle collection.

Slurry aerosol particles exhibit many of the physical properties of solution aerosols, <u>i.e.</u> they are essentially an aqueous (or liquid) envelope transporting a mass under pneumatic conditions, but differ from solutions in that the mass is contained in the solid phase as small primary particles.

3.3.1 Non-Intrusive Laser Measuring Methods

The measurement of solution aerosols from a sample introduction system (SIS) has been performed by laser techniques for a number of years by several workers (55,56,86,96,101,109), although little has been reported on the measurement of slurry aerosols by this technique (86).

Laser diffraction methods are mainly based upon measurements of the forward diffracted light from a disperse suspension. The angle of diffraction is inversely proportional to the particle size and the intensity of the diffracted beam at any angle is a measure of the mean projected areas of particles of a specific size. The theory is given by Talbot (113). The Malvern instrument employed in the experiments described in section 3.4.1 is essentially based on the above principle and is described by Allen (94). It is of note that the instrument. covers the particle size range 2 to 200  $\mu$ m, with an estimate below 1.2  $\mu$ m based on a % mass distribution.

The theory behind the Aerometrics phase Doppler shift laser analyser, which was used in the experiments described in section 3.4.2, is beyond the scope of this chapter, but is discussed in a series of papers the most recent of which is (114). The instrument uses a combination of particle size interferometry and Doppler phase shift velocimetry from a dual cross beam laser analyser/detector system in order to characterise aerosols in the size range 1  $\mu$ m up to 3mm and velocities up to 100 m s<sup>-1</sup>. The system allows the collection of population count data in 50 channels each covering 0.74  $\mu$ m width with a lower range of 1  $\mu$ m to 37  $\mu$ m. Velocity-population, size-population and velocity-size distributions are available forms of data output.

#### 3.3.2 Intrusive Measuring Methods

The intrusive aerosol measuring techniques mentioned in section 3.3 have been used by a number of workers <u>e.g.</u> cascade impaction (102,103), electrostatic precipitation (103), aerosol in gel collection (104), salt particle collection (115), with varying degrees of success. For slurry aerosols the filtration technique (68) and the aerosol trap or bottle collection technique (82,83,86) have been used to assess the size range of the solid particles carried by the aqueous envelope.

The cascade impactor (Figure 3.3, reference 94) used in the experiments described in section 3.5 was of the Andersen stack sampler design. The sampler contains nine jet plates each having a pattern of precision drilled orifices. The nine plates, separated by 2.5 mm inconel 0-ring spacers, divide the sample into eight fractions or particle size ranges. The jets on each plate are arranged in concentric circles which are offset on each succeeding plate. The size of the orifices is the same on a given plate but is smaller for each succeeding downstream

Diagram of the Andersen Cascade impactor.



Therefore, as the sample is drawn through the sampler at a plate. constant flow rate the jets of gas flowing through any particular plate direct the particulates toward the collection area on the downstream plate directly below the circles of jets on the plate above. Since the jet diameters decrease from plate to plate the velocities increase such that whenever the velocity imparted to a particle is sufficiently great its inertia will overcome the aerodynamic drag of the turning airstream and the particle will be impacted on the collection surface. Otherwise, the particle remains in the airstream and proceeds to the next plate. Since the particle deposit areas are directly below the jets. seven of the plates act as both jet stage and collection plate. Thus, the first plate is only a jet stage and the last plate is only a collection plate. Calibration of the sampler is referenced to unit density (1 g cm<sup>-3</sup>) spherical particles so that the aerodynamically equivalent sized particles collected on each stage are always identical for any given flow range. For this reason a sample containing a mixture of shapes and densities is fractionated and collected according to its aerodynamic characteristics and is aerodynamically equivalent in size to the unit density spheres collected on each specific stage during calibration.

Aerosols are drawn into the stack sampler by means of a vacuum line which is connected to the outlet of the impactor stack. The draw is set and metered in order to isokinetically sample the aerosol <u>i.e.</u> to match the velocity of the air being drawn at the inlet nozzle with the gas carrying the aerosol. For a gas issuing from an injector of diameter  $d_i$  at a flow rate  $Q_i$  the velocity matching flow rate for the

cascade impactor  $Q_{c}$  with an inlet nozzle of diameter d<sub>c</sub> is given by equation 3.8.

$$Q_c = Q_i d_c^2 / d_i^2$$
 (3.8)

Calibration tables supplied with the impactor allow the particle size fraction collected on each collection plate to be calculated for a specific flow rate  $Q_c$ .

The bottle collection technique, used in the experiments described in section 3.5, is based upon the channelling of aerosol slurry particles into a small bottle containing a small quantity of an aqueous solution of 0.1% m/v SHMP to maintain dispersion of the solid slurry particles collected. Particle sizing is then performed, for example by a Coulter Counter.

# 3.4 THE MEASUREMENT OF AEROSOL DROPLET SIZE USING NON-INTRUSIVE LASER TECHNIQUES

Two laser instrumental techniques were used to study aerosol size distributions from solutions and slurries at specific points along the nebuliser to injector assembly. A preliminary investigation was performed using a Malvern 2600/3600 particle sizer VA2 (Malvern Instruments Ltd., Spring Lane, Malvern, England) and an in-depth study using an Aerometrics phase/Doppler spray analyser (Aerometrics Inc., PO Box 308, Mountain View, California, U.S.A.).

3.4.1 Aerosol Distributions Measured by a Malvern 2600/3600 VA2

# 3.4.1.1 Experimental

Solutions of 0.1% m/v sodium hexametaphosphate (SHMP) and 1% m/v slurries of the ground ore J+L4 (dispersed in 0.1% m/v SHMP) were pumped at a flow rate of 0.8 ml min<sup>-1</sup> to an Ebdon high-solids V-groove PTFE nebuliser (PS Analytical, Sevenoaks, Kent, U.K.) of the design shown in Figure 3.1. The gas orifice of the model used was 300  $\mu m$ diameter. The particle size distribution of the starting slurry. ground by the microniser method, is shown in Figure 3.4. The aerosols produced at an argon flow rate of 1.5  $1 \text{ min}^{-1}$  were directed across the He/Ne laser beam and close to the 63 mm focal plane lens fitted to the Malvern analyser. Aerosols were measured some 20 mm from the face of the nebuliser (into still air) and the results are shown in Figure 3.5. Solution and slurry aerosols were also measured at the 4.5 mm exit of a Scott type double pass spray chamber (DPSC, ex Polyvac E1000 design, Hilger Analytical, Margate, Kent, U.K.), the design of which is shown in Figure 3.6. The model independent method of calculating the aerosol distribution was selected from the Malvern instrument as this is most appropriate for multi-modal systems and aerosols which contain a large percentage of fines.

#### 3.4.1.2 Results and Discussion

The particle size distributions (% mass in band against particle size) of aerosols from the nebuliser alone (Figure 3.5) covered the size range 1.5 to 55  $\mu$ m with peaks (modes) at 10-13  $\mu$ m and 18-23  $\mu$ m. This range is comparable to that produced by a concentric glass nebuliser (101,105) and a V-groove nebuliser of identical design (96) but is

FIGURE 3.4







By weight aerosol distribution (Malvern) of a 0.1% m/V sodium



Diagram of Scott-type double pass spray chamber.



Glass wall : 1.5 mm thick

slightly larger than that found for a conespray nebuliser (105). A direct and critical comparison with aerosol distributions from the literature is, however, difficult because the design of the nebuliser <u>e.q.</u> concentric, Babington, V-groove, crossflow, gas orifice size, etc. and its operating conditions, <u>i.e.</u> gas back pressure, gas flow rate, liquid flow rate, gas type, together with the properties of the solvent used, <u>i.e.</u> viscosity, vapour pressure, surface tension, density, all influence the mechanisms involved with aerosol production (105).

The particle size distribution of the solution aerosol measured at the exit of the double pass spray chamber (DPSC, Figure 3.7) shows that the spray chamber filters out the large size fraction and modifies the distribution by the processes outlined in section 3.2. The range of particle size has been reduced to 2 to 23  $\mu$ m with peaks at 2.5-3.9  $\mu$ m and 5-8  $\mu$ m. The diameter of the exit orifice of the DPSC was 4.5 mm. The aerosol distribution is very similar to that obtained by Norman (96) from solution aerosols exiting from a 4 mm injector/Scott type DPSC system measured using a Malvern 3300 laser particle size instrument.

A comparison of the aerosol distributions produced from slurries and solutions (Figure 3.7) shows no significant difference. This indicates that the processes which form and modify the aerosol in the nebuliser/ DPSC system are the same for both under the conditions used. Unfortunately, no information concerning the magnitude of these processes (<u>e.g.</u> from particle density number, particle volume flow and flux) is available from the Malvern instrument. A more important fact however is the limiting range of the Malvern instrument as previously stated. While information is given down to 1.2  $\mu$ m together with an indication of the fines less that 1.2 $\mu$ m it is reported (101,105) that measurements

FIGURE 3.7



at this size are not quantitative for certain types of laser instrument. Diffraction effects from particles below 2 to 3 µm require correction factors as the particle size approaches that of the wavelength of the measuring radiation (0.63  $\mu$ m for a He/Ne gas laser as used in the Malvern instrument). Hence a tail-off in response is noted at the finer end of a distribution (<  $3 \mu m$ ) as the diffraction measurement passes from the near-forward angle Fraunhoffer diffraction range to the colligative scattering dependency of the Mie range. The presence of ultra-fine particles  $(d_p \rightarrow A_{He/Ne})$  can result in spuriae (angular dependence,  $\pi d_{\rho} / \alpha$  intensity) which may be detected and lead to anomalous results. Because the data presented is normalised it is noted that the contribution from the fines is therefore shown in a degraded form which alters the overall distribution. This effect is compounded by the presentation of the data as % volume or mass (Malvern gives % mass) which weights the distribution towards the larger particle sizes and loses the contribution from the fines. The measurement of analytical aerosols using techniques that are responsive to the region below 3 µm (cascade impactor (102,103); Mie scattering (104); electrical analyser (103)) show a significant contribution from fine particles. Aerosol measurement was therefore continued using an instrument that is representatively responsive to particles down to 1  $\mu$ m.

# 3.4.2 Aerosol Distribution Measured by an Aerometrics Phase/Doppler Spray Analyser.

3.4.2.1 Experimental and Results

Solutions of 0.1% m/v sodium hexametaphosphate (SHMP) and 1% m/v slurries (dispersed in 0.1% SHMP) of the ground ore SA1/Cl20 were pumped at a liquid flow rate of 0.8 ml min<sup>-1</sup> to an Ebdon V-groove

<sup>70</sup>

nebuliser made of Kel-F (PS Analytical, Sevenoaks, Kent, U.K.) to the design shown in Figure 3.1. The gas orifice size was 210  $\mu$ m. The particle size distribution of the starting slurry (ground by the microniser method) is shown in Figure 3.8. Aerosol frequency distributions were measured at argon gas flow rates of 0.5 l min<sup>-1</sup> up to 1.5 l min<sup>-1</sup> at various positions in the sample introduction assembly for two systems.(i) A single pass spray chamber and (ii) a double pass spray chamber, both with 2 and 3 mm bore injectors.

The single pass spray chamber (SPSC) shown in Figure 3.9 was of the ARL conical design (ARL, Crawley, Sussex, U.K.) without an impact bead. The DPSC was of the design shown in Figure 3.6. The experiments undertaken for the measurement of aqueous aerosols are listed in Tables 3.2 and 3.3.

Non-aqueous aerosol particle sizes were also measured. This was part of an exercise to elucidate the cause of positive interference on the plasma emission signal of silicon present as a lipophilic surfactant in an organic solvent (White Spirit/xylene, 1:1 v/v). One possible cause was considered to be the sample introduction system with the possibility that the surfactant was modifying the aerosol size distribution compared with standard solutions. To test this theory, the size distribution of organic liquid aerosols were measured as emitted from a 2mm injector/DPSC system. A gas flow rate of 0.8 l min<sup>-1</sup> and sample flow rate of 0.8 ml min<sup>-1</sup> were employed with samples of white spirit/ xylene (l:l v/v) without and with the surfactant (l00  $\mu$ g ml<sup>-1</sup>) and after dilution (l/250) of the surfactant-containing sample with 1:1 white spirit/xylene mixture. Table 3.4 lists the experiments performed for the measurement of organic medium aerosols.



By volume particle size distribution of the BP sulphide ore, SA1/C120, used in the Aerometrics laser aerosol measurement experiments.



FIGURE 3.9

Diagram of single pass spray chamber. ARL design without impact bead.



TO PLASMA

As previously stated, the size data output of the laser phase Doppler spray analyser is presented as a population frequency versus size distribution. The contribution from the fine particles can therefore be viewed together with the bulk of the distribution. The frequency distributions (counts vs size) for all the experiments are shown in Figures 3.10 to 3.16 and are cross referenced to Tables 3.2 to 3.4. Critical population data from the distributions is given in Tables 3.5, 3.7 and 3.9.

While a population distribution can indicate what is occuring mechanistically to an aerosol in transport terms under certain conditions, it is noted that the intensity of an emission signal from an analyte in the central channel of a plasma is dependent upon the mass transported. For monodensitic aerosols (solutions) the mass transported, per unit aerosol size band, is directly proportional to the volume transported (mass = density x volume) and when expressed as a percentage (% volume in size band) will give the same distribution. The theory for transformation of frequency data to other forms of distribution (% surface, volume, mass, etc.) can be found in Allen (94). Both tabular and graphical data of % volume versus particle size were calculated from the population frequency distributions (experiments 1 to 46) using an in-house written computer programme (Appendix 1). These results are shown in Figures 3.17 to 3.35 and Tables 3.6, 3.8 and 3.10 and are cross referenced in Tables 3.2 to 3.4. The Aerometrics analyser also gives information on the aerosol particle density (Number of particles per  $cm^3$ ), volume flux ( $cm^3$  per second per  $cm^2$ ) and mean particle velocity (metres per second) of the aerosols measured. This affects a semi-quantitative measure of the loss processes in the sample introduction system. These results are shown in Tables 3.6, 3.8 and 3.10.

|       | <b></b> | <b>^</b> | 2 |
|-------|---------|----------|---|
| - TAI | SLE.    | - S -    |   |
|       | _       |          | _ |

.

:

| Experiment<br>NO. | Aerosol<br>Measurement           | Samplo                   | Gas<br>Plows  | Measurement Position | Particle       | Size Distri                            | bution Pig     | UTOS .        |
|-------------------|----------------------------------|--------------------------|---------------|----------------------|----------------|--|----------------|---------------|
|                   |                                  |                          | Rato<br>1 min |                      | Population     |  | Volume         |               |
| 1                 | Nebulișer<br>Alone               | Water                    | 0.75          | Smm from Euco        | Pig. 3. 10(a)  | Pig.3.17(a)                            |                |               |
| 2                 |                                  | 0.1% SHMP <sup>(1)</sup> | 0.75          | 5mm from faco        | (b)            | ( <del>c</del> )                       |                | Fig. 3.25(a   |
| 3                 |                                  | 0.1% SHMP                | 1.5           | 5mm from faco        | (c)            | (c)                                    |                | a             |
| 4                 |                                  | 0.1% SHMP                | 0.75          | 20mm from fuce       | (d)            | <b>Fig.3.18</b> (a)                    |                |               |
| 5                 |                                  | 14 Slurry <sup>(g)</sup> | 0.75          | 20mm from face       | (e)            | (c)                                    |                |               |
| 6                 |                                  | 0.1% SHMP                | 1.5           | 20mm from face       | (f)            | (c)                                    |                |               |
| 7                 |                                  | 0.1% SHMP                | 0.75          | 132mm from faco      | (g)            | Pig.3.19(a)                            |                |               |
| 8                 | _                                | 0.18 SHMP                | 1.5           | 132mm from face      | · (h)          | (b)                                    |                |               |
| 9                 | Nebulisor<br>and SPSC            | 0.1% SHMP                | 0.75          | At Exit of 4mm Dia.  | Fig. 3. 11 (a) | Fig. 3.19(c)                           |                | Pig. J. 24 (a |
|                   |                                  |                          | <u> </u>      |                      | Fig.3.12(a)    | ······································ |                |               |
| 10                | As above<br>with 2mm<br>Injector | 0.1% SHMP                | 1.5           | Tip of Injector Exit | Pig. 3. 11 (b) | Fig.3.20(a)                            | Pig. 3. 21 (a) |               |
| 11                | -                                | 1% slurry                | 1.5           | Tip of Injector Exit | (c)            |  | (ь)            |               |
| 12                |                                  | 0.11 SHMP                | 1.1           | Tip of Injector Exit | (d)            | Fig. 3. 20(b)                          |                |               |
| 13                |                                  | 0.1% SHMP                | 0.75          | Tip of Injector Exit | (e)            | (c)                                    | Pig. 3. 21 (c) | Pig. 3. 24(b  |
| 14                |                                  | 1% slurry                | 0.75          | Tip of Injector Exit | (f)            |  | (d)            |               |
| 15                |                                  | 0.11 SHMP                | 0.5           | Tip of Injector Exit | (g)            | Pig. 3. 20 (d)                         |                |               |
| 16                | As above<br>with Jmm<br>injector | 0.1% SHMP                | 1.5           | Tip of Injector Exit | Fig. 3. 12(b)  | Fig. 3. 22 (a)                         | Pig. 3. 23(a)  |               |
| 17                |                                  | 1% slurry                | 1.5           | Tip of Injector Exit | (c)            |  | (D)            |               |
| 18                |                                  | 0.1% SHMP                | 1.1           | Tip of Injector Exit | (d)            | Pig. ]. 22(b)                          |                |               |
| 19                |                                  | 0.11 SHMP                | 0.75          | Tip of Injector Exit | (e)            | (c)                                    | Pig. 3. 23 (c) | Pig. 3. 24 (c |
| 20                |                                  | 14 slurry                | 0.75          | Tip of Injector Exit | (E)            |  | (d)            |               |
| 21                |                                  | 0.1% SHMP                | 0.5           | Tip of Injector Exit | (0)            | Pho 3 22(4)                            |                |               |

٠

Table of Experiments Used in the Measurement of Aerosols from Various Sample Introduction Systems.([]Nebuliser and Single Pass Spray Chamber (SPSC), 2mm and 3mm injectors.

.

(1)SHMP = sodium hexametuphosphate solution (0.1 % m/V)

(2)Slurry = In-house sulphide ore dispersed in SHMP solution

.

.

.

.

.
| Experiment<br>No. | Acrosol<br>Moasurement            | Sample                   | Gas<br>Plow   | Measurement Position                         | Purticlo 5    | ize Distrit           | oution Pigu    | 1.68          |               |
|-------------------|-----------------------------------|--------------------------|---------------|--|---------------|-----------------------|----------------|---------------|---------------|
|                   |                                   | •                        | Rato<br>1 min |  | Population    |                       | • Ve           | olume         |               |
| 22                | Nobuliser<br>with inner           | 0.1% SHMP <sup>(1)</sup> | 0.75          | Exit from 15mm Dia.<br>Inner Pass of 132mm   | Fig.3.13(a)   | Fig. J. 26 (a)        | Fig. J. 25 (c) |               |               |
| 27                | pass                              | 0.11 SHMP                | 1.5           | longen                                       | (b)           | (c)                   | (d)            |               |               |
|                   |                                   |                          |               |  | ·             |                       |                |               |               |
| 24                | Nebuliser<br>with DPSC            | 0.11 SHMP                | 0.75          | Exit of 4.5mm Dis.                           | (c)           | Pig. 3. 26(c)         | Pig. 3. 27 (a) | Fig. 3. 29(a) | Fig. 3. 33 (d |
| 25                |                                   | 18 Slurry <sup>(1)</sup> | 0.75          |  | (d)           |                       | (b)            |               |               |
| 26                |                                   | 0.11 SHMP                | 1.5           |  | (e)           | Fig. 3.26 (d)         | (c)            | Pig.3.29(c)   | Fig. 3. 33 (c |
| 27                |                                   | 18 Slurry                | 1.5           |  | (f)           |                       | (d)            |               |               |
| 28                | As Abovo<br>with 2mm<br>injector  | 0.1% SHMP                | 1.5           | Tip of Injector Exit                         | Fig. J. 14(a) | Fig. 3.28(a)          | Pig. 3. 30 (a) | Fig. J. 29(d) |               |
| 29                |                                   | 11 Slurry                | 1.5           |  | (d)           |                       | (ь)            |               |               |
| 30                |                                   | 0.1% SHMP                | 1.1           |  | (c)           | Fig. <b>J.</b> 28 (b) |                |               |               |
| 31                |                                   | 18 Slurry                | 1.1           |  | (d)           |                       |                |               |               |
| 32                |                                   | 0.11 SHMP                | 0.75          |  | (e)           | Fig. 3. 28(c)         | Pig.3.30(c)    | Fig.3.29(b)   | Fig.3.35(c    |
| 33                |                                   | 18 Slurry                | 0.75          |  | (f)           |                       | (d)            |               |               |
| 34                |                                   | 0.1% SHMP                | 0.5           |  | (g)           | Fig. 3.28(d)          |                |               |               |
| 35                | As Above<br>with 3mm<br>injector  | 0.18 SHMP                | 1.5           | Tip of Injector Exit                         | Fig. 3.15(a)  | Pig. 3. 31 (a)        | Pig. 3. 32(a)  |               | Pig. 3. 33 (a |
| 36                |                                   | 11 Slurry                | 1.5           | •  | (D)           |                       | (d)            |               |               |
| 37 .              |                                   | 0.11 SHMP                | 1.1           |  | (c)           | Pig. 3. 31 (b)        |                |               |               |
| 38                |                                   | 0.18 SHMP                | 0.75          |  | (d)           | (c)                   |                |               | Pig. 3. 33(b  |
| 39 .              |                                   | 0.11 SHMP                | 0.5           |  | (a)           | Fig. 3. 31 (d)        |                |               |               |
| 40                | As Above<br>with Jaam<br>injector | 14 Slurry                | 0.75          |  | (E)           |                       | Pig. 3. 32 (d) |               |               |
| 41                |                                   | 0.11 SHMP                | - 0.75        |  | (g)           |                       | (c)            |               |               |
| 42                | As Above<br>with 3mm              | 0.1% SHMP                | 1.5           | Tip of 3mm Injector<br>but at edge of stream | (h)           |                       |                |               | Pig. 3. 35 (d |

TABLE 3.3

. .

:

.

(1) SHMP + sodium hexametaphosphato solution (0.11 m/V) .

(2) Slurry = In-house sulphide ore dispersed in SHMP solution.

•

•

•

.

•

Table of experiments used in the measurement of organic liquid aerosols from various sample introduction systems (III) Double pass spray chamber, 2 mm injector

;

| Expt | Aerosol                | Sample                   | Gas               | flow                     | Measurement            | Particle siz            | e           |             |
|------|------------------------|--------------------------|-------------------|--------------------------|------------------------|-------------------------|-------------|-------------|
| no.  | measurement            |                          | r:<br>1 (         | ate<br>min <sup>-l</sup> | position               | distribution<br>figures |             |             |
|      |                        |                          |                   |                          |                        | Population              | %Volu       | me          |
| 43   | Nebuliser<br>with DPSC | White spir               | it                | 0.8                      | Tip of 2mm<br>injector | fig.3.16(a)             | fig.3.34(a) | fig.3.35(a) |
| 44   | and 2mm<br>injector    | Wt spt/xyl<br>l:l v/v    | ene               | 0.8                      | exit                   | (b)                     | (b)         | (b)         |
| 45   |                        | Above+100µ<br>of surfact | _₁<br>g_ml<br>ant | 0.8                      |                        | (c)                     | (c)         |             |
| 46   |                        | l/250 Dilu<br>of above   | tion              | 0.8                      |                        | (d)                     | (d)         |             |
| 32   |                        | 0.1% SHMP<br>in water    | (1)               | 0.75                     |                        | (e)                     |             | fig.3.35(c) |

(1) SHMP = sodium hexametaphosphate solution.

| Puperimont | Population Co              | unt Data for Aer         | osols Measur                 | ed from Nebu                | liser and S             | ingle Pass             | Spray | Chambe              | r (SPS | ic)   |
|------------|----------------------------|--------------------------|------------------------------|-----------------------------|-------------------------|------------------------|-------|---------------------|--------|---|
| No.        | Adrosol<br>Measurement     | Sampio                   | Gas<br>Flow<br>Rate<br>1 min | Pop. Mean<br>Diameter<br>µm | Distrib.<br>Rango<br>µm | Distrib.<br>Mode<br>µm | % Pc  | −£25<br>۲۳۳<br>1.81 | 2.55   | Rutio of Population<br>at 1.1µm to Mode<br>as 8 |
|            | Nebuliser<br>alone Smm (1) | Water                    | 0.75                         | 9.0                         | 1.1-17                  | 7.0                    | 2.1   | 2.3                 | 2.4    | 28 .  |
|            |                            | 0.1% SHMP <sup>(2)</sup> | 0.75                         | 9.7                         | 1.1-18                  | 8.5                    | 1.6   | 1.5                 | Z.4    | 24  |
|            |                            | 0.1% SHMP                | 1.5                          | 8.8                         | 1.1-16                  | 9.2                    | 3.9   | 2.8                 | 3.3    | 51  |
|            | Nebuliser<br>alone 20mm    | 0.1% SHMP                | 0.75 .                       | 8.3                         | 1.1-16                  | 7.0                    | 1.9   | 1.9                 | 3.3    | 22  |
|            |                            | 18 Slurry                | 0.75                         | 8.4                         | 1.1-16                  | 7.4                    | 1.6   | 2.1                 | 2.7    | 19  |
| •          |                            | 0.1% SHMP                | 1.5                          | 7.5                         | 1.1-16                  | 5.5                    | 2.4   | 2.0                 | 3.7    | 30  |
|            | Nobuliser<br>alone 132mm   | 0.1% SHMP                | 0.75                         | 8.9                         | 1.1-19                  | 7.0                    | 0.5   | 0.9                 | 2.1    | 6   |
| l          |                            | 0.1% SHMP                | 1.5                          | 6.8                         | 1.1-17                  | 6.3                    | 1.8   | 2.6                 | 3.9    | 18  |
|            | Nebuliser +<br>SPSC Exit   | 0.1% SHMP                | 0.75                         | 13.7                        | 1.1-19;<br>22-50        | 9.2                    |       | 3.9                 | 4.4    | (46)(3)   |
| 0          | Above + 2mm<br>Injector    | 0.1% SHMP                | 1.5                          | 6.3                         | 1.1-12.5                | 6.3                    | 3.6   | 4.8                 | 5.2    | 35  |
| 1          |                            | 1% Slurry                | 1.5                          | 5.9                         | 1.1-12.2                | 5.5                    | 4.9   | 6.4                 | 5.4    | 39  |
| 2          |                            | 0.11 SHMP                | 1.1                          | 7.5                         | 1.1-14                  | 7.7                    | 1.4   | 2.8                 | 2.7    | 13  |
| 3          |                            | 0.1% SHMP                | 0.75                         | 8.7                         | 1.1-16.6                | 7.7-10                 | 0.8   | 0.5                 | 1.4    | 8   |
| 4          |                            | 18 Slurry                | 0.75                         | 8.3                         | 1.1-16                  | 8.5                    | 1.0   | 1.1                 | 1.8    | 9   |
| 5          |                            | 0.1% SHMP                | 0.5                          | 8.4                         | 1.1-18                  | 9.2                    | 0.6   | 1.2                 | 1.1    | 6.5   |
| 6          | Above + 3mm<br>Injector    | 0.1% SHMP                | 1.5                          | 8.3                         | 1.1-15                  | 7.7(-9.3)              | 1.2   | 1.1                 | 2.0    | 12  |
| .7         |                            | 18 Slurry                | 1.5                          | 8.0                         | 1.1-15.5                | 9.2(-7.7)              | 0.9   | 1.6                 | 2.7    | 9.6   |
| 8          |                            | 0.1% SHMP                | 1.1                          | 8.8                         | 1.1-16                  | 7.7                    | 2.2   | 2.1                 | 2.3    | 25  |
| 9          |                            | 0.1% SHMP                | 0.75                         | 8.3                         | 1.1-16                  | 7 and 9.2              | 1.9   | 2.1                 | 2.8    | 23  |
| 0          |                            | 1% Slurry                | 0.75                         | 9.2                         | 1.1-16                  | 8.5                    | 0.9   | 1.3                 | 1.2    | 10  |
| 21         |                            | 0.1% SHMP                | 0.5                          | 8.6                         | 1.1-16                  | 7.7and 9.2             | 1.4   | 1.6                 | 0.7    | 16  |

TABLE 3.5

(1)= Distance measured from face of nebuliser

.

(2)= SHMP - Sodium hexametaphosphate solution

.

| Experiment<br>No. | Acrosol<br>Measurement       | Sample                   | Gas<br>Plow<br>Rato<br>I min | Volume<br>Mean<br>Dia.<br>µm | Vol. I<br>Dia j | lode<br>Im | Runge<br>µm |         | Number<br>Density                      | Volumo<br>Flux    | Particle<br>Maan              |
|-------------------|------------------------------|--------------------------|------------------------------|------------------------------|-----------------|------------|-------------|---------|--|-------------------|-------------------------------|
|                   |                              |                          |                              |                              | d(1)            | d(2)       | d(1)        | d(2)    | / cm <sup>2</sup><br>x 10 <sup>2</sup> | / cm s cm<br>x 10 | Velocity<br>/ms <sup>~1</sup> |
|                   | Nebulisor (2)<br>alono 5mm   | Wuter                    | 0.75                         | 13.2                         | 14              | 29-32      | 4-18.5      | 18.5-37 | 15.4                                   | 30.3              | 9.3                           |
| 2                 |                              | 0.1% SHMP <sup>(1)</sup> | 0.75                         | 13.5                         | 14.8            | 26-31      | 4-20.7      | 20-37   | 16.4                                   | 31                | 8.6                           |
|                   |                              | 0.1% SHMP                | 1.5                          | 11.5                         | 12.5-15.5       | 24-30      | 4-20.5      | 20-31   | 7.5                                    | 13.7              | 34.4                          |
|                   | Nebuliser(2)<br>alone 20mm   | 0.11 SHMP                | 0.75                         | 10.8                         | 11.1-14         | 23-28      | 3.5-20.7    | 21-33   | 16                                     | 15                | 8.4                           |
| 5                 |                              | 18 Slurry                | 0.75                         | 11.3                         | (11.8)14        | 25.9       | 3.5-20.3    | 20-33   | 14.4                                   | 15.7              | 8.5                           |
| j                 |                              | 0.11 SHMP                | 1.5                          | 9.6                          | 11.8(15.5)      | 25         | 3-20.7      | 20-27   | 21                                     | 11.2              | 20.8                          |
| 1                 | Nobuliser (2)<br>alone 132mm | 0.11 SHMP                | 0.75                         | 12.4                         | 14.8            | 25.7       | 4.5-20      | 20-36   | 4.0                                    | 9.6               | 3.5                           |
| l                 | ·                            | 0.1% SHMP                | 1.5                          | 9.5                          | 12.5            | 25-26      | 3-19        | 19-35   | 7.2                                    | 6.8               | 5.3                           |
|                   | Nebulisor +<br>SPSC Exit     | 0.1% SHMP                | 0.75                         | 20.6                         | 14.1            | 37         | 5-20.6      | 20-52   | 9.7                                    | 127               | 1.2                           |
| 10                | Above +<br>2mm Injector      | 0.1% SHMP                | 1.5                          | 7.7                          | 8.1-9.6         | (14.8)     | 2.1-17.7    | `       | 3.5                                    | 2.0               | 6.6                           |
| 1                 |                              | 14 Slurry                | 1.5                          | 7.3                          | 7.3-9.6         | (14.8)     | 2.0-16      |         | 3.5                                    | 1.5               | 6.7                           |
| 2                 |                              | 0.1% SHMP                | 1.1                          | 9.0                          | 10.3            | (13.3)     | 2.9-17.7    | (29-31) | 3.7                                    | 3.2               | 5.2                           |
| 3 ·               |                              | 0.1% SHMP                | 0.75                         | 10.2                         | 11.1            | (21-26)    | 4.0-19.9    | (20-27) | 3.6                                    | 4.4               | 3.6                           |
| 4                 |                              | 18 Slurry                | 0.75                         | 9.9                          | 11.8            | (14.8)     | 3.7-21      | (21-26) | 4.7                                    | 4.8               | 3.7                           |
| 5                 |                              | 0.11 SHMP                | 0.5                          | 10.3                         | 11.1            | (27.3)     | 3.8-23      | (23-37) | 4.1                                    | 5.5               | 2.5                           |
| 6                 | Abova + 3mm                  | 0.11 SHMP                | 1.5                          | 9.9                          | 10.3            | (23.6)     | 3.2-19.2    | (20-30) | 3.6                                    | 4.9               | 4.4                           |
| 7                 | Injector                     | 11 Slurry                | 1.5                          | 9.5                          | 11.1            |            | 3.2-21.4    | (20-24) | 4.2                                    | 5.1               | 4.4                           |
| 8                 |                              | 0.11 SHMP                | 1.1                          | 11.4                         | 11.0            | 25.1       | 3.4-21.4    | 21-37   | 3.7                                    | 6.5               | 3.6                           |
| 9                 |                              | 0.1% SHMP                | 0.75                         | 11.1                         | 12.5            | 26-29      | 3.8-20.7    | 21-37   | 4.6                                    | 7.3               | 2.6                           |
| :0                |                              | 14 Slurry                | 0.75                         | 11.7                         | 12.5            | 23-29      | 4.0-22.2    | 22-37   | 6.8                                    | 13.5              | 2.5                           |
| 21                |                              | 0.11 SHMP                | 0.5                          | 11.0                         | 11.8-14.8       | 24-30      | 3.8-20      | 20+36   | 5.0                                    | 9.2               | 1.8                           |

TABLE 3.6

\$ Volume and Velocity Data for Acrosols Measured from Nebuliser and Single Pass Spray Chamber (SPSC)

Values in parentheses refer to shoulder peaks on a main peak (mode) and very minor second distributions d(1) and d(2) refer to the bimodal distributions of the aerosols. (d2 can however show multimodality).

(1) SHMP = sodium hexamotaphosphate solution (0.1% mN)

(2) Distance measured from face of mebulisers.

.

.

.

:

| Experiment<br>No, | Aerosol<br>Messurement                   | Sample                   | Gas<br>Flow         | Pop.<br>Mean | Distrib.<br>Range | Distrib.<br>Mode | N Pc<br>at: | pulati       | ton  | Ratio of Pop. at<br>1.1µm to Mode Am |
|-------------------|--|--------------------------|---------------------|--------------|-------------------|------------------|-------------|--------------|------|--------------------------------------|
|                   |  |                          | l min <sup>-1</sup> | μ <u>π</u>   | μο                | <u>حم</u>        | 1.1         | ×μ:<br>_1.01 | 2.55 | ۱.                                   |
| 2                 | Nebuliser<br>alone 5cm(2).               | 0.18 SHMP <sup>(1)</sup> | 0.75                | 9.7          | 1.1-18            | 8.5              | 1.6         | 1.5          | 2.4  | 24                                   |
| 3                 |  | 0.11 SHMP                | 1.5                 | 8.8          | 1.1-16            | 9.2              | -3.9        | 2.8          | 3.3  | 51                                   |
| 22                | Nebuliser<br>Inner Pass (3)              | 0.18 SHMP                | • 0.75              | 9.5          | 1.1-18            | ,                | 2.0         | 2.2          | 2.3  | 26                                   |
| 23                |  | 0.11 5KMP                | 1.5                 | 9.6          | 1.1-16            | 9.2              | 2.9         | 2.2          | 1.)  | 35                                   |
| 24                | Nebuliser •<br>DPSC Exit<br>(4.5rm Dia-) | 0.18 SHMP                | 0.75                | 9.7          | 1.1-17            | 9.9              | 0.7         | 1.3          | 1.3  | 6                                    |
| 26                |  | 0.1% SHMP                | 1.5                 | 7.4          | 1.1-14.5          | 7.0              | 2.2         | 2.3          | 2.1  | 20                                   |
| 25                |  | 18 Slurry                | 0.75                | 9.9          | 1.1-15            | 9.2              | 1.0         | 0.7          | 1.2  | 9                                    |
| 27                |  | 11 Slurry                | 1.5                 | 7.8          | 1.1-14.5          | 6.3              | 1.3         | 1.5          | 2.5  | 12                                   |
| 28                | As above +<br>Zmm Injector               | 0.11 SHMP                | 1.5                 | 6.6          | 1-1-14            | 5.5              | 6.3         | 5.2          | 4.8  | 72                                   |
| 29                |  | 18 Slurry                | 1.5                 | 6.6          | 1.1-14.4          | 4.8              | 5.0         | 6.2          | 4.8  | 56                                   |
| 10                |  | 0.1% SHMP                | 1.1                 | 6.2          | 1.1-12            | 6.2              | 3.7         | 4.5          | 5.7  | 31                                   |
| 11                |  | 18 Slurry                | 1.1                 | 6.3          | 1.1-12.5          | 4.8              | 3.4         | 4.0          | 6.7  | 31                                   |
| 32                |  | 0.1% SHMP                | 0.75                | 5.1          | 1.1-10.7          | 4.8              | 4.7         | 7.2          | 1.1  | 31                                   |
| 22                |  | 18 Slurry                | 0.75                | 5.1          | 1.1-10.7          | 4.8              | 5.8         | 6.9          | 7.4  | 48                                   |
| 14                |  | 0.11 SHMP                | 0.5                 | 4.9          | 1.1-9.2           | 4.8              | 2.9         | 4.2          | 7.5  | 17                                   |
|                   | As Above +<br>3mm Injector               | 0.11 SHMP                | 1.5                 | 5.1          | 1.1-10.8          | 4.8              | 5.2         | 6.2          | 1.1  | 38                                   |
| 16                |  | 18 Slurry                | 1.5                 | 5.4          | 1.1-11            | 5.5              | 4.6         | 3.9          | 8.1  | 37                                   |
| 17                |  | 0.11 SHMP                | 1.1                 | 6.6          | 1.1-13            | 5.9              | 2.1         | 2.3          | 3.8  | 17                                   |
| 18                |  | 0.18 SHMP                | 0.75                | 7.0          | 1.1-14            | 7                | 1.2         | 0.8          | 1.4  | 9                                    |
| 39                |  | 0.11 SHMP                | 0.5                 | 6.9          | 1-1-13            | 6.3              | 0.7         | 0.9          | 1.9  | 5                                    |
| 10                |  | 18 Slurry                | 0.75                | 5.5          | 1.1-11            | 5.5              | 2.0         | 3.3          | 3.7  | 11                                   |
| 41                |  | 0.11 SHMP                | 0.75                | 5.5          | 1.1-11            | 5.5              | 2.0         | 2.3          | 3.6  | 11                                   |
| 42                | As Above<br>but edge of<br>Jon stream    | 0.11 SHMP                | 1.5                 | 5.1          | 1.1-11            | 4.8              | 2.1         | 4.8          | 1.1  | 18                                   |

(1)SHMP - Sodium hexametaphosphate solution (0.1% m/V)

..

(2) Distance measured from face of nebuliser

(3) Dimensions of inner pass from DPSC, 15mm Dia. # 132mm long

| <u> </u>         | Volume and Vel                                  | LOCILY Data for Ae       | COSOLS Meas                 | ured from      | Inner and ( | Duter Passes | of Double | Pass Spray ( | Chesber (              | DPSC I         |                  |
|------------------|---|--------------------------|-----------------------------|----------------|-------------|--------------|-----------|--------------|------------------------|----------------|------------------|
| Experisent<br>No | Aerosol<br>Measurament                          | Sample                   | Gas<br>Flow                 | Voluze<br>Hean | Vol. Hode   | Die.         | Distrib.  | Range        | Number<br>Density      | Volume<br>Flux | Particle<br>Mean |
|                  |   |                          | Rete<br>1 min <sup>-1</sup> | Die.<br>بت     | 4(1)        | d(2)         | 4(1)      | 4(2)         | /c=<br>10 <sup>2</sup> | /cm cm         | Velocity<br>/m#  |
| 2                | Nabuliser<br>slone 5mm(2)                       | 0.1% SHMP <sup>(1)</sup> | 0.75                        | 13.5           | 34.8        | 26-31        | 4-20.7    | 20-37        | 16.4                   | 31             | 8.6              |
| 1                |   | 0.1% SKMP                | 1.5                         | 11.5           | 12.5-15.5   | 24-30        | 4-20.5    | 20-31        | 7.5                    | 13.7           | 34.4             |
| 22               | Nebuliser<br>• Enner<br>Pass (Some<br>x 132cms) | 0.14 SHMP                | 0.75                        | 12.9           | 11.8-15.5   | 21.5-37.5    | 3.5-19    | 19-36        | 8.7                    | 2.1            | 0.25             |
| 23               |   | 0.14 SHMP                | 1.5                         | 13.0           | 9.6-12.5    | 30.3         | 3.5-17.7  | 18-36        | 8.6                    | 2.5            | 0.36             |
| 24               | Nebuliser +<br>DPSC Exit<br>(4.5mm Dia)         | 0.11 SHMP                | 0.75                        | 12.8           | 12.5-14.8   | 26.6         | 5-20      | 20-37        | 2.0                    | 4.3            | 0.9              |
| 26               |   | 0.1% SHMP                | 1.5                         | 9.9            | 9.6         | 25.1         | 3.5-20    | 20-34        | 2.0                    | 2.2            | 1.7              |
| 25               |   | 14 Slurry                | 0.75                        | 12.4           | 10.3        | 24.4-32.5    | 4.5-18.5  | 18-36        | 3.0                    | 8.6            | 0.95             |
| 27               |   | 14 Slurry                | 1.5                         | 10.2           | 8.8(11.1)   | 23-32.5      | 3.5-20    | 20-36        | 2.2                    | 2.7            | 1.7              |
| 28               | As shows •<br>7mm Injector                      | 0.14 SHAP                | 1.5                         | 8.9            | 9.6-11.1    | 26.6         | 2.4-19.2  | 20-36        | 3.3                    | 3.1            | 9.7              |
| 29               |   | 14 Slurry                | 1.5                         | 9.1            | 8.8(11.1)   | 26.6         | 2.4-19.2  | 20-36        | 2.8                    | 3.0            | 9.9              |
| 30               | •   | 0.1% SHMP                | 1.1                         | 7.9 '          | 9.5         | 23.6         | 2.0-17    | 17-36        | 2.7                    | 1.9            | 7.9              |
| 31               |   | 14 Slurry                | 1.1                         | 8.5            | 8.8-11.1    | 27.3         | 2.0-17.7  | 18-34        | 3.8                    | 3.1            | 7.9              |
| 32               |   | 0.14 SHMP                | 0.75                        | . 4.2          | 6.6-7.4     | 17           | 1.6-14    | 14-17        | 4.3                    | 1.2            | 5.6              |
| 33               |   | 14 Slutry                | 0.75                        | 6.7            | 6.6         | 28           | 1.6-17    | 17-28        | 4.4                    | 1.6            | 5.6              |
| 34               |   | 0.1% SHMP                | 0.5                         | 5.7            | 6.1         | (15.5)       | 1.6-14    | (14-15.5)    | 9.0                    | 1.2            | 3.6              |
| 35               | As above +<br>]mm Injector                      | 0.18 SHMP                | 1.5                         | 6.)            | 6.6-8.1     |              | 1.7-16.2  | •••••        | 3.7                    | 1.0            | 6.5              |
| 36               |   | 18 Slurry                | 1.5                         | 6.5            | 7.4-8.1     |              | 1.7-15.5  | •••••        | 4.2                    | 1.1            | 6.3              |
| 37               |   | 0.11 SHMP                | 1.1                         | 8-1            | 8.1-8.5     | (31.8)       | 2.3-16    | {16-35}      | 4.3                    | 2.4            | 4.9              |
| 38               |   | Q.18 SHMP                | 0.75                        | 8.3            | 8.1-11.1    | (25.9)       | 2.9-17    | {17-26}      | 2.5                    | 1.9            | 3.3              |
| 39               |   | 0.11 SHMP                | 0.5                         | 7.9            | 8.8         |              | 2.8-19    |              | 3.9                    | 1.0            | 2.2              |
| 40               |   | 18 Slurry                | 0.75                        | 6.5            | 6.6         |              | 2.0-15    |              | 3.4                    | 1.2            | 3.3              |
| 41               |   | 0.18 SHMP                | 0.75                        | 6.2            | (6.6)7.4    |              | 2.0-11    |              | 4.3                    | 1.2            | 3.2              |
| 42               | As above<br>but edge of<br>Jam stream           | 0.18 SHMP                | 1.5                         | 6.0            | 6.6         | •••••        | 2-14.8    |              | 4.6                    | 1.4            | 3.3              |

Values in parenthesis refer to shouldsr peaks on a main peak (mode) and very minor second distributions. d(1) and d(2) refer to the bimodal distributions of the serosols (d(2) can however be multimodal).

(1)SHMP - codium hexametaphosphate solution (0.11 m/V)

. .

(2) Distance measured from face of nebuliest

Population count data for organic liquid aerosols measured from 2mm injector/double pass spray chamber (DPSC)

.

.

•

| Expt.<br>No. | Aerosol<br>measurement | Sample   | Cas flow<br>rate<br>min <sup>-1</sup> | Pop. Mean<br>dia. | Distr.<br>range | Distr.<br>mode | %Рор  | ulatio<br>xµm | n at: | Ratio of Pop.<br>at l.l µm to |
|--------------|------------------------|--|---------------------------------------|-------------------|-----------------|----------------|-------|---------------|-------|-------------------------------|
|              |                        | •  |                                       | hm                | μm              | hw             | 1.1   | 1.81          | 2.55  | mode as %                     |
| 43           | Nebuliser<br>DPSC and  | White spirit   | 0.8                                   | 6.9               | 1.1-12          | 7.0            | 1.5   | 2.7           | 3.4   | 10                            |
|              | 2mm injecto            | r  |                                       |                   |                 |                |       |               |       |                               |
| 44           |                        | wt.spt/xylene<br>l:l v/v                                   | 0.8                                   | 8.2               | 1.1-17          | 7.0            | 4.7   | 3.6           | 3.6   | 53                            |
| 45           |                        | Above +<br>surfactant                                      | 0.8                                   | 8.2               | 1.1-18          | 7-8.5          | 3.3   | 3.7           | 3.8   | 42                            |
| 46           |                        | <pre>l/250 dilution of above with l:l wt.spt/ xylene</pre> |                                       | 8.7               | 1.1-16.5        | 7              | 3.4 3 | 9.0 3         | 9.5 L | +2                            |
| 32           |                        | 0.1% SHMP (1)<br>in water                                  | 0.75                                  | 8.7               | 1.1-16.6        | 7.7-10         | 0.8   | 0.5           | 1.4   | 8                             |

(1)SHMP = sodium hexametaphosphate solution.

82

.

•

-

.

% Volume and velocity data for organic liquid aerosols measured from 2mm injector/double pass spray chamber (DPSC)

.

| Expt.<br>No. | Aerosol<br>measurement                 | Sample   | Gas flow<br>rate<br>l min <sup>-1</sup> | Vol.mean<br>dia.<br>µm | . Vol<br>d(1) | mode<br>d(2)<br>Im | Distr. ra<br>d(l)<br>µm | ange N<br>d(2) | o. density<br>/cm <sup>-3</sup><br>x10 <sup>2</sup> | Vol.flux<br>/cm <sup>3</sup> s <sup>-1</sup> cm <sup>-2</sup><br>x10 <sup>-4</sup> | Particle<br>mean velocity<br>/m s <sup>-1</sup> |
|--------------|--|--|---|------------------------|---------------|--------------------|-------------------------|----------------|---|--|---|
| 43           | Nebuliser,<br>DPSC and<br>2mm injector | white<br>spirit  | 0.8                                     | 8.1                    | 8.1           | (16.2)             | 2.4-15.5                | (15.5-17)      | 5.3   | 2.8  | 4.3   |
| 44           | 0                                      | white<br>spirit<br>/xylene<br>l:l v/v                      | 0.8                                     | 11.6                   | 11.1          | 30-34              | 3.3-18.5                | 18.5-37        | 11.9  | 16.4   | 4.4   |
| 45           |  | Above +<br>surfac-<br>tant                                 | 0.8                                     | 11.4                   | 11.8          | 37                 | 3.3-20                  | 20-37          | 10.0  | 12.5   | 4.5   |
| 46           |  | <pre>1/250 dilution of above with 1:1 wt.spt/ xylene</pre> | 0.8                                     | 12.0                   | 11.8          | 34                 | 3.5-19.2                | 20-37          | <b>9.8</b>  | 14   | 4.5   |
| 32           |  | 0.1%<br>SHMP <sup>1</sup> in<br>water                      | 0.75                                    | 6.2                    | 6.6-7.4       | 17                 | 1.6-14                  | 14-17          | 4.3   | 1.2  | 5.6   |

d(1) and d(2) refer to the bimodal distributions of aerosols (d(2) can however be multimodal)

(1) SHMP = sodium hexametaphosphate solution.

Population size distributions of aerosols produced by a high solids nebuliser at a carrier gas flow rate of 0.75 (a, b, d, e, g) and 1.5 (c, f, h)  $1 \text{ min}^{-1}$  from water (a), 0.1% m/V SHMP solution (b, c, d, f, g, h) and 1% m/V slurry (e) measured at 5mm (a, b, c), 20mm (d, e, f) and 132mm (g, h) from the nebuliser face.



Population size distributions of aerosols measured from a single pass conical spray chamber (a) and above a 2mm injector (b to g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f) and 0.5 (g)  $1 \min^{-1}$  carrier gas flow rate using 0.1% m/V SHMP solution (a, b, d, e, g) and 1% slurry (c, f).



Population size distributions of aerosols measured from a single pass conical spray chamber (a) and above a 3mm injector (b to g) at 1.5 (b, c), 1.1 (d), 0.75 (a, e, f) and 0.5 (g)  $1 \text{ min}^{-1}$  carrier gas flow rate using 0.1% m/V SHMP solution (a, b, d, e, g) and 1% slurry (c, f).



Population size distributions of aerosols measured from an inner pass chamber (a, b) and double pass spray chamber (c to f) at 0.75 (a, c, d) and 1.5 (b, e, f) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, b, c, e) and 1% m/V slurry (d, f).

25.2

25.2

13.2

13.2

f

e

37.3

37.3



Population size distributions of aerosols measured from a double pass spray chamber with 2mm injector at 1.5 (a, b), 1.1 (c, d), 0.75 (e, f) and 0.5 (g) 1 min<sup>-1</sup> carrier gas flow rate using 0.1% m/V SHMP solution (a, c, e, g) and 1% m/V slurry (b, d, f).



Population size distributions of aerosols measured from a double pass spray chamber with 3mm injector at 1.5 (a, b, h), 1.1 (c), 0.75 (d, f, g) and 0.5 (e)  $1 \text{ min}^{-1}$  carrier gas flow rate using 0.1% m/V SEMP solution (a, c, d, e, g, h) and 1% m/V slurry (b, f). Aerosol distribution (h) measured at edge of 3mm injector stream.



Population size distributions of organic liquid aerosols measured from a double pass spray chamber with 2mm injector at a gas flow rate of 0.8 l min<sup>-1</sup> (a) white spirit, (b) white spirit-xylene mixture (1:1), (c) white spirit-xylene mixture containing 100µg ml<sup>-1</sup> of surfactant, (d) 1/250 dilution of (c), (e) aqueous aerosol (0.1% SHMP) produced under similar conditions for comparison.





% volume size distributions of aerosols produced by high solids nebuliser at 0.75 (a, b) and 1.5 (c) 1 min<sup>-1</sup> carrier gas flow rate using water (a), 0.1% m/V SHMP solution (b, c), and measured 5mm from nebuliser face.



a





% volume size distributions of aerosols produced by high solids nebuliser at 0.75 (a, b) and 1.5 (c)  $1 \text{ min}^{-1}$  carrier gas flow rate using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b) measured 20mm from nebuliser face.



а

b



С

% volume size distributions of aerosols produced by a high solids nebuliser (a, b), measured 132mm from nebuliser face, and single pass conical spray chamber (c) at 0.75 (a, c) and 1.5 (b)  $1 \text{ min}^{-1}$ carrier gas flow rate using 0.1% m/V SHMP solution.









% volume size distributions of aerosols measured from a single pass conical spray chamber with 2mm injector at a carrier gas flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5 (d)  $1 \text{ min}^{-1}$  using 0.1% m/V SEMP solution.



% volume size distributions of aerosols measured from single pass conical spray chamber with 2mm injector at a carrier gas flow rate of 1.5 (a, b) and 0.75 (c, d)  $1 \text{ min}^{-1}$  using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).



% volume size distributions of aerosols measured from single pass spray chambër with 3mm injector at a carrier gas flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5 (d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.



% volume size distributions of aerosols measured from single pass conical spray chamber with 3mm injector at a carrier gas flow rate of 1.5 (a, b) and 0.75 (c, d)  $1 \text{ min}^{-1}$  using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).



% volume size distributions of aerosols measured from a single pass conical spray chamber alone (a), with 2mm injector (b) and 3mm injector (c) at a carrier gas flow rate of 0.75 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.









% volume size distributions of aerosols measured from a high solids nebuliser (a, b) and the inner pass from a double pass spray chamber (c, d) at a carrier gas flow rate of 0.75 (a, c) and 1.5 (b, d) 1 min<sup>-1</sup> using 0.1% SHMP solution.



% volume size distributions of aerosols measured from the inner pass of a double pass spray chamber (a, b) and from a double pass spray chamber (c, d) at a carrier gas flow rate of 0.75 (a, c) and 1.5 (b, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.



% volume size distributions of aerosols measured from a double pass spray chamber at a carrier gas flow rate of 0.75 (a, b) and 1.5 (c, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).







С

% volume size distributions of aerosols measured from a double pass spray chamber with 2mm injector at a carrier gas flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5 (d)  $1 \text{ min}^{-1}$  using 0.1 m/V SHMP solution.



% volume size distributions of aerosols measured from a double pass spray chamber (a, c) and double pass spray chamber with 2mm injector (b, d) at a carrier gas flow rate of 0.75 (a, b) and 1.5 (c, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.



% volume size distributions of aerosols measured from a double pass spray chamber with 2mm injector at a carrier gas flow rate of 1.5 (a, b) and 0.75 (c, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).



% volume size distributions of aerosols measured from double pass spray chamber with 3mm injector at a carrier gas flow rate of 1.5 (a), 1.1 (b), 0.75 (c) and 0.5 (d)  $1 \text{ min}^{-1}$  using 0.1% m/V SHMP solution.



% volume size distributions of aerosols measured from a double pass spray chamber with 3mm injector at a carrier gas flow rate of 1.5 (a, b) and 0.75 (c, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution (a, c) and 1% m/V slurry (b, d).



% volume size distributions of aerosols measured from a double pass spray chamber with 3mm injector (a, b) and from a double pass spray chamber alone (c, d) at a carrier gas flow rate of 1.5 (a, c) and 0.75 (b, d) 1 min<sup>-1</sup> using 0.1% m/V SHMP solution.



% volume size distributions of organic liquid aerosols measured from a double pass spray chamber with 2mm injector at a gas flow rate of 0.8 l min<sup>-1</sup>. (a) white spirit, (b) white spirit-xylene mixture (1:1), (c) white spirit-xylene mixture containing 100 $\mu$ g ml<sup>-1</sup> of surfactant, (d) 1/250 dilution of (c) with mixture.



% volume size distributions of organic aerosols (a) white spirit, (b) white spirit-xylene mixture (1:1), and aqueous aerosols (c, d) 0.1% m/V SHMP solution, measured from a double pass spray chamber with 2mm injector at a gas flow rate of 0.8 1 min<sup>-1</sup> (a, b, c) and a 3mm injector at 1.5 1 min<sup>-1</sup> (d). Aerosol (d) measured at edge of stream from injector.



The population count distributions (Figures 3.10 to 3.16) show in many cases that the contribution from 3  $\mu$ m particles and less is significant. Values of up to 20% are noted for the cumulative % population below 3  $\mu$ m for some aerosols (Figures 3.14 (e), Table 3.7 experiment 32, Figures 3.15 (a), Table 3.7 experiment 35) but generally fall in the region of 5 to 15%. In some cases the distribution extends below the 1.1  $\mu$ m size cut-off of the instrument. The extent to which this loss of information occurs can be gauged from the data in Tables 3.5, 3.7 and 3.9, which show the percentage population at 1.1, 1.8 and 2.5  $\mu$ m together with the ratio of the counts at 1.1  $\mu$ m to that of the distribution mode expressed as a percentage. As these figures increase the distribution shows a greater contribution from fine particles and hence the greater the loss of population information below 1.1  $\mu$ m <u>e.g.</u> Figure 3.14 (a) Table 3.7 experiment 28, Figure 3.16 (b) Table 3.9 experiment 44).

A comparison of the % volume data with the population data shows how markedly different the distributions are. The dependence of the particle volume upon the cube of the diameter ( $\Pi d_p^{-3}/6$ ) dictates that the weighting of the volume distribution versus particle diameter is towards a larger size than that of the population distribution. This results in a shift of the size mean, mode and range of the distribution, together with a reduction in the contribution from the fine particles. Few examples are seen where the contribution from 3  $\mu$ m particles and less exceed a cumulative value of 2% by volume. This effect is put into perspective when it is considered that the volume of one 10  $\mu$ m particle is equal to the volume of 1000, 1  $\mu$ m particles. One further consequence of the cubic dependence of the volume on the diam-

eter is the development of multi-modal % volume distribution from the essentially mono-modal population distribution. This is especially seen where the rate of decrease in population with increase in particle size is small and shallow gradients exist over the size range 16 to 30  $\mu$ m.

(a) Nebuliser and single pass spray chamber (SPSC) aerosols

Tables 3.5 and 3.6 show the relevant % population and volume data respectively from the solution and slurry aerosol distributions produced by the nebuliser at various flow rates and those emitted from the SPSC fitted with and without 2 and 3 mm injectors. From the nebuliser little or no difference is seen between aerosols of water and 0.1% m/v SHMP solutions (experiments 1 and 2, Figures 3.10(a) and (b)) determined 5 mm from the nebuliser face at a gas flow rate of 0.75 l min<sup>-1</sup>. The population data (Table 3.5) shows that for a constant distance from the face (5, 20, 132 mm) the contribution from fine particles increases with gas flow rate (0.75 to 1.5  $1 \text{ min}^{-1}$ ), indicating that more efficient aerosol formation takes place at higher gas flow rates. (Theory predicts the argon gas velocity reaches a maximum of 276 m s<sup>-1</sup>, the sonic velocity of Mach 1, at a gas flow rate of 0.65 to 0.7 l min<sup>-1</sup> through a 200  $\mu$ m orifice (105). A shift of the frequency mean and mode size to smaller diameters is consistent with this. The maximum of the population range is not significantly changed. The volume data (Table 3.6) also shows this shift to finer size. The multi-modal volume distributions (Figures 3.17(b) and (c), Figures 3.18(a) and (c), Figures 3.19(a) and (b), experiments 2, 3, 4, 6, 7 and 8) show how the modes, designated  $d_1$  and  $d_2$  from left to right in the distribution, change in proportion in the manner expected with an increase in gas flow rate, <u>i.e.</u>  $d_1$  increases,  $d_2$  decreases. The mean particle velocity also increases with increase in gas flow rate
(constant distance), showing a value of 34 m s<sup>-1</sup> at 1.5 l min<sup>-1</sup> gas flow rate and 8.6 m s<sup>-1</sup> at 0.75 l min<sup>-1</sup> gas flow rate (5 mm distance).

A comparison of the aerosols produced by the nebuliser from a solution (0.1% SHMP) with that from a 1% slurry shows little or no difference between their population distributions (experiments 4 and 5, Tables 3.5 and 3.6, Figures 3.10 (d) and (e), Figures 3.18 (a) and (b)). This indicates that the presence of 1% m/y solid material does not significantly influence the mechanism of primary droplet formation and confirms the result previously obtained using the Malvern laser sizer.

When a conical design single pass spray chamber (SPSC) is fitted to the nebuliser a marked change in the aerosol, measured at the 4 mm exit, is seen (Figures 3.11 (a), Figures 3.19 (c), experiment 9, Tables 3.5 and 3.6). The contribution from larger particles is significantly increased such that the volume data is dominated by the secondary ( $d_2$ ) distribution (range 20 to 52  $\mu$ m, mode 37  $\mu$ m). The primary mode,  $d_1$ , which is broad (10 to 14  $\mu$ m), lies in a primary distribution of range 5 to 20  $\mu$ m and is approximately 1/8 of the area of the secondary distribution. The range and mode of  $d_1$  however compares well with the range and mode of the primary ( $d_1$ ) distribution from the nebuliser alone (experiment 2, Figure 3.17 (b)) produced under the same flow conditions. The increase in the proportion and range of large particles can be attributed to particle recombination (109); confinement of the aerosol by the spray chamber results in the coagulation mechanisms outlined in section 3.2.

The effect on an aerosol from adding 2 and 3 mm injectors to the SPSC can be seen from the data in Tables 3.5 and 3.6 (experiments 9, 13, 19, 2 mm: Figures 3.11 (a) and (e), Figures 3.24 (a) and (b); 3 mm: Figures

3.12 (a) and (e), Figures 3.24 (a) and (c)). At 0.75 1 min<sup>-1</sup> the population data shows the aerosol distribution, after the 2 mm injector, is narrower than after the SPSC alone (post 2 mm : 1.1 - 16  $\mu$ m; pre 2 mm 1.1 - 50  $\mu$ m). Loss of the very large and some fine particles results in a shift of the mean to a smaller diameter (13.7 to 8.7  $\mu$ m). The mode however is affected very little, suggesting that the aerosol modification occurs outside a common mode range (8 to 10  $\mu$ m). The volume data shows the contrast between the aerosols before and after the 2 mm injector in even greater relief. Virtually no secondary distribution (d<sub>2</sub>) is seen after the 2 mm injector and a reduction in the mean and mode diameters results (20.6 to 10.2  $\mu$ m; 14.1 to 11.1  $\mu$ m respectively). A decrease in the number density (1/3 value) and volume flux (1/29 value) is also noted despite the increased mean particle velocity and decreased cross sectional area of the exit point.

The post 3 mm injector aerosol (experiment 19), while reducing the contribution from the large particles seen in the SPSC exit aerosol, does not restrict the distribution to the same extent as the 2 mm injector. The bimodality (Figure 3.24 (a) and (c)) of the SPSC aerosol is maintained, but the relative proportions of the distribution modes (d<sub>1</sub> and d<sub>2</sub>) are reversed. (SPSC d<sub>2</sub> = 8 x d<sub>1</sub>; 3 mm, d<sub>2</sub> x 1.2 = d<sub>1</sub>). The range of the d<sub>2</sub> distribution is contracted from 52-20  $\mu$ m to 37-21  $\mu$ m.

Table 3.11 outlines the relevant volume and population data for aerosols produced at 0.75 1 min<sup>-1</sup> and measured 5 mm from the nebuliser face, 5 mm from the SPSC exit and 5 mm from the tips of the 2 and 3 mm injectors.

# TABLE 3.11

Aerosol volume and population data from the nebuliser and the single pass spray chamber (SPSC) with and without 2 and 3 mm bore injectors at a gas flow rate of 0.75  $1 \text{ min}^{-1}$  argon.

| Aerosol   | Nebuliser            | SPSC     | Injector | bores |
|---|----------------------|----------|----------|-------|
|   | (5mm from face)      | (exit)   | 2 mm     | 3 mm  |
| Number density cm <sup>-3</sup> (x10 <sup>2</sup> )                 | 16.4                 | 9.7      | 3.6      | 4.6   |
| Vol. flux rate cm <sup>3</sup> s <sup>-1</sup> cm <sup>-2</sup> (x1 | .0 <sup>4</sup> ) 31 | 127      | 4.4      | 7.3   |
| Vol. mean size µm   | 13.5                 | 20.6     | 10.2     | 11.1  |
| Vol. mode size µm   | 14.8                 | 14.1(37) | 11.1     | 12.5  |
| Population mean µm  | 9.7                  | 13.7     | 8.7      | 8.3   |
| Population mode µm  | 8.5                  | 9.2      | 7.7-10   | 7-9.2 |

It can be seen from the flux rate that the SPSC produces and concentrates the large particles even though the number density is half that from the nebuliser alone. As a result, the greatest volume ( $\propto$  mass) loss occurs due to the presence of the injectors. The 3 mm injector allows a greater volume flux transfer than the 2 mm injector and this is reflected in the larger volume mean and mode sizes. Volume transport efficiencies are estimated to be of the order of 3.5% for the 2 mm injector and 5.7% for the 3 mm injector. This effect is consistent with the injector acting as a filter which has been discussed on a theoretical basis by Sharp (109).

Both the 2 and 3 mm post injector aerosols show an increase in the proportion of larger particles when the gas flow rate is decreased from 1.5 to 0.5 l min<sup>-1</sup> (Tables 3.5 and 3.6). This trend, while consistent with a ballistic/turbulent loss process appears to be due to different mechanisms which are dependent upon the injector and gas flow rate used. The 2 mm injector aerosols are primarily monomodal (Figures 3.20) (a) to (d)) and as the gas flow rate decreases from 1.5 to 0.75 l min<sup>-1</sup> the bulk of the mode shifts to larger size. From 0.75 to 0.5 l min<sup>-1</sup> the main mode is similar but with the development of a secondary mode distribution from 20 µm to 36 µm. The 3 mm injector aerosols are multimodal (Figures 3.22 (a) to (d)) and show an increase in the contribution from the secondary mode distribution (with loss in primary mode) with a decrease in gas flow rate (1.5 l min<sup>-1</sup>,  $d_2 \ll d_1$ ; 0.5 1 min<sup>-1</sup>, d<sub>2</sub>  $\sim$  d<sub>1</sub>). Only a very slight shift occurs in the primary mode  $(d_1)$  distribution towards larger size diameters with decrease in flow rate. The number densities for both the 2 and 3 mm injector aerosol series are of similar magnitude  $(3.5 - 5 \times 10^2 \text{ cm}^{-3})$  and increase very slightly with a decrease in flow rate (more pronounced in

3 mm aerosol series). The volume flux rate increases as expected, knowing that an increased contribution from large particles occurs with a decrease in gas flow rate. At a given gas flow rate the 3 mm injector aerosols show a greater contribution from larger particles than the 2 mm injector aerosols and show up to twice the volume flux rate as a result.

A comparison between aerosols produced from 1% slurries and 0.1% SHNP solutions, under the same conditions of gas flow rate and injector bore, show little difference in distribution mean sizes, modes, size range, velocity, number density and volume transport data (2 mm, Figures 3.21 (a) to (d), Figures 3.11 (b), (c), (e), (f), Tables 3.5, 3.6, experiments 10, 11, 13, 14; 3 mm, Figures 3.23 (a) to (d), Figure 3.12 (b), (c), (e), (f), Tables 3.5, 3.6, experiments 16, 17, 19, 20). This indicates that the magnitude of those mechanisms which govern the formation and loss processes of an aerosol during transportation from the nebuliser through the SPSC to the tip of an injector are very similar for solutions and slurries.

(b) Double pass spray chamber (DPSC) aerosols

Tables 3.7 and 3.8 show the critical population and volume data obtained from aerosols that were measured exiting from an inner pass (Figure 3.6), a DPSC and 2 and 3 mm injectors. The aerosol exiting from a tube of the dimensions of the inner pass (15 mm ID x 132 mm long) was measured at two gas flow rates (0.75 and 1.5 1 min<sup>-1</sup>) the results are shown in Tables 3.7 and 3.8 (experiments 22 and 23) and Figures 3.13 (a) (b) and 3.26 (a) (b). Both the population and volume data show only small differences between the aerosols formed at 0.75 and 1.51 min<sup>-1</sup>. This suggests that the turbulent nature of the gas

flows within the inner pass (due to re-entrainment, diffusion, overexpansion, contraction and velocity changes) result in one or two mechanistic loss processes which dominate the system (turbulent induced impaction, recirculatory deposition). These are of such magnitude as to erode the differences normally seen with aerosols at different flow rates in larger spray chambers (e.g. SPSC).

The similar values of number densities and volume flux for the two gas flows compared with the starting values for the nebuliser alone (experiments 2 and 3 Table 3.8) together with the disproportionate velocity mean values would appear to confirm this turbulent theory. This effect may also be due to the inner pass being of a high aspect ratio (length/diameter = 8.8:1) which accentuates the loss processes compared with a low aspect ratio pass (e.g. length/diameter 1:1).

The aerosols measured above the 4.5 mm diameter exit of the DPSC at 0.75 and  $1.5 \ 1 \ min^{-1}$  gas flow rates (experiments 24 to 27, Figures 3.13 (c) to (f) and 3.27 (a) to (d), Tables 3.7 and 3.8) show a decrease in both population and volume mean values with increase in flow rate. The increase in fine particles and loss of larger particles together with the shift of the distribution mode  $(d_1)$  to the left as the gas flow rate is increased is readily seen in the population and volume distributions. As the aerosol data from the inner pass is similar for the two gas flow rates, the development of the obviously different distributions seen at the exit of the double pass is a result of the aerosol negotiating the turn from the inner pass to the outer pass and traversing the length of the outer pass to the exit ( $\backsim$  90 mm). It may be conjectured that the loss of particles at the higher flow rate is a result of ballistic impaction on the end wall of the spray chamber. If gravitational forces were dominant the trend would be reversed.

The aerosols produced from 1% slurries (experiments 25 and 27) measured at the exit of the DPSC (gas flow rates 0.75 and 1.5 1 min<sup>-1</sup>) are very similar in population and volume data to those aerosols produced from solutions (0.1% SHMP) under the same conditions (Figures 3.13 (c) to (f), Figures 3.27 (a) to (d), Tables 3.7 and 3.8, experiments 24 to 27).

Experiments 28 to 34 in Tables 3.7 and 3.8 (Figures 3.14 (a) to (g) and Figures 3.28 (a) to (d)) show the relevant population and volume data for aerosols measured above a 2 mm injector/DPSC assembly at gas flow rates of 1.5 to 0.5 1 min<sup>-1</sup>. It can be seen that the population mean size decreases with decrease in gas flow rate (6.6 to 4.9  $\mu m)$  while the mode changes very little (5.5 to 4.8 µm); a result of contraction of the range, i.e. loss of both large and fine particles, but with a greater loss of larger. This is again a manifestation of the filtering process by an injector. The volume mean and mode sizes show the same trend with decrease in gas flow rate (9 to 5.7 µm and 10.4 to 6.1 µm respectively). Volume size contraction is also seen (2.4 - 19.2 µm to 1.6 to 14  $\mu\text{m})$  together with a shift of the primary distribution. A small, ill-defined secondary distribution  $(d_2)$  seen at 1.5 1 min<sup>-1</sup> decreases to nothing at 0.5 l min<sup>-1</sup>. The loss of volume transport with decrease of gas flow rate is reflected in the aerosol volume flux rates, which decrease to 1/3 of the value when the gas flow is reduced from 1.5 to 0.5 l min<sup>-1</sup>.

The aerosol distributions measured at the exit of the DPSC alone and at the tip of the 2 mm injector (Tables 3.7, 3.8, Figures 3.29 (a) to (d), experiments 24, 26, 28, 32) under the same flow conditions (0.75 and 1.5 1 min<sup>-1</sup>) show marked differences. At 0.75 1 min<sup>-1</sup> gas flow rate the secondary distribution (d<sub>2</sub>) is reduced to nothing and the primary

distribution  $(d_1)$  is shifted to smaller particle diameters. This shift is also seen in the population distribution. At 1.5 l min<sup>-1</sup> the secondary distribution is reduced but not lost, while the primary distribution is little changed.

The presence of the 2 mm injector modifies the population and volume distributions of an aerosol exiting the DPSC but, more of note, the trend seen between mean size and gas flow rate is reversed, <u>i.e.</u> as the gas flow increases the mean size and range increases, which is suggestive of gravitational effects. One explanation for this may be that the presence of a restriction (2 mm injector) results in an increase in particle residence time (along the outer pass and near the restriction), allowing some deposition to occur due to sedimentation forces. This may be accentuated by particle coagulation effects, particularly near the neck of the restriction. This would remove the very large particles (secondary distribution decrease) but the primary distribution will move to the right (larger size) as the gas flow rate increases.

Slurry (1% m/v) aerosols measured under the same conditions as solutions (0.1% m/v SHMP) show the same trends and very similar population and volume distribution data (experiments 28 to 34, Tables 3.7, 3.8, Figures 3.14 (a) to (g), Figures 3.30 (a) to (d)).

Experiments 35 to 42 in Tables 3.7 and 3.8 show the relevant population and volume data for aerosols measured above a DPSC with a 3 mm injector. The population data shows that the mean and mode sizes increase with a decrease in gas flow rate. A loss of fines and shift of the distribution to larger size is evident. This is reflected in the volume data (mean and mode of  $d_1$ ) where the trend is also an

inverse relationship between flow rate and particle size. Little or no secondary volume distribution  $(d_2)$  is seen with the 3 mm injector. The change in distribution with flow rate is similar to that seen in the experiments 24 to 27 with the DPSC alone suggesting that the 3 mm injector is large enough to manifest the ballistic-type loss effects previously seen. At 1.5 and 0.75 l min<sup>-1</sup> gas flow rates on passing from the DPSC through the 3 mm injector the secondary mode  $(d_2)$  is lost but also the primary distribution  $(d_1)$  is shifted to smaller diameters (injector filtration process).

The volume data show that as the gas flow rate changes from 1.5 1 min<sup>-1</sup> down to 0.5 1 min<sup>-1</sup>, the aerosol number density and volume flux rate changes little over the range.

Experiment 42 (Table 3.7, 3.8, Figures 3.15 (h) and 3.35 (d)) was performed to show the effect of measuring an aerosol at the edge of the stream exiting from a 3 mm injector. Slight differences can be seen in the population and volume data between this aerosol distribution and that of a centre line measurement (experiment 35). However the major difference is noted to be the velocity mean value  $(3.3 \text{ m s}^{-1})$  which is half the value of experiment 35 (6.5 m s<sup>-1</sup>) measured under the same gas flow conditions. This is an example of the particles following the gas velocity profile where  ${\tt V}_{n}$  is a maximum at the centre and due to viscosity effects approaches zero at the inside surface of the injector wall. As previously found with the 2 mm bore injector, aerosols produced from 1% slurries and measured above the 3 mm injector show no significant differences in distribution to those produced from solutions (0.1% SHMP) under the same gas flow conditions (experiments 35, 36, 40, 41, Tables 3.7, 3.8, Figures 3.15 (a) (b) (f) (g) and 3.32 (a) to (d)).

A comparison between the distribution data for aerosols exiting from 2 and 3 mm bore injectors under the same flow conditions shows a size cross-over effect. This is due to the direct (2 mm) and inverse (3 mm) proportionality of the aerosol mean, mode and volume flow with that of the gas flow rate. At low gas flows,  $0.5 - 0.75 \ 1 \ min^{-1}$ , the 3mm injector introduces a greater volume flux and proportion of larger particles (fewer fines) than the 2 mm injector. At high gas flows (1.5 1 min<sup>-1</sup>) the positions are reversed. Overall the largest particles ( $\propto$  volume flow and flux) are introduced to a plasma using a 3 mm injector at 0.5 to 1.1 1 min<sup>-1</sup> or a 2 mm injector from 1.1 to 1.5 1 min<sup>-1</sup> gas flow rates. To remove fines from the system it is preferable to use the 3 mm injector but not at high gas flow rates.

Table 3.12 shows the volume data for aerosols produced at 0.75 at  $1.5 \ 1 \ min^{-1}$  gas flows measured from a nebuliser, through an inner pass and DPSC to the tip of a 2 and 3 mm injector.

An estimation of the volume transport losses and overall efficiency of the sample introduction system may be gained from an examination of the figures in Table 3.12. In terms of flux rate it is seen that the greatest loss occurs at the nebuliser/inner pass stage where at  $0.75 \ 1 \ min^{-1}$  only some 7% of the original sample from the nebuliser passes out of the inner pass. This figure may be higher when the total cross sectional area of the aerosol is taken into account at 5 mm from the nebuliser face and at the exit of the inner pass. When the aerosol flux rates from the 2 and 3 mm bore injectors are considered, transport values of 3.9 and 6.1% of the original aerosol (5 mm from the nebuliser face,  $0.75 \ 1 \ min^{-1}$ ) are obtained. As the cross sectional area of the 3 mm injector is greater than that of the 2 mm injector, the efficiency

|  |                         |      | Меа                 | surement | <u>t Positi</u> | on                  |      |      | •    |     |      |     |
|--|-------------------------|------|---------------------|----------|-----------------|---------------------|------|------|------|-----|------|-----|
|  | Distance from Nebuliser |      | Spray Chamber Exits |          |                 | Injector Exit Bores |      |      |      |     |      |     |
|  | 51                      | nm   | 2                   | 0mm      | Inner           | Pass Exit           | DPSC | Exit | 2    | m   | 31   | ານກ |
| Gas Flow Rate/l min <sup>-1</sup>  | 0.75                    | 1.5  | 0.75                | 1.5      | 0.75            | 1.5                 | 0.75 | 1.5  | 0.75 | 1.5 | 0.75 | 1.5 |
| Number Density/ $cm^{-3}$ (x10 <sup>2</sup> )  | 16.4                    | 7.5  | 16 <sup>-</sup>     | 21       | 8.7             | 8.6                 | 2.0  | 2.0  | 4.3  | 3.3 | 2.5  | 3.7 |
| Volume Flux Rate/cm <sup>3</sup> s <sup>-1</sup> cm <sup>-2</sup><br>(x 10 <sup>-4</sup> ) | 31                      | 13.7 | 15                  | 11.2     | 2.1             | 2.5                 | 4.3  | 2.2  | 1.2  | 3.1 | 1.9  | 1.0 |

Volume Data Measured from Aerosols at the Nebuliser, Inner Pass Exit, DPSC Exit and top of the 2 and 3mm Bore Injectors at Gas Flow Rates of 0.75 and 1.5 1 min 1.

.

.

•

# TABLE 3.12

.

. :

122

.

.

.

.

.

of the 3 mm injector on a total volume transport basis is estimated to be 3 to 4 times greater than the 2 mm at 0.75 l min<sup>-1</sup> gas flow rate. At 1.5 l min<sup>-1</sup> the efficiences of the two injectors are similar.

Table 3.7 shows that the nebuliser alone (experiments 2 and 3) produces an aerosol with a population range of 18 µm down to just below 1 µm. The mode of this distribution is of the order 8 to 10 µm with a mean of similar size. The volume data (Table 3.8, experiments 2 and 3) shows the significant range to be 4 to 40 µm with a primary mode (d<sub>1</sub>) of 12 to 15 µm and a secondary mode (d<sub>2</sub>) of 24 to 30 µm. From section 3.2.2, equation 3.2, the Nukiyama-Tanasawa equation (110) empirically describes the Sauter mean size, d<sub>s</sub> (volume to surface ratio) of an aerosol formed under certain conditions. Substitution of the terms with those figures for aqueous aerosol formation at 1.5 and 0.75 1 min<sup>-1</sup> of argon <u>i.e.</u> velocity v = 276 m s<sup>-1</sup> (105),  $\sigma$  = 74.2 dyn cm<sup>-1</sup>,  $\mathbf{P} = 0.99$  g cm<sup>-3</sup>,  $\eta = 0.01$  P,  $\mathbf{Q}_{i} = 1.4 \times 10^{-2}$  cm<sup>3</sup>s<sup>-1</sup>,  $\mathbf{Q}_{g} = 25$  and 12.5 cm<sup>3</sup>s<sup>-1</sup> (1.5 and 0.75 1 min<sup>-1</sup> gas flow rates).

calculated d<sub>s</sub> ( $\mu$ m) observed d<sub>s</sub> ( $\mu$ m)

At 0.75 l min<sup>-1</sup> 52 18.4

At 1.5 l min<sup>-1</sup> 30 14.7

Equation 3.2 tends to overestimate the Sauter mean diameter for aerosols produced by the V-groove nebuliser. Only in the case of the higher flow rate  $(1.5 \ 1 \ min^{-1})$  does the Sauter mean value coincide with the upper range of the volume distribution. The equation does however show the trend of more efficient aerosol formation (finer size) as the flow rate increases.

Figure 3.6 displays the dimensions of the Scott type DPSC used in the experiments, in particular the turning point where the aerosol changes direction (180°) from the inner pass to the outer pass and on to the spray chamber exit. Cut-off diameters (50% penetration) for particles undergoing the termed "centrifugal loss process" can be calculated from equation 3.3 (112). Substituting in values for the terms  $\eta = 221 \times 10^{-6}$  P.,  $W_i = 0.75$ cm (minimum)and 1.6cm (maximum), n = 1 (minimum),  $P_p - P_g = 0.99$  g cm<sup>-3</sup>,  $V_{ip} = 4.2$  and 2.1 cm s<sup>-1</sup>, (1.5 and 0.75 1 min<sup>-1</sup>) then the minimum d<sub>c</sub> value calculated is 76 µm.

No particles of this size range are seen exiting from the inner pass, which shows a measured maximum particle size of 36  $\mu$ m. A value of 5 for the term n (no. of revolutions) would be required before the d<sub>c</sub> value would be comparable to the measured size maximum. There is also some uncertainty in the value for V<sub>ip</sub>. However the large difference between the measured and calculated size suggests that centrifugal loss processes are not dominant.

Equation 3.7 shows the relationship between stopping distance and particle radius for a given particle velocity. Substituting in the measured inner-pass exit velocity of particles, 36 cm s<sup>-1</sup> at 1.5 1 min<sup>-1</sup> gas flow and the maximum aerosol particle size measured at that flow rate 36  $\mu$ m then with P<sub>1</sub> = 0.99 g cm<sup>-3</sup> and N<sub>g</sub> = 221.7 x 10<sup>-6</sup> P equation 3.7 yields a stopping distance 1<sub>s</sub> of 0.12 cm.

The value of 0.12 cm represents the distance travelled by the particle when directed into a static atmosphere. The inner pass however guides the particles into an expansion/flow reversal area which is in constant motion and far from static. The change in gas velocity, down to

4.2 cm s<sup>-1</sup> at the outer pass dictates, from equations 3.5 and 3.7, that ballistic impaction will occur for particles of 120  $\mu$ m in size at the impaction surface some 3.3 cm from the inner pass. Due to a lack of knowledge about the flow lines in this region, the relative magnitudes of the possible loss processes, <u>i.e.</u> flow line interception, turbulent and recirculation impaction, gravitational and centrifugal deposition, are unknown and calculations based upon these theoretical considerations are only accurate to within an order of magnitude (109). However, the trends shown by the aerosol particle size distributions with flow rate for the DPSC with and without a 3 mm injector suggest that flow line and recirculation effects are important.

Using the dimensions of the DPSC (Figure 3.6) and substituting into equation 3.1 for the Reynolds number to ascertain whether, theoretically, laminar or turbulent flow is present along the outer pass to the exit, the following values of Re were obtained. With  $P = 1.78 \times 10^{-3} \text{ g cm}^{-3}$ ,  $V = 4.16 \text{ cm s}^{-1}$  (1.5 l min<sup>-1</sup>), 1.39 cm s<sup>-1</sup> (0.5 l min<sup>-1</sup>),  $\eta = 221.7 \times 10^{-6} P$  and d = 2.77 cm (calculated from the cross-sectional area of the annulus of travel along the outer pass and expressed as a pipe of diameter 'd' having the same area) then Re = 93 at 1.5 l min<sup>-1</sup> and 31 at 0.5 l min<sup>-1</sup>.

This indicates that laminar flow is theoretically present along the outer pass to the exit of the spray chamber. For particles to obey Stokes law, a Reynolds number of less than 1 is required (109). At a flow rate of 1.5 1 min<sup>-1</sup> a gas velocity of 4.2 cm s<sup>-1</sup> is calculated along the outer pass to the exit, which gives a threshold particle diameter in excess of 60  $\mu$ m (0.2 Re). The particle number (K<sub>p</sub>), equation 3.4, which is required to be less than 3.3 for an aerosol particle to be considered in uninterrupted laminar flow, is calculated

to be 1.3 for a 40  $\mu$ m particle. As K<sub>p</sub> decreases with diameter, all particles below 40  $\mu$ m can be considered eligible under the conditions used. Equations 3.5 and 3.6 (110) estimate the terminal settling diameter d<sub>TV</sub> and 50% cut-off diameter, d<sub>c50</sub>, due to gravitational effects in a laminar flow system. The values calculated for the outer pass-to-exit gas stream are shown in Table 3.13.

 $V_g$  is the gas velocity in the outer pass region of the spray chamber and  $T_r$  is the residence time for a particle to travel the 90 mm from just in front of the impaction wall to the DPSC exit. Only particles that can remain above the outer surface of the inner pass were considered. Those which drop below the crown of the outer surface are considered 'lost' due to the settling forces and would theoretically have little chance of rising up to the exit point. It can be seen that the values for the 50% cut-off diameter, d<sub>c50</sub>, are similar to those values found for the mean population and volume diameters of aerosols exiting a double pass spray chamber with and without a 2 mm injector. (Table 3.7, experiments 28 to 34 and Table 3.7, experiments 24 to 27). The terminal settling diameters compare favourably with the range seen for the secondary mode (d<sub>2</sub>) of the % volume distributions but are much higher than the bulk of the population distribution particle diameters.

The coincidence of the mean particle diameters measured in the aerosols with those  $(d_{c50})$  calculated to be limited by settling effects in a laminar flow system indicates that for this design of spray chamber the gravitational loss process cannot be ruled out. It is not possible to estimate from the experimental data the magnitude of any single loss process along the outer pass.

# **TABLE 3.13**

Settling diameters  $d_{\rm TV}$  and  $d_{\rm C50}$  calculated for the outer pass at four flow rates

| Flow rate/l min <sup>-l</sup> | V <sub>g</sub> /cm s <sup>-1</sup> | T <sub>r</sub> /s | d <sub>TV</sub> /µm | d <sub>c50</sub> ∕µm |
|-------------------------------|------------------------------------|-------------------|---------------------|----------------------|
| 1.5                           | 4.2                                | 2.2               | 41.2                | 8.4                  |
| 1.1                           | 3.0                                | 3.0               | 35.3                | 7.2                  |
| 0.75                          | 2.1                                | 4.3               | 29.1                | 5.9                  |
| 0.5                           | 1.4                                | 6.5               | 23.8                | 4.9                  |

It is of note that while the inner pass is shown to be in a turbulent state and calculations suggest, together with some experimental evidence, that the outer pass region settles to a laminar flow state the degree or extent of turbulence at the flow reversal point (inner to outer passes with expansion chamber and impaction wall) is unknown.

While a number of workers have investigated aerosol droplet distributions by laser diffraction techniques (86, 96, 101, 104, 109) it is evident that each nebuliser, spray chamber and injector system produces a unique droplet distribution which is also dependent upon the conditions employed, i.e. gas and liquid flow rates (and possibly the laser instrument used). This is readily seen in the work by Olsen and Strasheim (104), who measured the aerosols emitted from a Plasma therm torch coupled to a DPSC and using four different nebulisers, the result being four totally different population and volume distributions. Routh (101) measured the median droplet diameter and volume distributions of aerosols produced by six nebuliser/spray chamber/injector systems. Routh noted the decrease in median diameter with both increase in gas flow rate and position along the sample introduction system. The same trends are seen in the series of experiments 1 to 42. The aerosol median diameters measured by Routh using the nebuliser/ conical spray chamber/injector system are smaller ( $\sim 5 \ \mu m$ ) than any of the mean values found using a similar conical spray chamber assembly  $(7-10 \ \mu\text{m})$ . This may be due to the absence of an impact bead in the spray chamber and the use of a larger bore injector (2-2.2 mm) in the experiments 9 to 15. The distribution ranges are however similar (2 to 27 μm).

In the six combinations of sample introduction, Routh also included the measurement of aerosols from a Perkin-Elmer cross-flow nebuliser/Scott

DPSC and injector. The range (2 to  $18 \ \mu$ m) and median particle diameter (5  $\mu$ m) are comparable to those seen in experiments 32 to 34 which used a DPSC with 2 mm injector at 0.75 and 0.5 1 min<sup>-1</sup> flow rate (range 1.6 to 17  $\mu$ m, volume mean size 5.7 - 6.7  $\mu$ m).

(c) Organic Aerosols

Tables 3.9 and 3.10 show the relevant population and volume data obtained from organic liquid aerosols measured at the exit of a 2 mm injector /DPSC assembly (experiments 43 to 46, Figures 3.16 (a) to (d) and 3.34 (a) to (d)). For comparison the data for an aqueous aerosol produced under similar conditions is also shown (experiment 32, Figures 3.16 (e) and 3.35 (c)). The population data shows that the addition of xylene to the white spirit to form a 1:1 mixture results in a broadening of the distributions (from 12 to 17  $\mu$ m), an increase in fines and shift of the mean diameter to larger particle size. The mode however is not affected. The volume data shows a marked difference between the white spirit and the 1:1 white spirit/xylene mixture. The mean diameter and mode of the distribution are moved to larger particle size and the volume distribution becomes multimodal with a secondary distribution (d\_) up to 37  $\mu m$  . A doubling of the number density is also evident, together with a five-fold increase in the volume flux. These effects are a result of the physical properties of the liquids themselves, i.e. surface tension, viscosity, vapour pressure and density, which also accounts for the different population and volume distributions and data obtained from the aqueous system. For a more detailed study the reader is directed to work by Browner and Boorn (116) and Sharp (105).

The experimental series 43 to 46 was initially set up to ascertain if the presence of the silicon-based lipophylic surfactant modified the particle size distribution of the organic aerosol and its volume flow rate. Both population and volume data indicate that there is no significant difference between aerosols produced from a 1:1 white spirit/xylene mixture with and without the surfactant. The positive interference from the plasma signal for those solutions which contained the surfactant is therefore presumably due to a chemical/matrix effect in the plasma.

3.4.2.3 Conclusions

Both population and volume distribution data are necessary for a mechanistic study to be made of the formation and transportation of aerosols in a sample introduction system. A phase/Doppler spray analyser provides this information in the critical region 1 to 40  $\mu$ m together with velocity characterisation. Population distributions of primary aerosols are monomodal and cover the range 20  $\mu$ m down to below 1  $\mu$ m. Mean and mode particle diameters are of the order 7 to 10  $\mu$ m. Volume distributions are multimodal with an increased particle size range from 3 up to 37  $\mu$ m. Volume mean sizes are of the order of 13  $\mu$ m. Increasing the gas flow rate from 0.75 to 1.5 1 min<sup>-1</sup> increases the efficiency of aerosol formation and decreases the particle size (hence an increase in the contribution from fines).

When an aerosol is contained in a conical SPSC (without impact bead) the population distribution shows an increase in particle size range and mean diameters which can only be accounted for by particle coagulation effects.

The presence of an injector modifies the particle size distribution, causing the loss of the larger particles, reducing the range (population range 18  $\mu$ m down to below 1.1  $\mu$ m) and moves the population particle size mean and mode values to the region 6 to 9  $\mu$ m (volume data 7 to 11  $\mu$ m). A 3 mm injector allows a greater fraction of larger aerosol particles to pass to a plasma (8 to 9  $\mu$ m mean values) than a 2 mm injector (6 to 8  $\mu$ m mean values). On a % volume basis this effect is more pronounced (2 mm, 7 to 10  $\mu$ m mean values; 3 mm, 10 to 12  $\mu$ m), showing a greater contribution from the secondary mode (20 to 36  $\mu$ m). As a consequence the volume ( $\propto$  mass) flux of an aerosol from a 3 mm injector is twice that from the 2 mm injector. It is noted that the mean particle size decreases with increase in gas flow rate, which can be explained in terms of ballistic/turbulent impaction.

Aerosols formed from 1% m/v slurries show no significant differences to those formed from solutions (0.1% SHMP) under the same flow conditions, whether at the nebuliser or exiting from a 2 or 3 mm injector/SPSC system.

The double pass spray chamber study showed that the aerosol that exits from an inner pass has a similar distribution to that of the primary aerosol from the nebuliser, the population and volume mean particle diameters being very close in value. Increasing the gas flow rate  $(0.75 \text{ to } 1.5 \text{ l min}^{-1})$  has little effect on the population and volume mean values of the aerosols exiting from an inner pass and is an indication of the dominant turbulent forces that exist in this region. The loss in volume flux terms due to turbulent induced impaction is however very high and values suggest this to be the major loss point in the sample introduction system. Aerosols measured at the exit of the DPSC show similar population (9.5-10  $\mu$ m) and volume (12-13  $\mu$ m) means to

those from the inner pass at a flow rate of 0.75 l min<sup>-1</sup>. At 1.5 l min<sup>-1</sup> flow rate the population mean particle size decreases to 7-8  $\mu$ m (from volume data 10  $\mu$ m), suggesting a ballistic loss process is taking place. This is also seen in the population range, which decreases slightly when going from the inner pass to the DPSC exit at the higher gas flow rate.

As with the SPSC, the presence of an injector modifies the aerosol distribution from a DPSC, decreasing the population mean and mode particle size to 5-7  $\mu$ m in both cases and decreasing the particle size range. Mechanistically the 3 mm acts differently to that of the 2 mm injector. The 3 mm injector allows an increase in the population mean and mode particle sizes with a decrease in the gas flow rate and may be acting like the large exit (4.5 mm) from the DPSC, i.e. allowing the turbulent/ballistic processes seen with the DPSC alone to be the dominant loss mechanism. The 2 mm injector shows an increase in both population and volume mean particle diameters with increase in flow rate. The mode diameters also show this trend. One explanation is that the more restrictive 2 mm bore causes an increase in residence time for particles and allows gravitational effects to become significant. Theoretical calculations show that the gas train from the outer pass to the exit is in laminar flow and that settling diameters for 50% loss (5 to 8  $\mu m)$  are of the same order as those mean diameters measured exiting the spray chamber/injector system (5 to 7 µm).

Aerosols formed from 1% m/v slurries show no significant difference to those formed from solutions (0.1% SHMP) under the same conditions. This was found to hold throughout the DPSC sample introduction system, even to the mechanistically different effects seen with the 2 and 3 mm injectors.

The organic aerosols measured above the 2 mm injector/DPSC system show a marked difference to those of aqueous aerosols produced under similar conditions. The white spirit aerosol is noted to be very different to that of a 1:1 white spirit/xylene aerosol, the latter showing a broader distribution with a shift of the mode (volume) and mean values to larger particle size. The presence of the lipophilic silicon-based surfactant in the 1:1 white spirit/xylene medium does not significantly modify an aerosol produced from the medium alone.

# 3.5 THE MEASUREMENT OF SLURRY SOLID PARTICLE SIZE IN AEROSOLS USING INTRUSIVE IMPACTOR TECHNIQUES

### 3.5.1 Introduction

The cascade impactor method was chosen because it would theoretically allow those parameters concerning slurry aerosols to be calculated, (i) aerosol sizes, (ii) solid particle sizes, and (iii) transport efficiences.

The theory and design of the impactor is outlined in Section 3.3.2.

3.5.2 Experimental

A Mark III Andersen stack sampler (Andersen Samplers Inc., Atlanta, Georgia, U.S.A.) was positioned above the exit point of a 3 mm bore injector which was connected to a Scott type double pass spray chamber (DPSC) as shown in Figure 3.36. The stack sampler was fitted with a pre-impactor attachment in order to separate and collect aerosol particles of over 12  $\mu$ m in size and allow those below 12  $\mu$ m to be

FIGURE 3.36

Diagram of the Andersen stack sampler and double pass spray chamber arrangement used for the cascade impactor experiments.



collected as fractions on pre-weighed glass fibre papers sitting on the plates in the impactor body. Slurries of 2.5 and 5% m/v concentration were used in these experiments and were prepared by the microniser method outlined in Chapter 2. These were fed to a Kel-F Ebdon nebuliser (PS Analytical Sevenoaks, Kent, UK) by a peristaltic pump at a flow rate of 0.8 ml min<sup>-1</sup>. Various argon flow rates were used to convey slurry aerosols to the cascade impactor, 0.75 to 1.6  $l \min^{-1}$ flow rate, and total isokinetic sampling was performed. All the solid material collected by the impactor was weighed and transport efficiencies were calculated, based upon these values and the pre- and postnebuliser starting slurry weights. For comparison, a 1% m/v sodium chloride solution aerosol produced at 0.76 l min<sup>-1</sup> gas flow rate was collected. The metered draw for the cascade impactor was supplied by a 1/2 HP laboratory compressor fitted with an in-line calibrated flow meter. All solid particle sizes were measured on a Coulter Counter TAII.

## 3.5.3 Results and Discussion

The particle size distribution of the 5% ore starting slurry (SA1/C120) and that of the redispersed solid fractions from the cascade impactor matched to the 1.6 1 min<sup>-1</sup> argon flow rate experiment are shown in figures 3.37 and 3.38. It is seen that the particle size range of the ore from the cascade impactor, 0.7 to 5  $\mu$ m, is markedly different from the starting slurry, 0.7 to 12  $\mu$ m. The modes of the two distributions are also different; the impactor collected material being finer, 1 to 2  $\mu$ m, than the starting slurry, 3 to 4  $\mu$ m. Figure 3.39 shows the % mass fractions collected by the impactor against aerosol size. The solid size ranges shown in Figure 3.38 do not correlate exactly with the

aerosol size fractions shown in Figure 3.39 except in trend. In most cases the aerosol size is smaller than the solid particle size.

Two possible explanations for this result are the effects of extensive evaporation of the liquid envelope from the slurry particles on leaving the injector and the unknown density of the slurry aerosol, i.e. large deviation from the theoretical  $1 \text{ g cm}^{-3}$ . The former explanation is most likely because the slurry aerosol particle passes from a saturated argon atmosphere in the injector at a gas flow rate of 1.6 l min<sup>-1</sup> to normal laboratory air in the impactor at a flow rate of 17 l min<sup>-1</sup> (in order to isokinetically sample the total aerosol). By the time impaction takes place, a dry or near-dry slurry particle may have been collected. Hence, while the % mass fraction versus aerosol size graphs do not show accurate aerosol size, they do serve to show the comparative grading of the aerosol fractions collected. It is of interest to note that the pre-impactor which theoretically separates aerosol particles over 12 µm from the bulk, collected some 18% by mass of the total solid particles, none of which were over 5 µm in size. This trend is seen in all the mass fraction graphs relating to the first series of 2.5 and 5% m/v slurry experiments (Figures 3.39 to 3.42).

When a finer starting ore slurry (2.5% m/v) was conveyed to the impactor (Figure 3.43) at an argon flow rate of 0.75 l min<sup>-1</sup>, the particle size distribution of the solids collected on the plates (Figure 3.44) show that representative size transportation occurred. The range and mode being very close in both sets (range 0.7 to 6  $\mu$ m; mode l to 2  $\mu$ m). It is therefore indicated that under the above conditions representative transportation of a slurry takes place, with respect to particle size, when the maximum solid particle size is below 5  $\mu$ m and the mode of the distribution is below 3  $\mu$ m.

FIGURE 3.37

By volume particle size distribution of the starting ore slurry, 5% m/V SA1/C120, used in Cascade impactor study (i).



FIGURE 3.38

By volume particle size distributions of ore fractions collected by Cascade impactor (study(i)) from aerosol exiting a double pass spray chamber with 3mm injector at 1.6 l min<sup>-1</sup> gas flow rate.



By weight aerosol size distribution of 5% m/V ore slurry, SA1/C120, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 1.6 l min<sup>-1</sup> gas flow rate.



FIGURE 3.40

By weight aerosol size distribution of 5% m/V ore slurry SA1/C120, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 0.85 l min<sup>-1</sup> gas flow rate.



FIGURE 3.41

By weight aerosol size distribution of 2.5% m/V ore slurry SA1/C120, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 1.6 l min<sup>-1</sup> gas flow rate.





By weight aerosol size distribution of 2.5% m/V ore slurry SA1/C120, collected by Cascade impactor (study (i)) from aerosol exiting double pass spray chamber with 3mm injector at 0.85 1 min<sup>-1</sup> gas flow rate.



FIGURE 3.43

By volume particle size distribution of the starting ore slurry, 2.5% m/V SA1/C120, used in Cascade impactor study (ii).



FIGURE 3.44

By volume particle size distributions of ore fractions collected by Cascade impactor (study (ii)) from aerosol exiting a double pass spray chamber with 3mm injector at 0.75 1 min<sup>-1</sup> gas flow rate.



FIGURE 3.45

By weight aerosol size distributions of (a) 2.5% m/V ore slurry SA1/C120, collected by Cascade impactor (study (ii)) and (b) 1% m/V sodium chloride solution from aerosol exiting a double pass spray chamber with 3mm injector at 0.75 1 min<sup>-1</sup> gas flow rate.



The % mass fraction against aerosol size distribution for the finer 2.5% ore slurry  $(0.75 \ 1 \ min^{-1})$  is shown in Figure 3.45 together with the mass fraction distribution for the 1% m/v sodium chloride solution collected under the same conditions. While the distributions are very different, the slurry being coarser due to the presumed evaporation effects previously mentioned, the mass transfer efficiency (MTE) of the two experiments is the same. As mass transfer efficiency, in this case, is designated

as:

then representative mass transport is also indicated for fine slurries .compared with solutions.

Table 3.14 shows the mass transfer efficiencies for the experiments performed with the cascade impactor.

The % MTE values in Table 3.14 indicate that mass transfer efficiency increases with gas flow rate. This effect has been noted by a number of workers (109, 110, 117), but is dependent upon the feed rate of the solution being constant. The % MTE decreases with increased feed rate for a constant gas flow (109, 110). The increase in MTE with gas flow rate is attributed to the increase in nebuliser efficiency resulting in a finer aerosol distribution, with fewer losses in the SIS. The range of the MTE values at the gas flow rates shown compare more than

# **TABLE 3.14**

# Mass transport efficiences<sup>1</sup> (MTE) calculated from cascade impactor studies

| % Slurry (m/v)           | Argon flow rate l min <sup>-1</sup> | % MTE |  |  |
|--------------------------|-------------------------------------|-------|--|--|
| 5                        | 1.6                                 | 173   |  |  |
| 2.5                      | 1.6                                 | 1.97  |  |  |
| 5                        | 0.85                                | 0.48  |  |  |
| 2.5                      | 0.85                                | 1.12  |  |  |
| ,                        |                                     |       |  |  |
| 2.5                      | 0.75                                | 0.76  |  |  |
| 1% NaCl Sol <sup>n</sup> | 0.75                                | 0.77  |  |  |

1. calculated from equation (3.9) constant liquid flow rate 0.8 ml min<sup>-1</sup>.

۰.
favourably with those of Kato (117), Ebdon and Cave (58), Cull <u>et al.</u> (102), and Browner and Boorn (89), showing values of 0.5 to 2%. Considering the range of different systems used by the above workers, <u>e.q.</u> concentric and Babington nebulisers, double and single pass spray chambers, 1 to 2 mm bore injectors, feed rates of 0.5 to 2 ml min<sup>-1</sup> and gas flows of 0.5 to 1.5 1 min<sup>-1</sup>, the values obtained would appear to be typical and are a further indication of the close modelling of solutions by slurries under the conditions used.

3.5.4 Conclusions

It is necessary for certain ores, which are multicomponent and therefore polydensitic, to be ground to less than 5 to 6 µm before representative transportation, in terms of particle size, of the starting slurry can occur. Fine slurries of this nature show comparable mass transfer efficiency with solutions indicating that simple solutions can be used for calibration, assuming that no atomisation effects are present in a plasma.

## 3.6 THE MEASUREMENT OF SLURRY SOLID PARTICLE SIZE IN AEROSOLS USING THE INTRUSIVE BOTTLE COLLECTION METHOD

3.6.1 Introduction

In order to establish if gas flow rate and injector bore affected the distribution of solid particles reaching the plasma, a series of experiments varying the above parameters was undertaken.

#### 3.6.2 Experimental

An Ebdon nebuliser (V-groove type, PS Analytical, Sevenoaks, Kent, U.K.), Scott double pass spray chamber and injectors with bore diameters 1.1, 2.2, 3.2 and 3.6 mm were used in the experiments. Slurries of 5% m/v were prepared in 0.1% m/v sodium hexametaphosphate solution from the post Tema mill-ground ore J+L4. In order to disperse the dry-ground coarse ore (particle size range 0.6 to 40  $\mu$ m), slurry concentrates were immersed in an ultrasonic bath for three minutes prior to dilution.

A peristaltic pump (Watson and Marlow) was used to deliver 2.9 ml min<sup>-1</sup> of the stirred slurry to the nebuliser and a regulated argon supply transported the slurry aerosol through the spray chamber to the various injectors. The particles were then collected by channelling the aerosol through a flexible plastic pipe to a solution of 0.1% SHMP (to maintain the dispersion) contained in a 30 ml Nalgene bottle. An in-line needle valve flow meter controlled the flow of argon to the nebuliser and gas flow rates of 0.66, 1.73 and 3.4 1 min<sup>-1</sup> were used. The particle size distributions were measured on a Coulter Counter TAII.

3.6.3 Results and Discussion

The distribution results are shown in graphical form in Figures 3.46 to 3.49. Table 3.15 cross-references the figures to the experiments undertaken.

## TABLE 3.15

• •

.

# Table of cross-referenced figures to the aerosol bottle collection experiments performed

|          |              | Gas Flow Rate / 1 min <sup>-1</sup> |                  |
|----------|--------------|-------------------------------------|------------------|
| Injector | 0            | 0.66 1.73                           | 3.4              |
| Bore/mm  |              |                                     |                  |
| 1.1      | fig 3.46 (a) | fig 3.46 (b) fig 3.46               | (c) fig 3.46 (d) |
| 2.2      | fig 3.47 (a) | - fig 3.47                          | (b) fig 3.47 (c) |
| 3.2      | fig 3.48 (a) | fig 3.48 (b) fig 3.48               | (c) fig 3.48 (d) |
| 3.6      | fig 3.49 (a) | fig 3.49 (b) fig 3.49               | (c) fig 3.49 (d) |

F

150

.

,

By volume particle size distributions of 5% ore slurry, J+L4, acquired by the bottle collection method from aerosols exiting a double pass spray chamber with 1.1mm injector at gas flow rates (b) 0.66, (c) 1.73, (d) 3.4 l min<sup>-1</sup> together with starting slurry distribution (a).



FIGURE 3.47

By volume particle size distributions of 5% m/V ore slurry, J+L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 2.2 mm injector at gas flow rates (b) 1.73, (c) 3.4 l min<sup>-1</sup> together with starting slurry distribution (a).



152

By volume particle size distributions of 5% m/V ore slurry, J+L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 3.2mm injector at gas flow rates (b) 0.66, (c) 1.73, (d) 3.4 1 min<sup>-1</sup> together with starting slurry distribution (a).



FIGURE 3.49

15

By volume particle size distributions of 5% m/V ore slurry, J+L4, acquired by the bottle collection method, from aerosols exiting a double pass spray chamber with 3.6mm injector at gas flow rates of (b) 0.66, (c) 1.73, (d) 3.4 l min<sup>-1</sup> together with starting slurry distribution (a).

Ξ.



DIAMETER µm

In most cases the particle size range of the post-injector material is between 0.6 and 6.3  $\mu$ m and differs markedly from the broad starting slurry distribution (0.6 to 40  $\mu$ m). All the post-injector distributions show a loss in the fraction of slurried material above the 6 to 8  $\mu$ m channel and a gain in the fraction of smaller size material, 0.63 to 5  $\mu$ m, compared with the slurries before nebulisation.

The position of the distribution maxima (mode) is not significantly changed by the size of the injector bore and in most cases the mode of the distribution from the post-nebulised material is the same as that of the starting slurry. The shape of the distribution mode from the post-nebulised slurries also models that of the starting slurry.

For a constant bore size, 2.2, 3.2 and 3.6 mm, an increase in gas flow rate, 0.66 up to 3.4 l min<sup>-1</sup> increases the contribution from the larger size particles and decreases the percentage volume value of the mode of the distribution.

Small differences are seen, however, in the modes of the distributions exiting the 1.1 mm injector at different gas flow rates. One possible explanation is that for a 1.1 mm injector any flow rate above  $1.5 \ 1 \ min^{-1}$ is turbulent (Reynolds number >2300) and the flow pattern for the particles is different above and below the critical flow rate. While no change is observed in the mode of the distributions exiting the 2.2 mm injector it is of note that the gas flow through this bore at 1.7 1 min<sup>-1</sup> is calculated to be laminar, but at 3.4 1 min<sup>-1</sup> the flow is turbulent.

The ore used (J+L4) in the study is a mixture of eight major minerals each with a separate density (2 to  $8^{\circ}$  g cm<sup>-3</sup>) and particle size dist-

ribution. The distribution collected at the top of the injector is the result of many different effects, <u>e.g.</u> primary aerosol formation, turbulent and laminar flow, gravitation, impaction, centrifugation, drag and inertia, each acting to different degrees. Also the suspension medium, water, is associated with the particles, usually present as a coating, which alters the particle size and density of the solid analyte being transported to the plasma. As yet no single model fully describes the processes which occur within a double pass spray chamber for even simple solutions. However it is evident from the transport experiments previously described that slurry aerosols can model solutions closely, even to the change in solid particle distribution within an aqueous envelope that is changing distribution.

3.6.4 Conclusions

The study shows that the particle size distribution of the post injector material is very different to that of the starting slurry. A marked decrease in particles over 6 to 8  $\mu$ m is evident from the distributions and this maximum is little changed with flow rate and injector bore. The mean and fine fraction of the distributions are however dependent upon flow rate and bore size; an increase in either resulting in a shift towards a larger size fraction exiting the injector.

## CHAPTER 4

## ELEMENTAL ANALYSIS OF SOLIDS BY ... SLURRY ATOMISATION PLASMA EMISSION SPECTROMETRY.

#### 4.1 INTRODUCTION

The introduction of solid samples in slurry form into plasmas has, as previously outlined in Chapter one, been performed by a number of workers (45,46,58,79,82). The samples analysed for major, minor and trace elemental constituents have covered a broad variety of materials which include plastics (96), zeolites (75), coals (81), rocks (84), minerals (83, 86) and wear oils (76). Several naturally occurring and processed materials yield full recoveries (slurry value over known value equals unity) for some elements by the slurry technique using simple calibration solutions. It has also been noted that for many samples the chemical type, form and particle size of the material are important criteria (82, 86). Full elemental recoveries will only be obtained using aqueous calibration if two conditions are met.(i) The mass transport per unit time of a particular element associated with the slurry equals that of the element in a calibration solution of equal concentration and ii) the atomisation and excitation processes of the slurry particles model those of the calibration solutions. The fundamental questions of transport phenomena have been discussed in detail in Chapter 3 and illustrate the importance of solid particle size with respect to mass transport. Any supposed effects due to the atomisation and excitation processes of the slurry particles in a plasma are, however, difficult to quantify due to the possible presence , of transportation phenomena.

This chapter describes the experimental work concerned with the elucidation of both transportation and atomisation effects for a variety of different solid samples in slurry form using plasma source atomic emission spectrometry. In order to observe these effects well characterised mono and poly-densitic materials, some of a 'hard' and/or refractory nature were chosen for the experiments. Interpretation of these effects was therefore made possible from the elemental recoveries compared with calibration solutions.

4.2 INSTRUMENTATION

In this study three commercially available plasma emission spectrometers were used. Two of these instruments were of the inductively coupled (IC) design (25), the Plasmakon S-35 (Kontron Spektralanalytik, Eching, W. Germany) and the ARL 35000 (ARL, Crawley, Sussex, UK), and one of the direct current design (42), the Spectraspan IIIA (ARL, Crawley, Sussex, UK). These instruments are briefly described in sections 4.2.1, 4.2.2 and 4.2.3 respectively.

Basically an inductively coupled plasma atomic emission spectrometer can be divided into five sections.

- (i) Power supply and radio frequency (RF) generation
- (ii) Plasma torch and gas supply
- (iii) Sample transportation
- (iv) Wavelength selection and emission detection
- (v) Data acquisition and processing.

A simple schematic diagram is shown in Figure 4.1



Drain

The power to the four turn, round section, water cooled copper load coil is supplied by a 3.5 kW maximum, 27.12 MHz crystal controlled RF generator which includes a fully automatic tuning capacitor for load matching.

The concentrically mounted torch, Figure 4.2 is of the large Greenfield type and comprises a composite PTFE/glass fibre (60:40) base fitted with a one-piece quartz coolant and auxiliary body, 29 mm OD and 25 mm OD respectively. A separate injector of 3 mm bore is located in the two-piece base.

The all argon gas supply to the torch is regulated by three mass flow controllers and these come under manual control, as does the RF power generator, after the plasma has been initiated by the high voltage tesla coil under the automatic start-up programme. Samples are introduced to a Kel-F high solids, V-groove nebuliser (Ebdon type, PS Analytical, Sevenoaks, Kent, UK) by a peristaltic pump (Gilson Minipuls 2, Luton, Beds, UK) and the aerosol generated with the argon flow is transported through an in-house constructed double pass glass spray chamber to the injector.

Radiation from the plasma is focused on and directed to the entrance slit of the monochromator with a computer controlled periscope arrangement consisting of two spherical mirrors. The viewing zone within the plasma can be accurately positioned from the top of the load coil to a vertical point six centimetres above it. Wavelength selection is accomplished with a 0.6 metre Czerny-Turner grating monochromator which is under computer control. An angle encoder, which incorporates

an optoelectronic counting system, transmits the grating position to the computer and is capable of selecting a wavelength to within 0.0015 nm. The selected wavelength passes through the exit slit and onto a side window photomultiplier (Thorne-EMI 9781A) which measures the intensity of the radiation. By stepping the supply voltage ( $\sim$ 550-950 V) to the photomultiplier its response can be altered to cover a wide range of intensities.

An on-board computer, based on the Z-80 microprocessor, controls the start-up conditions for plasma formation, the monochromator drive, periscopic viewing position, photomultiplier voltage and data presentation/storage together with a number of associated mathematical calculations <u>e.g.</u> peak emission maxima, signal to background ratio maxima against viewing height and line calibration. Information is displayed on a monitor in graphical form or on a dot-matrix printer.

4.2.2 The ARL 35000 IC Plasma

The ARL 35000 ICP (ARL, Crawley, Sussex, UK) is a sequential instrument similar to the Kontron S-35. Power to a three turn, round section, water cooled copper load coil is supplied by a 2.5 kW maximum, 27.12 MHz RF generator (Henry Radio, California, USA) of the closed loop design. The torch is of the all-quartz small 'Fassel' type with a coolant tube of 20 mm OD and a 'tulip' design auxiliary tube. One piece torches with a fixed 1.5 mm bore injector and two piece with interchangeable injectors up to 3 mm bore are used. The all argon gas supply is controlled with a three stage precision regulator. Pressure is regulated to  $\pm$  0.05 psi and gas flow is controlled with low thermal coefficient porous plugs.

Aqueous sample aerosols such as those formed from dissolved minerals (fusion analyses), are generated by an all glass concentric pneumatic nebuliser (J E Meinhard Associates, California, USA) of various orifice designs (Types A to C). The aerosol then passes through an all glass single pass spray chamber (ARL, Crawley, Sussex, UK) to the injector. An argon humidifier and tip washer extend this type of nebuliser's tolerance to increased levels of dissolved salts.

For slurry analyses an Ebdon nebuliser was used with this instrument together with the ARL single pass and Scott-type double pass spray chambers.

Wavelength selection is achieved with a 1 metre grating monochromator of the Czerny-Turner design.Wavelength scanning is achieved by deflecting the diffraction grating with a sine bar drive and a stepper motor which is computer controlled. The computer is capable of reproducing selected wavelengths to within  $\pm$  0.0056 nm. There is no optical or translational facility for changing the viewing zone within the plasma and the radiation is directly focused onto the entrance slit set 15 mm above the load coil. The intensity of the selected radiation is measured using a side window photomultiplier which is also under computer control and offers 15 stepped levels of amplification.

Signals from the photomultiplier are processed by a DEC PDP-11/03 digital processor unit which controls the instrument. Operator interface is achieved through a terminal keyboard with monitor and DEC writer.

## FIGURE 4.2

..

Diagram of Greenfield-type inductively coupled plasma torch.



4.2.3 The Spectraspan IIIA Direct Current Plasma

The three electrode direct current plasma emission spectrometer was described in detail by Decker (42) and can be divided into five sections.

- (i) Power source
- (ii) Electrode assembly
- (iii) Sample transportation
- (iv) Wavelength selection and emission detection
- (v) Data acquisition and processing.

The Spectraspan IIIA direct current sequential spectrometer possesses a lkW maximum direct current power source nominally run at 60 volts and 7 amps. This supplies the three electrode assembly, comprising two graphite anodes and a stabilising tungsten cathode, with the energy necessary to sustain a plasma from the argon gas passing concentrically around the electrodes. The sample is introduced to the instrument by a peristaltic pump which supplies a ceramic cross-flow design nebuliser. The aerosol formed in the argon flow is transported via the cyclonelike spray chamber to the large (10 mm bore) injector tube. This directs the sample into the apex, formed between the two anodes, of the inverted Y-shaped plasma. The emission from this region is focused on and passes through the entrance slit to the monochromator. The electrode assembly sits on a two-dimensional translation table which governs the position of the plasma relative to the monochromator entrance slit.

The wavelength selection is governed by a 0.75 metre Echelle grating monochromator (79 grooves/mm) operated at high order (30 - 120) with a

30° prism for order separation. The design is noted for its higher spectral resolution and dispersion while also being compact. Wavelength selection is manually controlled. The radiation is detected, through a cassette mask, by a photomultiplier. Amplification of the signal is manually selected in ten steps and an on-board dedicated microprocessor directly processes the signal data. The microprocessor controls the counts display, integration, calibration and concentration modes used in data processing.

4.3 MINERAL ANALYSIS BY SLURRY ATOMISATION PLASMA EMISSION SPECTROMETRY 4.3.1 In-House Sulphide Ores.

Two samples of in-house sulphide ores (BP Research Centre, Sunbury-on-Thames, Middx, UK), designated J+L4 and SA1/C120 were received for analysis by the slurry technique. The ores were polydensitic, consisting of up to seven major and minor mineral components. These components are shown in Table 2.1 of Chapter 2 together with their measure of hardness (MOH). The procedure used to sample these ores and to prepare slurries is described in detail in Chapter 2.

4.3.1.1 Standardisation and preliminary slurry atomisation experiments

The elements of particular interest in these ores <u>i.e.</u> iron, zinc, copper, silver, and gold, were first determined by a fusion/dissolution technique (with the exception of gold which was determined by a fire assay technique) for characterisation and standardisation before subsequent slurry analysis. A sodium peroxide fusion was used to bring about dissolution of the high silica-bearing sulphide ores <u>i.e.</u> approximately 0.2g of the finely ground ores were accurately weighed into zirconium crucibles and 1 to 1.5g of sodium peroxide carefully added.

The covered crucibles were then admitted to a muffle furnace, held at  $650^{\circ}$ C and allowed to react for 20 to 25 minutes with occasional agitation. After cooling the contents of the crucibles were <u>carefully</u> reacted with 12.5 ml of concentrated nitric acid, 5 ml of 10% m/v tartaric acid and a little water  $(50 \text{ cm}^3)$ . The dissolution products were then boiled and, after cooling, were made up to just under 100 ml in a volumetric flask. These solutions were then left overnight to degas and made up to the mark next day. Calibration standards were prepared using matrix matched solutions with respect to the fusion reactants. Determination of iron, zinc, copper, and silver was performed using the ARL 35000 ICP spectrometer under the conditions shown in Table 4.1. The silver concentration was also determined using an IL Video 22 atomic absorption spectrometer and the silver resonance line at 338.289 nm.

Slurries of the ores SA1/C120 and J+L4 at 0.5 and 2% m/v solids loading were prepared by the bottle and bead method (10:1 m/m bead to sample ratio) over a 1 hour grinding period and stabilised in 0.1% m/v sodium hexametaphosphate solution. Determination of the iron, copper, zinc, and silver concentrations were performed using the Plasmakon S-35 ICP with the conditions shown in Table 4.2. A scandium internal standard was employed in both the samples and the simple calibration solutions.

#### 4.3.1.2 Results and discussion

The results from the determination of iron, zinc, copper, and silver in the fusion solutions are shown in Table 4.3. Interference from zirconium occurs on the primary silver line at 328.068 nm but not the secondary line, 338.289 nm. The primary silver line is of importance for trace analysis and the interference effect was studied further.

Plasma conditions used for the determination of iron, copper, zinc and silver in sulphide ore fusion solutions of J+L4 and SA1/C120 using the ARL 35000 ICP spectrometer

| Torch                              | 'Fassel' Size    |  |  |
|------------------------------------|------------------|--|--|
| Forward power/kW                   | 1.0              |  |  |
| Gas flow rates/l min <sup>-l</sup> |                  |  |  |
| Coolant                            | 12.0             |  |  |
| Auxiliary                          | 1.0              |  |  |
| Injector                           | 0.8              |  |  |
| Nebuliser type                     | concentric glass |  |  |
| Injector bore/mm                   | 1.5              |  |  |
| Viewing height/mm                  | 15               |  |  |
| Wavelengths/nm                     |                  |  |  |
| Iron II                            | 259.94           |  |  |
| Iron II                            | 259.837          |  |  |
| Copper I                           | 219.958          |  |  |
| Copper I                           | 327.396          |  |  |
| Zinc I                             | 213.856          |  |  |
| Silver I                           | 328.068          |  |  |

Plasma conditions used for the determination of iron, copper, zinc and silver in sulphide ore slurries J+L4 and SA1/C120 using the Kontron S-35 ICP spectrometer

| Torch .                       | 'Greenfield' size |
|-------------------------------|-------------------|
| Forward power/kW              | · 1.8             |
| Cas flow rates/ l min $^{-1}$ |                   |
| Coolant                       | 20.0              |
| Auxiliary                     | 0.8               |
| Injector                      | 1.9               |
| Nebuliser type                | Ebdon             |
| Injector bore/mm              | 3                 |
| Wavelengths/nm                |                   |
| Iron II                       | 238.204           |
| Zinc II                       | 206.191           |
| Copper I                      | 324.754           |
| Silver I                      | 328.068           |

..

.

The determination of iron, zinc, copper and silver in the minerals J+L4 and SA1/C120 (designated J and S) after a fusion/dissolution stage had been performed. Instrument used ARL 35000 ICP.

| Element               | Wavelength/nm | Э                    | S <sup>·</sup>       |
|-----------------------|---------------|----------------------|----------------------|
|                       |               |                      |                      |
| Fe%                   | 259.94        | 19.05 <u>+</u> 0.15  | 18.7 <u>+</u> 0.2    |
| Fe%                   | 259.837       | 18.6 <u>+</u> 0.2    | 18.2 <u>+</u> 0.4    |
| Zn%                   | 213.856       | 16.2 <u>+</u> 0.3    | 2.6 <u>+</u> 0.05    |
| Cu%                   | 219.958       | 0.345 <u>+</u> 0.005 | 0.37 <u>+</u> 0.005  |
| Cu%                   | 327.396       | 0.345 <u>+</u> 0.005 | 0.375 <u>+</u> 0.005 |
| Ag µg g <sup>−l</sup> | 338.289       | _ 253 <u>+</u> 10    | 119 <u>+</u> 7       |
| Ag*µg g <sup>-l</sup> | 328.068*      | 332 <u>+</u> 33      | 164 <u>+</u> 27      |

Silver determination using the IL Video 22 Atomic Absorption Spectrometer.

|                       | Wavelength/nm | J   | S   |
|-----------------------|---------------|-----|-----|
| Ag µg g <sup>−1</sup> | 338.289       | 232 | 114 |

\* Interference from zirconium identified.

Zirconium crucibles were used in the fusion step and quantification of the contamination was performed. These results are shown in Table 4.4. As zirconium is present in the ores and contamination from the crucibles during fusion is not constant a separate experiment was performed using silver and zirconium solutions to quantify the interference effect on the important primary silver line. Under the conditions used on the ARL 35000 ICP (Table 4.1) it was found that the presence of 130  $\mu$ g ml<sup>-1</sup> of zirconium in 100 ml of solution was equivalent to 1  $\mu$ g ml<sup>-1</sup> of silver using the 328.068 nm AgI line.

The results for the iron, zinc, copper and silver concentration in the ores, determined by the slurry technique, are shown in Table 4.5. The recoveries of these elements (the ratio of an analyte concentration found by the slurry technique to that of the known value) range from 56% for iron in J+L4 up to 84% for copper in SA1/C120. Particle size analysis of the slurries showed that only 4% by volume in the case of SA1/C120 and 5.5% by volume for J+L4 was greater than 8  $\mu$ m in size. However these increased to 48% and 32% by volume respectively for material greater than 3.1  $\mu$ m suggesting that mass transportation effects might have been present for the slurries.

The silver emission was monitored using the primary 328.068 nm atom line. While subsequent determinations of the zirconium contents of these ores (e.g. 90  $\mu$ g g<sup>-1</sup> for SA1/C120) indicated that at the levels present there would be little effect on the silver result, the possibility of zirconium interference due to contamination by the zirconia grinding beads had to be considered. Table 4.6 shows this interference on the 328.068 nm silver line when the bottle and bead method grinding time was increased and the silver content of the ores determined. Subsequent silver analyses were performed using the secondary 338.289 nm

The determination of zirconium in 100 ml solutions of J+L4 and SA1/C120 after performing a sodium peroxide fusion in zirconium crucibles.

| Element | Wavelength | J+L4(1)                   | SA1/C120(1)               | Blank Fusion           |
|---------|------------|---------------------------|---------------------------|------------------------|
| Zr      | 327.305 nm | 28-33 µg ml <sup>-1</sup> | 19-24 µg ml <sup>-1</sup> | 18 µg ml <sup>-1</sup> |

(1) Range covered by three fusion reactions

- -

The determination of iron, zinc, copper and silver in the minerals J+L4 and SA1/C120 (designated J and S) by slurry atomisation using the Plasmakon S-35 ICP

:

## % CONTENT

| Element               | Wavelength | J(slurry) | J(solution) | Recovery | S(slurry) | S(solution) | Recovery |
|-----------------------|------------|-----------|-------------|----------|-----------|-------------|----------|
|                       | nm         |           |             | %        |           |             | %        |
| Fe                    | 238.204    | 10.4      | 18.6        | 56       | 10.6      | 18.2        | 58       |
| Zn                    | 206.191    | 10.2      | 16.2        | 63       | 2.0       | 2.6         | 77       |
| Cu                    | 324.754    | 0.27      | 0.34        | 79       | 0.31      | 0.37        | 84       |
| Ag(µg g <sup>-l</sup> | )328.068   | (180)     | (253)       | 71       | (77)      | (119)       | 65       |

The determination of silver in the ores J+L4 and SA1/C120 by slurry atomisation ICP-AES. Slurries prepared by grinding with zirconia beads over 2 hour period. Wavelength monitored 328.068 nm.

Concentration of silver  $\mu g g^{-1}$ 

Sample 1 hour ground slurry 2 hour ground slurry Known Concentration

 J+L4
 180
 280
 253

 SA1/C120
 77
 187
 119

#### TABLE 4.7

Operating conditions used on the Spectraspan III d c plasma for analysis of solutions and slurries of in-house ores.

| Gas supply                            | argon (99.5% pure) |
|---------------------------------------|--------------------|
| Flow rate (total)/l min <sup>-l</sup> | 8                  |
| Nebuliser pressure/PSI                | 24                 |
| Nebuliser flow rate/l min $^{-1}$     | 4                  |
| Nebuliser type                        | cross flow         |
| Sleeve pressure/PSI                   | 50                 |
| Power supply/A (dc)                   | 7                  |
| Sample uptake/ml min <sup>-l</sup>    | 1.6                |

line. It is of note that the zirconia contamination which was present as a slurry atomised efficiently to give an interference even though it is a highly refractory oxide.

The gold contents of the ores, determined by fire assay and atomic absorption spectrometry were found to be 12.4  $\mu$ g g<sup>-1</sup> (J+L4) and 0.1  $\mu$ g g<sup>-1</sup> (SA1/C120). Slurry analysis showed that severe spectral interference from concomitant elements was present on the primary gold line (Au I 242.795 nm) and as the secondary line was found to be too insensitive (Au I 267.595 nm) no further determinations were undertaken for gold in these ores.

4.3.1.3 Slurry analysis by direct current plasma emission spectrometry

The sample introduction systems employed in direct current plasma emission spectrometry are noted for their tolerance to large particle sizes when slurry atomisation is employed (44, 56, 118). The use of single pass spray chambers with no baffles or impactors together with large (10mm) injector bores and high carrier gas (2.5 to 4 1 min<sup>-1</sup>) and liquid flow rates (1.6 to 10 ml min<sup>-1</sup>) results in greater transport efficiencies (up to 15%) compared with the conventional double pass spray chamber/injector assembly (up to 2%) used in ICP spectrometry.

The two ores J+L4 and SA1/C120 were analysed on the spectraspan IIIA direct current plasma (DCP) spectrometer for the elements iron, zinc and copper. The ores were analysed in two forms:

(i) as a solution after employing the fusion technique (1.5g  $Na_20_2 + 0.2g$  sample etc.) and

(ii) as 0.35% m/v slurries ground by the bottle and bead method for one hour with 0.1% m/v SHMP as dispersant.

The sodium peroxide fusion technique resulted in a sodium (easily ionised element, EIE) concentration of approximately 0.4 M (100ml final solution). From a graph, showing the effect of varying the concentration of an EIE in a solution matrix upon the response (emission) of an analyte excited by a DCP (118, enhancement curve), the 0.4 M sodium (or any alkalie EIE) region corresponds to the near plateau or very shallow slope of the enhanced emission curve. Hence small variations of any concomitant EIE within the sample would have little effect and the solution can be considered buffered. Calibration solutions were matrix matched for the sodium and acid contents of the fusion solutions while the slurries were buffered with neutralised sodium peroxide  $(Na_2O_2 + HNO_3)$ , added to the same concentration. The plasma conditions used with the Spectraspan IIIA are shown in Table 4.7

4.3.1.4 Results and discussion

The results of the determination of iron, zinc and copper in the ores J+L4 and SA1/C120 by slurry atomisation and in solution are shown in Table 4.8. The solution results compare well with those previously determined using the ARL 35000 ICP (Table 4.3). The slurry results show full recoveries for zinc and copper with improved recoveries for iron (76% for J+L4 and 92% for SA1/C120) compared with those results obtained from the slurry experiments performed on the Plasmakon S-35 ICP (Table 4.5). The particle size distributions of the slurries were similar to those previously obtained and described in section 4.3.1.2. The superior transport properties of the sample introduction system of the DCP system used (large single pass with 10mm injector) are

The determination of iron, zinc and copper in the minerals J+L4 and SA1/C120 (designated J and S) by slurry atomisation and in solution using the Spectraspan III d c plasma.

Ele- Wave-J(solution) J(slurry) %R\* S(solution) S(slurry) %R\* ment length/nm Fe% 240.488  $18.8 \pm 0.3$   $14.3 \pm 0.2$  76.1  $17.1 \pm 0.6$   $15.8 \pm 1.1$ 92.4 Zn% 213.856 16.3 <u>+</u> 0.1 16.5 <u>+</u> 0.5 101  $2.6 \pm 0.1$   $2.9 \pm 0.1$ 111 0.355<u>+</u>.005 100 Cu% 213.597 0.355+.005 0.36+ 0.01 0.39+ .005 108 \* Recovery, slurry value over solution value as percentage

## TABLE 4.9

Operating conditions used on the ARL 35000 ICP for the analysis of in-house ores (J and S) by slurry atomisation.

| Torch type                         | Fassel              |
|------------------------------------|---------------------|
| Forward power/kW                   | 1.5                 |
| Gas flow rates/l min <sup>-l</sup> |                     |
| Coolant                            | 16                  |
| Auxiliary                          | 1.5                 |
| Carrier                            | 1.7                 |
| Viewing height/mm                  | 15                  |
| Injector bore/mm                   | 3                   |
| Nebuliser type                     | Ebdon               |
| Spray chamber                      | Double pass (glass) |

suggested as being responsible for the near to full recoveries observed. While atomisation problems are more likely to be present in the DCP (a thermally cooler source) than in the ICP, full recoveries indicate that these phenomena were not significant. This may in part be due to the high dissolved salt content  $(1.5\% Na_2O_2 \text{ gives } 3.26\% NaNO_3)$ in 100 ml solutions), in both the calibration standards and the slurries, which is known to have an effect on the transport mechanisms. By near matching of viscosity, surface tension, density and mass flux the transport properties of the slurries are less likely to be influenced by the presence of particulate matter at a concentration of 0.35% m/v and would compare with the calibration solutions. The inherently high salt content of both the solution and slurry aerosols may also result in a near matching of their heat capacities and differences in atomisation efficiency are less likely to be seen in the relatively cooler thermal environment of the DCP.

4.3.1.5 Slurry analysis and matrix effects in the ICP

Slurry samples of the ore SA1/C120 at 0.1% and 1% m/v solids loading were prepared by the microniser technique as described in Chapter 2. These were stabilised in 0.1% m/v sodium hexametaphosphate solution. Multi-element standard solutions were prepared in order to determine the zinc, copper, iron, lead, zirconium and silver contents of the ground slurries.

A scandium internal standard was added to the calibration solutions but no SHMP dispersant in order to prolong the stability of the solution mixture (phosphate precipitation was prone to occur with time). The plasma conditions used for the calibration and slurry analyses are shown in Table 4.9. All analyses were performed on the ARL 35000

ICP with the SIS comprising a double pass spray chamber (Figure 3.6 Chapter 3), a 3mm bore injector and Ebdon nebuliser.

4.3.1.6. Results and discussion

During calibration of the instrument using solution standards it was noted that severe deviations from linearity were present for the atom lines of copper, zinc, lead and silver but not for the ion line of iron; the deviations displaying typical ionisation interference (as observed in atomic absorption spectroscopy). Scrutiny of the calibration table (Table 4.10) and the calibration plots for zinc, copper and lead (Figure 4.3(a),(b) and (c)) indicated that the presence of iron (at 100 and 200  $\mu$ gml<sup>-1</sup>) enhances the signals for the top standards of these three analytes. Figure 4.3(d) shows that the removal of 200  $\mu \text{gml}^{-1}$  of iron from the top lead standard results in the lead signal falling on to the extrapolated line made between the blank and bottom lead standard which contained no iron. From the ratio of the calibration slopes for each analyte, with and without iron present, the order of increasing deviation from linearity was found to be inversely proportional to the excitation potential of the analyte under investigation (i.e. as eV increases the deviation decreased). Matrix effects have been discussed by Thompson and Ramsey (119) and Kovacic et. al. (120) and references therein. As a solution to this effect was required in order to perform the slurry analysis the effect was investigated further. The high carrier gas flow rate  $(1.71 \text{ min}^{-1})$  though the 3mm bore injector into the Fassel-sized plasma was considered to be a contributing factor. Visualisation of the injector bullet in the plasma using 1000  $\mu$ g ml<sup>-1</sup> sodium solution showed that the top of the initial radiation zone (IRZ) was well above the fixed viewing height of 15mm for the monochromator. The high flow rate was considered to be

important in maintaining good transport for the slurry aerosol and hence experiments to elucidate this matrix effect centred on the inclusion of an internal standard (scandium) and on the addition of a buffering agent (an EIE, in this case sodium) together with variations in plasma forward power. Figure 4.4 (a) illustrates the effect of varying the forward power upon the emission from 20  $\mu$ g ml<sup>-1</sup> of scandium with and without the presence of 100 and 200  $\mu$ g ml<sup>-1</sup> of iron. There was no line emission from the iron stock solution at the scandium emission wavelength (402.04 nm) used. The effect from the addition of sodium, as SHMP, at the concentration used in the slurry suspensions (0.1% m/v) to that of a simple scandium solution is also shown. The enhancement effects are readily seen and are concentration dependent. Scandium therefore, cannot be used as an internal standard. Figure 4.4(b) illustrates the effect of varying forward power on the emission from 100  $\mu$ g ml<sup>-1</sup> of lead and shows that the presence of SHMP buffers out the effect of iron by its stronger "EIE effect". SHMP was therefore added to the calibration standards as an intrinsic EIE buffer and for matrix matching the solution. Analysis of the slurry SA1/C120 was then completed. A solution containing known amounts of all the elements, but without iron and zirconium, and including 0.1% m/v SHMP was also analysed to serve as a check on the calibration standards under buffered conditions. Table 4.11 shows the result of the slurry analysis and Table 4.12 the results of the solution check. The latter shows the SHMP solution was successful in buffering out the EIE effect of the iron. The slurry results show that with the exception of iron (75% recovery) near to full recoveries for the analytes were obtained. The high carrier gas flow rate was necessary to ensure good transportation for the majority of elements in the multi-mineral ore. The particle size distribution of the slurry (Figure 4.5) shows that 2.5% by volume of material was over 8 µm and some 13% over 5 µm.

-

Standards table used in the calibration of the ARL 35000 for the determination of Zn, Cu, Fe, Pbyand Ag in micronised slurry sample SA1/C120.

Concentration of analyte  $\mu g m l^{-1}$ 

Calibration

. .

| solution No. | Zn  | Cu | Fe  | РЬ  | Zr | Ag |
|--------------|-----|----|-----|-----|----|----|
| l (blank)    | 0   | 0  | 0   | 0   | 0  | 0  |
| 2            |     | 20 |     |     |    |    |
| 3            | 50  |    |     |     |    |    |
| 4            |     |    | 50  |     |    |    |
| 5            |     |    |     | 20  |    |    |
| 6            |     |    |     |     | 20 |    |
| 7            |     |    |     |     |    | 1  |
| 8            | 100 | 40 | 100 | 50  | 0  | 2  |
| 9            | 200 | 60 | 200 | 100 | 40 | 5  |

FIGURE 4.3

Calibration plots for zinc, copper and lead (a, b, c) showing the deviation from linearity of the bottom standard solution emission (no iron present) compared with the two top standards (iron present). Plot (d) shows lead top standard emission without iron present.



FIGURE 4.4

Graph showing the matrix effect of iron and surfactant (SHMP) concentration upon the net emission intensity of scandium (a) and lead (b) at 1150W and 1800 W forward power. Concentrations in  $\mu g m l^{-1}$ .








The determination of copper, zinc, iron, lead, zirconium and silver in the ore SA1/C120 by slurry atomisation using the ARL 35000 ICP.

| Element | Wavelength/nm | SA1/Cl20 (slurry)   | SA1/Cl20 (solution) |
|---------|---------------|---------------------|---------------------|
|         |               | % Cont              | cent                |
| Cu      | 219.958       | 0.337 <u>+</u> 0.02 | 0.37 <u>+</u> 0.005 |
| Zn      | 213.856       | 2.41 <u>+</u> 0.08  | 2.6 <u>+</u> 0.1    |
| Fe      | 259.94        | 13.7 <u>+</u> 0.06  | 18.2 <u>+</u> 0.8   |
| Pb      | 283.307       | 0.28 <u>+</u> 0.02  | 0.27 <u>+</u> 0.03  |
|         |               | μg g <sup>-</sup>   | 1                   |
| Zr      | 327.305       | 90 <u>+</u> 4       | 94 <u>+</u> 9 ·     |
| Ag      | 338.289       | 119 <u>+</u> 16     | 119 <u>+</u> 14     |

Results from the determination of elements of known concentration in solution containing sodium hexametaphosphate (SHMP) buffer.

|                     | Concentration of element (µg ml <sup>-1</sup> ) |      |       |      |       |     |  |  |
|---------------------|---|------|-------|------|-------|-----|--|--|
|                     | Cu  | Zn   | Fe    | Pb   | Zr    | Ag  |  |  |
| Known concentration | 40  | 100  | 0     | 50   | 0     | 2.0 |  |  |
| Concentration found | 39.7  | 96.5 | <0.01 | 47.2 | <0.02 | 2.3 |  |  |

#### **TABLE 4.13**

A comparison of the iron, zinc, copper and lead contents of the ore SA1/C120 as received and collected after transportation through a Scott-type double pass spray chamber and 3mm injector at a gas flow rate of 1.5 1 min<sup>-1</sup>

#### Ore sample

| Element | Starting sample | After transportation | After transportation |
|---------|-----------------|----------------------|----------------------|
|         | (dissolution)   | (dissolution)        | (slurry atomisation  |
|         |                 |                      | and emission)        |
| Fe %    | 18.2            | 14.2 <u>+</u> 0.4    | 13.7                 |
| Zn %    | 2.6             | 2.50 <u>+</u> 0.05   | 2.41                 |
| Cu %    | 0.37            | 0.32 <u>+</u> 0.04   | 0.34                 |
| РЬ %    | 0.27            | 0.27 + 0.01          | 0.28                 |

FIGURE 4.6

By volume particle size distributions of (a) starting ore slurry, SA1/C120, and (b) the solid fraction collected by Cascade impactor after passing through a double pass spray chamber with 3mm injector at gas flow rate 1.5 1 min<sup>-1</sup>.



4.3.1.7 Segregation phenomena in multi-component slurries

Analysis of slurries of the ores J+L4 and SA1/C120 has shown that near to full recoveries can be obtained for the elements zinc, copper, lead, zirconium and silver. Iron has, however, repeatedly shown reduced recoveries, typically 70 to 80% of the known content. In order to establish the mechanism for this shortfall <u>i.e.</u> whether it was due to transportation or atomisation effects, an experiment was performed to collect all the material carried to the top of an injector during nebulisation of the iron-bearing ore slurry.

A stirred 1% m/v slurry of SA1/C120, ground by the microniser method (Chapter 2) was peristaltically pumped at 1 ml min<sup>-1</sup> to an Ebdon nebuliser. The aerosol was then passed through a double pass spray chamber (ex polyvac E1000 type, Figure 3.6 Chapter 3) and 3mm injector at an argon gas flow rate of 1.5 1 min<sup>-1</sup> and into a cascade impactor arranged in such a manner as to isokinetically sample the whole aerosol (as described in section 3.5, Chapter 3). A volume of 280 ml of slurry was processed in this manner (over a 4.5 hour period) in order to collect sufficient material for fusion and analysis). The size fraction from the pre and main impactors were collected, mixed and sampled. A sodium peroxide fusion/dissolution step was then performed on the transported ore and the iron, zinc, copper and lead contents were determined against matrix matched calibration standards.

4.3.1.8. Results and discussion

The fusion/dissolution results are shown in Table 4.13 together with the starting sample dissolution results and those obtained by slurry

atomisation. Transportation effects are clearly indicated as the major cause of low iron recovery by the slurry technique for these ores. The particle size distributions of the slurry particles before and after transportation are shown in Figure 4.6 and are very similar, with over 95% of the material being less than 6µm. Representative transportation of the starting slurry distribution has occurred. It is suggested that the iron, which is mainly present as the dense  $(5.2q \text{ cm}^{-3})$ , hard (MOH of 6.5) mineral iron pyrites, is contained in the larger size fraction of the distribution; the result of a decreased efficiency of grinding. In contrast the lead, present as the dense galena (7.6 g cm<sup>-3</sup>) is soft (MOH of 2.5) and is likely to be efficiently ground and present in the finer fractions thereby giving full recoveries in transportation and as shown in the slurry emisson values equivalent atomisation to that of the calibration solutions. The possibility of a segregation effect has recently been mentioned by Verbeek and Brenner for geological materials (85) when analysed by the slurry technique.

4.3.1.9 The effect of injector bore on slurry emission recoveries

It has been shown by Ebdon and Collier (82) that both the type of spray chamber and the bore of an injector affects the recovery of an element from various size fractions of kaolin samples when aspirated by the slurry technique. Near to full recoveries were obtained from the finest fraction of kaolin (the majority of which was less than 2.5  $\mu$ m in size) when a single pass spray chamber and 3mm bore injector were employed. These effects are consistent with the transport phenomena described in detail in Chapter 3. As the iron recovery from the ores SA1/C120 and J+L4 has been shown to be transport dependent an experiment was performed to monitor the recovery of iron from a fine

slurry of SA1/C120 while varying the injector bore, the carrier gas flow rate and the viewing height.

A slurry of micronised ore, SA1/C120, containing iron at a concentration of 199  $\mu$ g ml<sup>-1</sup> was pumped to an Ebdon nebuliser, double pass spray chamber and injectors of 2 and 3mm bore, at carrier gas flow rates 0.6 1 min<sup>-1</sup> to 2.3 1 min<sup>-1</sup>. The iron ion line, 259.94nm was monitored at viewing heights which presented the optimum signal to background ratio and the net signal was then compared with that from a simple iron solution of equal concentration and matrix matched with SHMP dispersant. These experiments were performed on the Plasmakon S-35 ICP with a 'Greenfield size' torch while running at a forward power of 1500W.

#### 4.3.1.10 Results and discussion

The results from these experiments are shown in Table 4.14. As most slurry analyses are carried out using a carrier gas flow rate between 1.1 and 1.8 l min<sup>-1</sup> using a 3mm bore injector the iron recoveries are as previously found <u>i.e.</u> 70 to 80%. When using the 2mm injector with comparable flow rates the recoveries are much the same. Differences are, however, seen when flow rates are 'in extremus'. At high gas flows, 2 l min<sup>-1</sup> using the 2mm injector and 2.3 l min<sup>-1</sup> using the 3mm injector, the recoveries are elevated. This may be attributed to improved transport effects from the slurry compared with solution but also, and perhaps more importantly, at viewing heights of 18 to 19mm the recoveries may be attributed to matrix effects as the tip of the IRZ approaches the viewing zone. In this region the effects due to minor differences in matrix are more likely to be operative.

.

• •

.

.

The recovery of iron from a fine slurry of the ore SA1/C120 with variation in carrier gas flow rate, viewing height and injector bore. Analysis performed using the Kontron S-35 ICP at 1500W.

|                    | 2mm                        | bore       | 3mm bore  |            |  |
|--------------------|----------------------------|------------|-----------|------------|--|
| Injector flow/l mi | in <sup>-1</sup> %Recovery | Viewing '  | %Recovery | Viewing    |  |
|                    |                            | height(mm) |           | height(mm) |  |
| 0 4                | 100                        |            | ()        |            |  |
| 0.6                | 120                        | 12.0       | - (1)     | -          |  |
| 0.8                | 95.1                       | 12.0       | - (1)     | -          |  |
| 1.1                | 74.9                       | 15.1       | 79.3      | 12.7       |  |
| 1.4                | 72.4                       | 15.5       | 68.8      | 13.5       |  |
| 1.7                | 76.6                       | 16.2       | 70.2      | 18.4       |  |
| 2.0                | . 93.1                     | 18.4       | 77.9      | 19.1       |  |
| 2.3                | • -                        | -          | 86.8      | 19.8       |  |

(1) gas velocity at these low flow rates insufficient to punch plasma

.

In the case of the low gas flow rate, 0.6 l min<sup>-1</sup>, using the 2mm injector (it was not possible to punch the plasma at this low flow rate using a 3mm injector) the recovery may be explained due to transportation phenomena. Atomisation phenomena are, if present, likely to be of similar magnitude to that for ores transported through the 3mm injector at a flow rate of 1.3 to 1.4 l min<sup>-1</sup> (based on residence time/velocity of particles). The mass flux of the slurry aerosol would appear to exceed that of the calibration solution aerosol at 0.6 l min<sup>-1</sup> and may be a result of the distribution of solid fines in the slurry aerosol. The particle size distribution of the starting slurry was such that 95% was less than 5  $\mu$ m, 87% less than 2.5  $\mu$ m and 45% less than 1.26  $\mu$ m.

4.3.1.11 Multi-element simplex optimisation for ore slurry analysis.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is a multi-element technique which for routine analysis of solutions is generally operated with a single set of conditions. The versatility of the plasma source is such that good analytical performance is readily obtained and for most applications univariate searches of the running conditions are generally applied to achieve a sufficient performance. Since the work of Spendly <u>et. al.</u> (121) who introduced the principle of tracking the output from a system, as a set of points forming a simplex in factor space and continually forming new simplicies by reflecting one point in the hyperplane of the remaining points, the principle has grown, via the work of Nelder and Mead (122) and Deming and Morgan (123), into an optimisation technique for performance evaluation. As a result the use of simplex programs can help realise true optimum operating conditions from analytical instruments where the complexity of their interdependant, multi-component variables render the

univariate search technique inapplicable. The simplex technique has previously been used to monitor the performance of both IC plasmas and dc plasmas (71, 124) and this includes multi-element optimisation (125, 126). The flexibility of the simplex technique allows free rein for the 'figure of merit' and has been applied to single element slurry optimisation for the recovery of aluminium from coal slurries (100).

An investigation of multi-element simplex optimisation with slurry atomisation was undertaken using the in-house ore SA1/C120. Four elements were chosen, copper,zinc, iron and silver and their recoveries were monitored using the ARL 35000 ICP fitted with a single pass spray chamber with impact bead (ARL type), an Ebdon nebuliser and a 3 mm injector. Five parameters were varied <u>i.e.</u> forward power, solution feed rate, carrier gas flow rate and the coolant and auxiliary gas flow rates. The simplex program used was OPTIMA VIOOT, developed by Betteridge (126, BP Research Centre, Sunbury-on-Thames, Middlesex, UK). The response of each element in the slurry under various conditions was compared with that from the element of equal concentration in solution using the equation:

$$F(r) = \frac{I_s - B_s}{I_{sol} - B_{sol}} \times \frac{I_{sol} - B_{sol}}{B_{sol}}$$
(4.1)

where I<sub>s</sub> = Total emission intensity of slurry element at wavelengthλe I<sub>sol</sub> = Total emission intensity of solution element at wavelengthλe B<sub>s</sub> = Background emission intensity at elemental wavelength for slurry

B<sub>sol</sub> = background emission intensity at elemental wavelength for solution

 $F_{(r)}$  = Criterion of merit figure related to recovery

ideally the response required would be

$$\frac{I_s - B_s}{I_{sol} - B_{sol}} = 1 \quad (100\% \text{ recovery})$$

and the expression  $I_{sol} - B_{sol}$ 

is a weighting factor to stop the simplex going to low values of  $I_{sol}$ . The overall figure of merit (response  $F_{(T)}$ ) for the simplex at each step was calculated from the product of each of the element factors  $F_{(r)}$ .

$$F_{(T)} = F_{(r1)} \times F_{(r2)} \times F_{(r3)} \times F_{(r4)}$$
 (4.2)

This expression is unweighted.

#### 4.3.1.12. Results and discussion

While the stopping condition for the optimisation was not reached (5% relative), the maximum recoveries obtained are shown in Table 4.15 together with the running conditions which brought about these recoveries. The single pass spray chamber while used in an attempt to improve the mass transport of the slurry did result in plasma instability problems. Originally a SPSC without a spoiler was employed but severe condensing of the aerosol in the 3mm injector occurred. When a spoiler was introduced short term stability was improved but with time the aerosol gradually condensed again in the injector and occasionally was ejected, extinguishing the plasma. Starving the nebuliser by using low

Multi-element simplex optimisation (I) of slurry SAl/Cl20 for maximum recovery using the ARL 35000 ICP.

| Element       | Cu      | Zn      | Fe     | Ag      |
|---------------|---------|---------|--------|---------|
| Wavelength/nm | 219.958 | 213.856 | 259.94 | 338.289 |
| Recovery/%    | 85      | 81      | 72     | 95      |

• •

## Plasma Conditions

| Forward power /kW                           | 1.4                           |
|---|-------------------------------|
| Solution feed rate / ml min $^{-1}$         | 0.5                           |
| Carrier gas flow rate / l min <sup>-l</sup> | 1.7                           |
| Viewing height / mm                         | 15                            |
| Coolant gas / PSI                           | 32                            |
| Auxiliary gas / PSI                         | 32                            |
| Spray chamber                               | ARL single pass + impact bead |
| Injector bore / mm                          | 3                             |

. ·

Multi-element simplex optimisation (II) of slurry SA1/Cl20 for maximum recovery using ARL 35000 ICP

.

.

| Element        | Cu      | Zn      | Fe     | Ag      |
|----------------|---------|---------|--------|---------|
| Wavelength /nm | 219.958 | 213.856 | 259.94 | 338.289 |
| Recovery / %   | 95      | 92      | 92     | 103     |

· •

## Plasma Conditions

| Forward power /kW  | 1.5                       |
|--|---------------------------|
| Solution feed rate / ml min <sup>-1</sup><br>Carrier gas flow rate / l min <sup>-1</sup> | 0.84<br>0.95              |
| Viewing height / mm  | 15                        |
| Coolant gas / PSI  | 35                        |
| Auxiliary gas / PSI  | 30                        |
| Spray chamber  | Double pass spray chamber |
| Injector bore / mm   | 3                         |

.

liquid flow rates was found to be of benefit but restricted one of the simplex parameters.

The simplex was repeated using the same nebuliser but with a DSPC and 3 mm injector to help overcome some of the liquid transport problems. The response for each element was calculated using a slightly different equation:

$$F_{(r)} = \frac{I_{s} - B_{s}}{I_{sol} - B_{sol}} \times \frac{I_{s} - B_{s}}{B_{s}}$$
(4.3)

This allowed the slurry to solution response to find a maximum while weighting the slurry value to guide the simplex to greater recoveries and slurry signal. The maximum recoveries obtained from this experiment are shown in Table 4.16. As previously found, instabilities in the plasma limited the success of the experiment due to short term drift and the stopping condition for the optimisation was not reached. The improved recoveries seen in the second simplex experiment would suggest a closer match in transport efficiency between slurry and standard solutions; this being the result of using a different spray chamber as the slurries used for both simplexes were similar in particle size distribution.

#### 4.3.2 Canadian Certified Reference Ores

Two certified ores from the Canadian Certified Reference Materials Project, CCRMP, (CANMET, 555 Booth Street, Ottawa, Ontario, Canada) designated KCla and MPla were analysed by the slurry technique. The ores were polydensitic, containing up to 8 minerals in KCla and 13 in MPla.

These minerals are shown in Table 2.1 of Chapter 2 together with their measure of hardness (MOH).

## 4.3.2.1 Slurry atomisation experiments with KCla and MPla using the Plasmakon S-35 ICP

Slurries of 1.0% m/v were prepared from the 'as received' ores KCla and MPla by the bottle and bead method using a three hour grinding period. Eight elements were determined in these slurries using the Plasmakon S-35 ICP under the conditions shown in Table 4.17.

4.3.2.2 Results and discussion

Table 4.18 shows the results of the slurry analysis with KCla and MPla. Near to full recoveries are seen for the more volatile elements <u>i.e.</u> lead, zinc, and arsenic while the least volatile species, molybdenum, only shows about 14% recovery. While some transport effects would have to be considered for these materials (particle size analysis showed for KCla, 87% by volume less than 8µm and 75% less than 3µm while for MPla, 94% less than 8µm and 82% less than 3µm) the effect of selective volatilisation is suggested. A graphical representation of the recoveries of these elements against their heat of atomisation is shown in Figure 4.7 and the trend is indicative of a thermodynamic effect occurring within the atomisation process. Table 4.19 shows the values of heats of vaporisation,  $\Delta H_{vap}$  , for some of the minerals present in KCla and MPla from 2000 to 3500K together with the total enthalpy change on going from pure solid minerals at 298K to gaseous atoms at that particular temperature (calculated data obtained from the Central Thermodynamic Database system, David Campbell, MPB group, BP Research Centre, Sunbury-on-Thames, Middlesex, UK).

Operating conditions used on the Kontron S-35 ICP for the analysis of CRM ores KCla and MPla by the slurry technique.

| Torch                                | 'Greenfield size' |
|--------------------------------------|-------------------|
| Forward power / kW                   | 1.5               |
| Gas flow rates / l min <sup>-l</sup> |                   |
| Coolant                              | 16                |
| Auxiliary                            | 0.6               |
| Carrier                              | 1.9               |
| Injector bore / mm                   | 3                 |
| Nebuliser type                       | Ebdon             |

The determination of eight elements in the CANMET CRM ores MPla and KCla by slurry atomisation using the Kontron S-35 ICP.

| Element                 | Wavelength | Slurry              | Cert.value           | slurry                | Cert.value           |
|-------------------------|------------|---------------------|----------------------|-----------------------|----------------------|
|                         | /nm        |                     |                      |                       |                      |
| Cu%                     | 219.958    | 0.45 <u>+</u> 0.01  | 0.629 <u>+</u> 0.015 | 0.99 <u>+</u> 0.01    | 1.44 <u>+</u> 0.01   |
| Zn%                     | 213.856    | 33.7 <u>+</u> 0.5   | 34.65 <u>+</u> 0.15  | 16.7 <u>+</u> 0.2     | 19.02 <u>+</u> 0.10  |
| Ag%(µgg <sup>-1</sup> ) | 338.289    | 0.11 <u>+</u> 0.005 | 0.167 <u>+</u> 0.002 | (45 <u>+</u> 4)       | (69.7 <u>+</u> 2.2)  |
| Pb%                     | 283.306    | 2.27 <u>+</u> 0.03  | 2.24 <u>+</u> 0.03   | 3.7 <u>+</u> 0.05     | 4.33 <u>+</u> 0.03   |
| Sn%                     | 283.999    | 0.44 <u>+</u> 0.02  | 0.61 <u>+</u> 0.02   | 0.86 <u>+</u> 0.02    | 1.28 <u>+</u> 0.04   |
| Мо%                     | 379.825    |                     |                      | 0.004 <u>+</u> 0.0004 | 0.029 <u>+</u> 0.001 |
| As%                     | 234.984    |                     |                      | 0.74 <u>+</u> 0.02    | 0.84 <u>+</u> 0.02   |
| Fe*%                    | 259.954    | 8.6 <u>+</u> 0.2    | 10.9*                | 4.9 <u>+</u> 0.1      | 6.2*                 |

\*indicated values only

..

FIGURE 4.7

٠

Graph showing the correlation between the elemental heat of atomisation and the percentage recovery (E) obtained from the analysis of the CANMET ores KC1a and MP1a.

;



.

Heats of Vaporisation  $\Delta H_{(vap)}$  and total enthalpy change (TEC) data for some of the minerals in KCla and MPla over the temperature range 2000 to 3500 K

|             | K (d1.001         |           |                   |       |                   |         |                   |       |
|-------------|-------------------|-----------|-------------------|-------|-------------------|---------|-------------------|-------|
|             | Cha               | lcopyrite | Pyr               | ites  | Moly              | bdonite | Gale              | na    |
| Temperature | CuFeS             | 2         | FeS <sub>2</sub>  |       | MoS <sub>2</sub>  |         | PbS               |       |
| ĸ           | ∆H <sub>vap</sub> | TEC       | ∆H <sub>vap</sub> | TEC   | ∆H <sub>vap</sub> | TEC     | ∆H <sub>vap</sub> | TEC   |
| 2000        | 327.7             | 393.2     | 267.6             | 299.7 | 337.1             | 381.8   | 130.6             | 154.0 |
| 2500        | 317.7             | 403.8     | 265.2             | 307.7 | 333.4             | 389.6   | 128.4             | 159.8 |
| 3000        | 308.2             | 414.9     | 262.7             | 316.0 | 330.1             | 397.8   | 126.2             | 166.1 |
| 3500        | 299.3             | 426.6     | 260.2             | 324.5 | 327.4             | 406.6   | 124.1             | 172.9 |

| k | Cal | . mo | 1 | -1 |
|---|-----|------|---|----|
|---|-----|------|---|----|

|             | Cass              | iterite         | Sphal            | erite |                   |       |
|-------------|-------------------|-----------------|------------------|-------|-------------------|-------|
| Temperature | Si                | <sup>n0</sup> 2 | ZnF              | ēS    | MoO               | 3     |
| к           | ∆H <sub>vap</sub> | TEC             | $\Delta H_{vap}$ | TEC   | ∆H <sub>vap</sub> | TEC   |
| 2000        | 325.2             | 359.2           | 138.6            | 163.6 | 491.0             | 548.4 |
| 2500        | 322.0             | 367.5           | 136.5            | 168.7 | 486.0             | 558.5 |
| 3000        | 381.1             | 375.7           | 134.2            | 173.8 | 481.2             | 568.9 |
| 3500        | 313.5             | 383.8           | 131.8            | 178.9 | 477.1             | 580.0 |

These values show the same trend against recovery as previously found. It is of note that variations in recovery for the same mineral type indicate that atomisation phenomena cannot wholly explain the observed effects.

The emisson intensity from an atom line is known to be dependent upon the plasma operating conditions, specifically the forward power and the injector flow rate, together with the height of observation. Using the atom lines of copper and silver, 219.958 nm and 338.289 nm respectively the intensities from the finely ground 1% m/v slurries of the reference ores KCla and MPla (used previously) and from solutions containing the equivalent elemental concentration were monitored as a function of viewing height in the analyte channel of the plasma.

The running conditions were varied until the intensity scans from solution and slurry showed a point of coincidence for both analytes (Figures 4.8(a) and (b)). The viewing height was noted and the copper and silver contents of the slurries determined using simple aqueous standards and the new plasma conditions. These conditions are shown in Table 4.20 and the results of the slurry determination are shown in Table 4.21. While a compromise viewing height was used (13 mm) to determine the silver and copper content from Figure 4.8(a) and (b) it is seen that congruency of the solution and slurry emission lines occurs at 10mm height for copper and 18mm height for silver. It is of note that (i) at these high flow rates some matrix effects will begin to be seen in the viewing zone 10 to 20mm above the load coil and (ii) the viewing height emission profiles do not show a well defined maximum (peak). This is as if the atomisation process is spread out over a broad viewing region <u>e.g.</u> from around 8 mm up to 23mm in the case of

FIGURE 4.8

Viewing height emission profiles for equivalent concentrations of elements in solution and slurry (KCla) under plasma conditions which produce a cross over (a) silver, (b) copper.

.



New plasma operating conditions used for the determination of copper and silver in the ore slurries KCla and MPla.

| Forward power /kW                   | 2.0 |
|-------------------------------------|-----|
| Gas flow rates / lmin <sup>-l</sup> |     |
| Coolant                             | 18  |
| Auxiliary                           | 0.6 |
| Injector                            | 2.6 |
| Injector bore size /mm              | 3   |
| Viewing height / mm                 | 13  |

#### TABLE 4.21

The determination of copper and silver in ores KCla and MPla by slurry atomisation using the conditions shown in Table 4.20

|                      | KC1   | MPla   |      |
|----------------------|-------|--------|------|
|                      | Cu    | Ag     | Cu   |
| Cert.Ref.value/ %    | 0.629 | 0.167  | 1.44 |
| Slurry value/ %      | 0.569 | 0.19   | 1.27 |
| Recovery/ %          | 90.5  | 113    | 88.1 |
| Previous Recovery/ % | 71.5  | 65.8 . | 68.8 |

silver, thereby creating conditions for near coincidence (due to high particulate velocities/short plasma residence times)

4.3.2.3 Slurry atomisation experiments with KCla and MPla using the ARL 35000 ICP.

Slurries of 0.1 and 1% m/v were prepared from the ores, KCla and MPla, using the microniser method and a grinding period of 15 minutes. Six elements were determined in each slurry using the ARL 35000 ICP under the conditions shown in Table 4.22. In an attempt to improve slurry transport a single pass ARL conical spray chamber (without a spoiler) was used together with a 3mm bore injector and Ebdon high solids nebuliser.

4.3.2.4 Results and discussion

Table 4.23 shows the results from this experiment together with the calculated recoveries. The very low carrier gas flow rate  $(0.6 \ lmin^{-1})$  and liquid flow rate  $(0.4 \ mlmin^{-1})$  were employed to negate the recurrent problem of aerosol condensation in the injector and high aerosol/vapour loading of the plasma. While transport efficiencies were obviously increased for both solution and slurry, a relative reduction of the mass flux as a ratio of slurry over solution is indicated from the low recoveries. A low gas flow through the 3mm bore injector would result in longer particle residence times in the plasma (due to lower particle velocities) thereby reducing any atomisation effects.

Samples of KCla and MPla were ground for four hours by the bottle and bead method to investigate the effect of particle size upon recovery

Plasma running conditions used for the determination of six analytes in the ores KCla and MPla using the ARL 35000 ICP

| Torch                                 | 'Fassel' Type             |
|---------------------------------------|---------------------------|
| Forward power /kW                     | 1.4                       |
| Gas flow rates / l min <sup>-l</sup>  |                           |
| Coolant                               | 13                        |
| Auxiliary                             | 1                         |
| Carrier                               | 0.6                       |
| Injector bore /mm                     | 3                         |
| Nebuliser type                        | Ebdon                     |
| Liquid flow rate/ml min <sup>-1</sup> | 0.4                       |
| Spray chamber                         | ARL (conical) single pass |

-

# The analysis of KCla and MPla CRM ores by slurry atomisation using the ARL 35000 ICP

| Element           | Zn      | Pb     | Cu     | Ag       | Fe                   | Sn     |
|-------------------|---------|--------|--------|----------|----------------------|--------|
| Wavelength/nm     | 213.85  | 283.30 | 324.75 | 338.29   | 259.94               | 283.99 |
|                   |         |        | KCla % |          |                      |        |
| Certificate value | e 34.65 | 2.24   | 0.629  | 0.167    | (10.9)               | 0.61   |
| Slurry value      | 22.43   | 1.61   | 0.28   | 0.07     | 6.62                 | 0.36   |
| % Recovery        | 64.7    | 71.9   | 44.5   | 41.9     | 60.7                 | 59.0   |
|                   |         |        | MPla % |          |                      |        |
| Certificate value | e 19.02 | 4.33   | 1.44   | 69.7µg g | - <sup>1</sup> (6.2) | 1.28   |
| Slurry value      | 11.74   | 2.59   | 0.57   | 47.7µg g | - <sup>1</sup> 3.69  | 0.55   |
| % Recovery        | 61.7    | 59.8   | 39.6   | 68.4     | 59.5                 | 43.0   |

( ) indicated value only

Results from the determination of copper, iron, zinc and lead in the bottle and bead ground slurries KCla and MPla together with the copper and iron values from the ore SA1/Cl20. Analysis on ARL 35000 ICP

| Element     |      | KCla     |                    |      | MP1a  |                      | SA1    | /C120 |                    |
|-------------|------|----------|--------------------|------|-------|----------------------|--------|-------|--------------------|
|             | Slu  | rry Cert | . R <sup>*</sup> % | Slur | ry Ce | rt. R <sup>*</sup> % | Slurry | Cert  | . R <sup>*</sup> % |
| Cu%         | 0.35 | 0.629    | 55.6               | 0.84 | 1.44  | 58.3                 | 0.35   | 0.37  | 95.7               |
| Fe%         | 11.2 | (10.9)   | 102.7              | 6.8  | (6.2) | 109                  | 18.5   | 18.2  | 101                |
| Zn%         | 29.9 | 34.65    | 86.3 <sup>·</sup>  | 18.2 | 19.02 | 95.6                 |        |       |                    |
| Pb <b>%</b> | 2.2  | 2.24     | 98.2               | 3.6  | 4.33  | 83.1                 |        |       |                    |

\*R% Recovery as %

Cert. Certified reference value

. .

( ) Indicated value only

for these ores. The fine slurries were analysed to determine their copper, iron, zinc and lead contents using the plasma conditions shown in Table 4.22 with the exception of using a forward power of 1500W and gas flow rate of  $1.0 \ 1 \ min^{-1}$ . A newly constructed 3mm injector with a smooth contoured base and DPSC were employed in an attempt to reduce the problems of aerosol nucleation at the higher flow rate. These results are shown in Table 4.24 together with those found from the inhouse ore SA1/C120, ground and analysed under the same conditions. With the exception of the copper results for the ores KCla and MPla, near to full recoveries were obtained. In most cases the ground materials were 100% less than 6µm and 50% less than 2µm. It is of note that stability problems were still encountered with this sample introduction system which was manifest in the necessity to recalibrate frequently or renormalise by running standards either side of every sample.

4.3.3 Dolomite and Feldspar Certified Reference Materials

Samples of certified reference minerals, BCS 368 Dolomite (BCS, Middlesborough, UK) and NBS SRM 99a Feldspar (NBS, Washington, DC 20234, USA) were analysed by the slurry technique. Dolomite is essentially calcium magnesium carbonate  $(CaMg(CO_3)_2)$  and in nature the magnesium may be partially replaced by other cations (Dolomite forms a solid solution series with ankerite -  $Ca(Fe,Mg,Mn)(CO_3)_2)$ . Its density is between 2.85 and 2.95 g cm<sup>-3</sup> and is considered semi-hard (MOH 3.5 to 4). The Feldspars are a group name which include the granite, Rhyolite and Syenite rock system. The high potassium and sodium contents of this sample suggest that it is a 'Perthite' type being a mixture of sodium and potassium aluminosilicates (regular association of albite or oligoclase in a microline crystal host or possibly orthoclase). Its

density is usually 2.55 to 2.65 g cm<sup>-3</sup> and is very hard (MOH 6 to 6.5). Very minor quantities of other minerals are often associated with it but quartz can sometimes be present at percentage levels.

4.3.3.1 The analysis of Dolomite and Feldspar by slurry atomisation

Samples of BCS 368 Dolomite and NBS 99a Feldspar were ground, using the bottle and bead method, for four hours and prepared as both 0.1 and 1% m/v slurries. These were stabilised in 0.1% SHMP dispersant. Iron, aluminium, magnesium, calcium and manganese were determined by the slurry technique using simple calibration solutions. The analyses were performed on the Plasmakon S-35, using the conditions of 1500W forward power, 16 1 min<sup>-1</sup> and 0.6 1 min<sup>-1</sup> coolant and auxiliary flows, at various viewing heights and injector flows based on the optimum signal to background emission ratio from the solutions. The sample introduction system used was a double pass spray chamber and 3mm bore injector.

#### 4.3.3.2. Results and discussion.

The results of the slurry determination are shown in Table 4.25. While the iron ion line 259.837 nm was viewed under various running conditions to bring about full recovery from the Dolomite sample it was found that the atom line 371.993 nm gave nearly 95% recovery under normal running conditions (1.5 kW power, 1.8 1 min<sup>-1</sup> carrier gas flow rate). The viewing height, however, was 30 mm. Figure 4.9 shows a comparison of the iron atom and ion line viewing height emission profiles and displays how the iron atom emission rises to a maximum at 30 mm height as the flow rate increases. In comparison, at 1.7 to 1.8 1 min<sup>-1</sup> the iron ion line gave recoveries of 77 to 78% at 18 mm

|         |            |         |           | Dolomite | ж        | 1         | Feldspar % |          |
|---------|------------|---------|-----------|----------|----------|-----------|------------|----------|
| Element | Experiment | Wave- ( | Certified | Slurry   | Recovery | Certified | Slurry     | Recovery |
|         |            | length  | value     | value    | %        | value     | value      | %        |
|         |            | nm      |           |          |          |           |            | •        |
| Fe II   | 1          | 259.84  | 0.161     | 0.125    | 77.6     |           |            |          |
| Fe II   | 2          | 259.84  | 0.161     | 0.140    | 86.9     |           |            |          |
| Fe II   | 3          | 259.84  | 0.161     | 0.148    | 91.9     |           |            |          |
| Fe II   | 4          | 259.84  | 0.161     | 0.186    | 115.5    |           |            |          |
| Fe I    | 5          | 371.99  | 0.161     | 0.152    | 94.4     |           |            |          |
| Fe II   | 6          | 259.94  | -         | -        | -        | 0.042     | 0.065      | 153(1)   |
| A1 I    | 7          | 396.152 | 0.09      | 0.090    | 100      |           |            | 200      |
| Al I    | 8          | 396.152 | -         | -        |          | 10.85     | 8.7        | 80       |
| Al I    | · 9        | 396.152 | 0.09      | 0.095    | 105      |           | •••        | •••      |
| Mg I    | 10         | 285.213 | 12.6      | 12.04    | 95.6     |           |            |          |
| Ca II   | 11         | 317.933 | 22.0      | 19.5     | 88.6     | 1.53      | 1.29       | 84.4     |
| Mn II   | 12         | 257.61  | 0.0465    | 0.0416   | 89.4     |           |            |          |

:

## The analysis of Dolomite and Feldspar Certified Reference Materials by slurry atomisation ICP-AES.

| Experiment | Viewing Height/mm | Gas flow rate/lmin <sup>-1</sup> |
|------------|-------------------|----------------------------------|
| 1          | 18                | 1.7                              |
| 2          | 13                | 1.3                              |
| 3          | 19                | 2.3                              |
| 4          | 17                | 2.3                              |
| 5          | 30                | 1.8                              |
| 6          | 20                | 1.4                              |
| 7          | 27.5              | 1.8                              |
| 8          | 26.8              | 1.4                              |
| 9          | 27.8              | 1.4                              |
| 10         | 33.4              | 1.4                              |
| 11         | 18.8              | 1.4                              |
| 12         | 18                | 1.4                              |

.

(1) Contamination from grinding process.

.

.

.

.

.

FIGURE 4.9

Viewing height emission profiles from iron in BCS 368 Dolomite slurry using the iron ion line 259.94nm and iron atom line 371.993nm at low gas flow rate (1.3 l min<sup>-1</sup>) and high gas flow rate (2.3 l min<sup>-1</sup>).



viewing height. Calculations show an increase of nearly 45% for particle residence time in the plasma, based on the point of entry to the viewing position, when the atom line 371.993 nm is used. As all other transport conditions are the same, the near full recovery can be explained in terms of atomisation efficiency. It is of considerable note that, from Table 4.25, all elements that were determined at 1.4 to 1.8 l min<sup>-1</sup> carrier gas flow rate (normal solution conditions) using an atom line and high viewing positions *i.e.* Fe, Al, Mg between 27 and 33 mm, gave near to full recoveries in the Dolomite sample, while those determined using ion lines i.e. Fe, Ca, Mn, at normal solution viewing positions, 18 to 19 mm, gave recoveries of less than 90%. The particle size distribution of the Dolomite slurry was such that 90% (by volume) was under 2.6 µm and 100% under 5 µm. In contrast the harder Feldspar sample showed 55% under 2.6 µm and 100% under 10 µm and hence transport (and possibly atomisation) effects would be more pronounced (as shown by the aluminium recovery, 80%, using the atom line 396.152 nm at 27.5 mm viewing height).

#### 4.4. TRANSPORT AND ATOMISATION PHENOMENA FROM ALUMINA SLURRIES

While transportation effects may occur with many different slurried materials, depending upon the size of the solid matrix, atomisation phenomena are more likely to be present if the thermodynamic properties of the matrix demands a high energy input prior to excitation of a concomitant analyte. The high melting and boiling points of alumina (2345 and 3253 K respectively) together with the high enthalpy change required for alumina to undergo the following reaction:

$$A1_{2}0_{3}(solid) = 2 A1_{(gas)} + 3 0_{(gas)}$$
 (4.4)

at 3500 K,  $3.4 \times 10^6$  J mol<sup>-1</sup>, make this material a prime candidate for examination of atomisation effects. A theoretical approach to the decomposition of alumina particles in a plasma environment has been published by Allemand and Barnes (127) and for ceramic materials including alumina by Raeymaekers et al. (88).

4.4.1. The Determination of Aluminium in Alumina.

Two samples of alumina were used for the determination of aluminium by the slurry technique. One was an ultrafine (reported to have a mean particle size of 0.05  $\mu$ m) polishing alumina (BDH, Poole, Dorset, UK) while the other was a laboratory standard prepared for X-Ray fluorescence (BP Research Centre, Sunbury-on-Thames, Middx, UK) and very much coarser (up to 16  $\mu$ m particle size). An examination of both materials by powder X-Ray diffraction showed the major phase to be gamma alumina.

Samples of the two alumina materials were analysed by the slurry technique and after dissolution, by a sodium peroxide fusion/nitric acid attack, for aluminium. Three different particle sized alumina slurries were prepared by the bottle and bead method and stabilised in 0.1% m/v SHMP solution. The ultrafine alumina sample was ground for 15 minutes to produce the finest slurry while the coarser alumina sample was divided and ground for 15 minutes and 1 hour to produce a coarse slurry and an intermediate sized slurry respectively. The determination of aluminium in both solutions and slurries was performed using the Plasmakon S-35 ICP under the running conditions shown in Table 4.26 (a).

# ... TABLE 4.26

Plasma running conditions used on the Plasmakon S-35 ICP for the determination of aluminium in coarse, medium and fine alumina slurries and fusion solutions.

|                                    | (a)             | (b)             |
|------------------------------------|-----------------|-----------------|
| Torch                              | Greenfield type | Greenfield type |
| Forward power/kW                   | 1.5             | 1.5             |
| Gas flow rates/1 min <sup>-1</sup> |                 |                 |
| Coolant                            | 16 - 17         | 17              |
| Auxiliary                          | 0.5 - 0.6       | 0.6             |
| Carrier                            | 2.0             | 1.2             |
| Injector bore/mm                   | 3               | 3               |
| Nebuliser type                     | Ebdon           | Ebdon           |
| Viewing height/mm                  | 20 to 30        | 6.4             |
| Spray chamber                      | Double pass     | Double pass     |
| Al Wavelength/nm                   | 396.152         | 396.152         |
| Recovery/%*                        | 74              | 90              |
|                                    |                 |                 |

\* For medium particle size alumina slurry as defined in Table 4.27.

.

-

.

215

.

4.4.2. Results and Discussion.

The theoretical aluminium content of alumina is 52.94%. The fusion solutions gave the aluminium content of the alumina samples as 52.75+0.25. Table 4.27 shows the aluminium recoveries of the coarse, medium and fine alumina slurries together with their size distributions. While all slurries were over 90% (by volume) less than 8 um only the ultrafine slurry (100% less than 2.5 µm, the mode of the distribution less than 1 µm) gave near full recovery, indicating that both the transport and atomisation efficiencies of the slurry are very close to that of a solution. As the particle size increases the recovery for aluminium decreases. That a transport effect is present for the coarse alumina slurry can be seen in the particle size distributions of Figure 4.10, where a separate sample of the coarse alumina was ground for 15 to 20 minutes and collected at the tip of a 3 mm injector after passing through an Ebdon nebuliser and double pass spray chamber. Clearly, little material over 5 µm is seen after transportation while the starting slurry shows material up to 8 µm in size. It is of interest to note that the previously mentioned Dolomite BCS 368 sample, which was of a very fine particle size (100% less than 5 μm, 90% less than 2.6 μm), gave full recovery for the aluminium content by the slurry technique.

The atomisation efficiency of a coarse alumina slurry can be improved, relative to that of a solution by using a reduced carrier gas flow rate  $(1.2 \ 1 \ min^{-1})$ , through a 3 mm bore injector. The resultant increase in residence time for slurry particles improved the recovery of the medium size fraction álumina from 74% to 90%. These conditions are shown in Table 4.26(b).

Full recoveries are obtained when a slurry aerosol models that of a solution with respect to (i) the mass flux of the analyte under consideration, (ii) the aerosol mass flux and particle size distribution and (iii) the atomisation and excitation processes in the plasma environment.

That only the ultrafine slurries of alumina (less than 2.5 µm size) show this congruency with solutions is put in perspective when the fate of an aluminium (as nitrate) calibration solution aerosol is considered on a particle mass basis entering the plasma. Using the solution aerosol distribution that exits from a double pass spray chamber (Malvern aerosol study, Chapter 3, Figure 3.7) it is possible to calculate the maximum solid particle size distribution of aluminium oxide formed from the desolvation and decomposition process:

600K  $4A1(NO_3)_3 + XH_2O \longrightarrow 2A1_2O_3 + 12NO_2 + 3O_2 + XH_2O$  (4.6) Solution aerosol solid gas

using the equation 
$$d_c = d_A \cdot \left[\frac{(Y \cdot C_f)}{P_c}\right]^{1/3}$$
 (4.7)

where d<sub>c</sub> is the resultant solid particle diameter in  $\mu$ m (in this case for Al<sub>2</sub>O<sub>3</sub>), d<sub>A</sub> is the solution aerosol particle diameter in  $\mu$ m (in this case Al(NO<sub>3</sub>)<sub>3</sub> aerosol particles), Y is the weight in grams of the analyte per cm<sup>3</sup> of solution (in this case aluminium per cm<sup>3</sup> of solution Al(NO<sub>3</sub>)<sub>3</sub>), C<sub>f</sub> is the compound factor (the weight ratio of the resultant compound to analyte, in this case Al<sub>2</sub>O<sub>3</sub>/2Al) and P<sub>c</sub> is the density of the resultant compound in g cm<sup>-3</sup> (in this case 3.96 g cm<sup>-3</sup> for Al<sub>2</sub>O<sub>3</sub>).

The worst scenario is considered in that no ablation of the aerosol particle or solid occurs during the desolvation and decomposition processes. Figure 4.11 shows the relevant distributions and it can be seen that a 21  $\mu$ m size aerosol particle (maximum) containing aluminium at a concentration of 500  $\mu$ g ml<sup>-1</sup> (equivalent to the aluminium in the fine alumina slurries) would yield a maximum sized alumina particle of 1.27  $\mu$ m diameter. As only the ultrafine alumina approached this hypothetical solid distribution, it is to be expected that slurries prepared from this material would give near to full recoveries, compared with the coarser alumina samples.

Raeymaekers et al. (88) have recently measured the maximum size of solid particles that exit from a single pass spray chamber with injector using various size fractions of alumina in suspension (<10µm, 10 to 20 µm, 20 to 25 µm). Particles up to 17 µm in diameter were noted but no final solids distribution was given. The aluminium emission from these suspensions was compared with that from a solution containing an equal concentration of the analyte using an ICP under the conditions of 2.4 kW power and 1 1 min<sup>-1</sup> carrier gas flow. The relative response (designated here for convenience as recovery, R %) was considered in terms of evaporation efficiency. Experimental transport factors, however, were not taken into account. From their paper for 1 to 10  $\mu$ m sized particles, R = 75%, and for 10 to 20  $\mu$ m size, R = 20%. For a fine alumina suspension (95% less than 2.5 μm), however, full recoveries were obtained. Theoretical calculations based on their proposed evaporation model (where  $T_{gas}$  = 5000 K taken) suggest that full atomisation of alumina particles up to 10 µm in diameter should occur after travelling 20 mm through the plasma while for particles in the range 10 to 20  $\mu m$  size only 55% of material is atomised after travelling 30 mm through the plasma. This is in

FIGURE 4.10

By volume particle size distribution of ground alumina slurry before and after transportation through a double pass spray chamber with 3mm injector at a gas flow rate of 2 1 min<sup>-1</sup>.


#### FIGURE 4.11

By weight particle size distribution of aerosol exiting a double pass spray chamber and theoretical maximum alumina particle size produced by decomposition of  $500\mu g ml^{-1}$  aluminium nitrate aerosol of the same distribution.



#### TABLE 4.27.

Variation, with particle size, of the aluminium recovery (R%) from coarse, medium and fine alumina slurries.

% less than / µm. R% Slurry<sup>+</sup> 8 5 3 2.5 99 Fine 100 100 100 100 74 Medium 94 88 69 47 55 Coarse 93 77 46 25

+ See text for definition.

#### **TABLE 4.28**

Plasma running conditions used on the Plasmakon S-35 ICP for the measurement of the AlO emission band head (0-0) as a function of viewing height.

| Torch                             | Greenfield type |
|-----------------------------------|-----------------|
| Forward power/kW                  | 1.1 - 1.2       |
| Gas flow rates/lmin <sup>-l</sup> |                 |
| Coolant                           | 15              |
| Auxiliary                         | 0.6             |
| Carrier                           | 1.65            |
| Injector bore/mm                  | 3               |
| Nebuliser, type                   | Ebdon           |
| Spray chamber                     | Double pass     |
| AlO band head (0-0)/nm            | 484.22          |
| Viewing height/mm                 | 10 - 50         |

contrast to the experimental evidence of Monnig and Koirtyohann (128) who used a Mie scattering technique to follow aerosol particles of aluminium in solution (5000  $\mu$ g ml<sup>-1</sup>) through the plasma. Particles were seen to persist at the top of the initial radiation zone and into the normal analytical viewing zone. These were considered to be the presence of refractory alumina. As a 10  $\mu$ m diameter aerosol particle from 5000 ug ml<sup>-1</sup> aluminium in solution would produce a maximum sized alumina particle of about 1.3  $\mu$ m the evidence is that much smaller particles than those proposed by Raeymaekers <u>et al.</u> are able to withstand the thermal environment of the plasma.

# 4.4.3. The Measurement of AlO Emission in a Plasma from Solutions and Slurries.

Aluminium in solution may, upon entering a plasma, decompose to form the thermodynamically stable oxide,  $Al_2O_3$  as shown in equation 4.6. Aluminium is also known to form a stable molecular monoxide, AlO, in certain plasmas (arcs, flames, stars, (129)). As this oxide can persist in high temperature environments its presence and concentration at various points in the analyte channel of an ICP may give an indication of the atomisation (and later recombination) rate mechanism through which a decomposing alumina or aluminium-containing aerosol particle undergoes. Any differences between the AlO viewing height emission profiles from solutions and slurries may indicate a difference in the transportation and thermal breakdown of the alumina particles involved. No differences would indicate that both processes are similar.

Two slurries of alumina were prepared to give an aluminium concentration of 10,000  $\mu$ g ml<sup>-1</sup> (<2% m/v solids loading). One slurry was of

the ultrafine alumina grade (100% below 2.5  $\mu$ m) while the other was the coarse alumina used in the previous experiments. Both were ground for 10 minutes by the bottle and bead method in 0.1% m/v SHMP solution to bring about a primary particle dispersion. Using the plasma conditions shown in Table 4.28 the intense AlO emission band head (0-0) at 484.22 nm (129) was monitored from the slurries and a standard 10,000  $\mu$ g m1<sup>-1</sup> aluminium solution as a function of height above the load coil. The background was monitored at 484.10 nm.

#### 4.4.4. Results and Discussion

The well defined AlO band head emission (0-0) at 484.22 nm is shown in Figure 4.12 for a 2% m/v alumina slurry at 40 mm height. The ultrafine alumina and standard aluminium solution show near identical AlO emission profiles over the height range 10 mm to 40 mm (Figure 4.13). Again an indication of the ultrafine slurry and solutions having equivalent atomisation and transport mechanisms. The AlO emission from the coarse alumina against viewing height is shown in Figure 4.14 compared with that from the standard aluminium solution. The profiles show the effect of both transport, due to the reduced AlO emission over the entire range, and atomisation, as the profiles are different shapes. The coarse slurry shows a broader and flatter AlO emission (25 to 50 mm height) suggestive of atomisation effects that are dependent upon residence time. The particle size distribution of the starting coarse alumina slurry was such that 100% (volume) of material was below 16  $\mu m$  size, 94% below 8  $\mu m$ , 76% below 5  $\mu m$ , 41% below 3  $\mu m$  and 20% below 2.5 µm. The peak AlO recovery (ratio of AlO net emission from slurry over solution as percentage) is 50 to 52% (at 23 mm height). This is comparable to the aluminium recovery obtained previously for this coarse slurry i.e. 54 to 56% at 20 mm (396.152 nm Al atom line).

FIGURE 4.12

•

Wavelength emission scan across the 484.2 nm AlO emission band head obtained from aspirating a 1% m/V aluminium solution into the plasma and viewed at 40mm above load coil.





Graph showing the net intensity of the AlO emission band head, from a 2% m/V ultrafine alumina slurry and a solution of equivalent aluminium concentration, against viewing height in plasma.



FIGURE 4.14

Graph showing the net intensity of the AlO emission band head 484.2 nm, from a 2% m/V coarse alumina slurry and a solution of equivalent aluminium concentration, against viewing height in plasma.



It is of note that a study by Reeves <u>et al.</u> (130) of the stable monoxide emissions from ScO, VO, GdO and LuO (500  $\mu$ g ml<sup>-1</sup> solutions) showed peaks in the viewing profiles around 15 to 20 mm above the load coil. These experiments, however, were conducted with a Fassel size extended torch to reduce the ingress of air.

4.4.5. Atomisation Phenomena from Alumina Slurries.

The AlO emission study suggested that some time dependent atomisation phenomena may be present in some coarser alumina slurries. A greater appreciation of such effects may be gained from a comparison of the aluminium viewing height emission profiles (VHEP) from alumina slurries of varying particle size with those from a solution of equal aluminium concentration obtained under identical plasma operating conditions.

Coarse, medium and ultrafine alumina slurries (0.1% m/v) were prepared by the bottle and bead method in 0.1% m/v SHMP solution and their VHEP were monitored with the Plasmakon S-35 ICP using forward powers of 1.3 to 2 kW and carrier gas flow rates from 1.1 up to 3 1 min<sup>-1</sup>. Solutions of comparable aluminium content were monitored under the same conditions. The aluminium atom lines 308.22 nm and 396.152 nm were used.

4.4.6. Results and Discussion.

Figure 4.15 (a) shows the VHEP for ultrafine alumina and a 400  $\mu$ g ml<sup>-1</sup> Al solution obtained at 1.5 kW forward power and 2 l min<sup>-1</sup> carrier gas flow rate. The profiles are identical and the ratio of the emission responses (corrected for background) shows full recovery over the entire height range. Figure 4.15 (b) shows the VHEP from a coarse

alumina slurry and a solution of equal aluminium content to the starting slurry (2 kW forward power, 2.7 l min<sup>-1</sup> carrier gas flow rate). The recovery from 5 mm to 60 mm height is 50 to 60% and the profiles are very similar. No evidence for atomisation effects is seen and the reduced emission may be accounted for in terms of transport efficiency. The particle size of the coarse alumina slurry is stated in section 4.4.4.

Figure 4.16 shows the profiles obtained from a medium sized alumina slurry (distribution given in Table 4.27) compared with a solution of equal aluminium content using a forward power of 1.5 kW and injector flow rates of 1.1, 1.2 and 1.3 1 min<sup>-1</sup> (Figures 4.16 (a), (b) and (c) respectively). This slurry previously gave a recovery of 74% (1.5 kW and 2 1 min<sup>-1</sup>). By increasing the residence time it can be seen that at low viewing heights (5 mm) near coincidence of the profiles occur at 1.2 and 1.3 1 min<sup>-1</sup> flow rates. At 1.1 1 min<sup>-1</sup> flow rate the profiles begin to converge at a height of 27 mm and are indicative of time dependent atomisation processes. This viewing region compares well with that used previously to monitor atom line emissions from slurries to give near to full recoveries. However, at these low flow rates some sensitivity is lost due to the use of a 3 mm injector.

Parry (100) has shown that by employing simplex optimisation with a suitable figure of merit full recoveries for the aluminium content of a coal slurry can be realised. The running conditions under which full recoveries were obtained (Table 39 of reference 100) centred on high carrier gas flow rates (2.6 to  $3.0 \ 1 \ min^{-1}$ ), high auxiliary flow (up to  $1.8 \ 1 \ min^{-1}$ ), medium forward power (1.2 to  $1.5 \ kW$ ) and low viewing heights (5 to 14 mm). With the exception of the forward power these conditions are similar to those used to produce a cross over of the

VHEP for the analytes copper and silver in the CANMET ore slurries KCla and MPla.

In this alumina study the plasma running conditions obtained by Parry (Table 4.29) were used to produce VHEP from the medium particle size alumina slurry and solutions of equal aluminium content. These viewing profiles are shown in Figures 4.17 (a) to (c). It can be seen from Figures 4.17 (a) and (b) that the high carrier gas flow rates (2.7 and 3.0 l min<sup>-1</sup>) and power used (1.33 and 1.38 kW) cause the emission profiles to be flattened and broadened. No definite emission peak with viewing height was observed and this suggests that the atomisation and excitation processes are spread out in the analyte channel of the plasma. This effect occurs for both solutions and slurries (but the profiles are not identical). This may in part be due to a thermalising of the central channel which would cause the kinetic temperature gradient along this axis to be reduced. While the kinetic temperature may be increased at greater heights, this would be dependent upon the thermal energy transfer rate from the plasma body to the analyte channel. Atomisation and excitation processes may therefore be present higher in the plasma. It can be conjectured that one of two effects may be occurring.

(i) That atomisation of both solutions and slurries occurs low down in the plasma and that only the excitation processes are able to persist higher up in the plasma (thereby showing no improvement in recovery when greater viewing heights are used to observe emissions and failing to separate the transport and possible atomisation processes).

(ii) That both atomisation and excitation processes are able to persist higher up in the plasma and hence may show a coincidence point for solutions and slurries higher up (thereby indicating that at these high gas flow rates transport processes are similar for solutions and the medium sized alumina slurry).

Under the conditions used to produce profiles (a) and (b) the latter effect is suggested. Near coincidence of the aluminium emissions from solution and slurry is observed from 35 mm (Figure 4.17 (a)) and 40 mm (Figure 4.17 (b)). Certainly at the higher carrier gas flow rates used, the transport properties of both solution and slurry aerosols will be modified compared with conventional flow rates (1.5 1 min<sup>-1</sup>) as would the residence time of the particles (50% of conventional). Only a finer aerosol and solids distribution may therefore enter the plasma with a possible result that, at the velocities involved, decreased atomisation occurs for both solutions and slurries (reduction in emission, loss of sensitivity) but to different degrees.

Figure 4.17 (c) shows the effect of lowering the carrier gas flow rate (from 3.0 to 2.6 l min<sup>-1</sup>) and increasing the power to 1.5 kW. The peak emission point normally seen around 18 to 23 mm begins to re-emerge but the coincidence point is moved to a higher viewing position suggesting that atomisation of the solution aerosol occurs before that of the slurry. This is accentuated when the power is raised to 1.7 kW for the same carrier flow rate (Figure 4.17 (d)).

#### FIGURE 4.15

Viewing height emission profiles of the aluminium atom line, 396.152 nm, from (a) an ultrafine alumina slurry and solution and (b) a coarse alumina slurry and solution of equivalent aluminium content.



FIGURE 4.16

Viewing height emission profiles of the aluminium atom line, 308.215nm, from a ground alumina slurry and from a solution of equivalent aluminium content at gas flow rates of (a) 1.1, (b) 1.2 and (c) 1.3 l min<sup>-1</sup>.

•



VIEWING HEIGHT / cm

Plasma running conditions (Plasmakon S-35) used to produce the viewing height emission profiles shown in Figures 4.17 (a) to (d).

Gas flow rates/l min $^{-1}$ 

| Figure 4.17 | Forward power | Carrier | Auxiliary | Coolant |
|-------------|---------------|---------|-----------|---------|
|             | /k₩           |         |           |         |
| (a)         | 1.33          | ·2.7    | 1.7       | 22.3    |
| (b)         | 1.38          | ·3.0    | 1.6       | 22.6    |
| (c)         | 1.5           | 2.6     | 1.5       | 20.1    |
| (d)         | 1.7           | 2.6     | 1.5       | 20.1    |

• •

.

Ł

Ł

#### FIGURE 4.17

Viewing height emission profiles of the aluminium atom line, 396.152 nm, from a ground alumina slurry and from a solution of equivalent aluminium content produced at high gas flow rates with increase in forward power.



- 4.5. THE DETERMINATION OF MAJOR ELEMENTS IN CERAMIC MATERIALS BY SLURRY ATOMISATION.
- 4.5.1. The Recoveries of Zirconium from Fine Zirconia Powders.

Zirconia powder is a highly refractory material used in the production of ceramic goods (thermal insulators, furnace liners, crucibles and specialist engineering ceramics). As a consequence this stable, high melting point solid (3000 K) is not readily attacked by acids and alkalies and dissolution is generally brought about by use of fusion techniques and bomb digestions. Such a step can be circumvented in analysis if a slurry technique is employed. A preliminary study was undertaken to determine the feasibility of using slurry atomisation for the analysis of unground, as supplied, fine zirconia powder.

Four samples of fine zirconia powder  $(ZrO_2)$  were obtained for analysis (Magnesium Electron Ltd, Swinton, Manchester, UK). The samples, as received, were designated 1 to 4 and were stated to have mean particle size diameters  $(d_{50})$  of 0.58, 0.93, 1.65 and 1.99  $\mu$ m respectively. Subsamples (0.1 g) were shaken for 5 minutes, using the bottle and bead method, in 0.1% SHMP solution to remove agglomerates and produce a primary particle dispersion. These dispersions were introduced into the Plasmakon S-35 ICP and the zirconium emissions obtained at various plasma running conditions were compared with those from a solution of the dissolved powder sample of equal concentration. Particle size distributions of the dispersions were measured using the Coulter Counter TAII and 30  $\mu$ m size orifice tube.

Sample 1, which was stated to be the finest of the powders (d  $_{50}$  = 0.58  $\mu$ m) was used to determine the plasma conditions necessary to bring about the greatest recovery. Table 4.30 shows the overall change in zirconium recovery (70 to 78%) which was little affected by the conditions. The particle size distributions of the zirconia dispersions, 1 to 4, are shown in Table 4.31 and all are fairly broad. While the supplied  $\mathsf{d}_{50}$  mean size values suggest that the powders are fine, in practice the spread of the distributions shows material up to 6  $\mu m$  is present in all samples. The d<sub>50</sub> values are also larger than stated <u>i.e.</u> samples 1 to 4 show  $d_{50}$  dispersion values of 1.1, 1.36, 2.2 and 1.9 µm respectively, although this difference may be a function of the dispersion system or the particle sizing technique used. Material below 0.63 µm size was however also present. Table 4.30 also shows the recoveries obtained from slurried samples 2, 3 and 4, under identical conditions to slurried sample 1, based upon the response from the dissolved samples. It is of note that the total percentage of material below 2  $\mu m$  size for each sample correlates well with the recovery for zirconium (Table 4.30). As particles up to 5 µm size are known to reach the plasma through the double pass spray chamber and 3 mm injector (the solids distribution being partly dependent upon the density of the transported material, 5.6 - 5.9 g cm<sup>-3</sup>) transport effects may only account in part for the reduced recoveries. This is put into perspective when it is considered that temperatures up to 5000 K may be necessary to atomise zirconia. The material which reached the plasma did, however, atomise to give 70 to 80% recovery.

The effect of plasma running conditions upon the recovery of zirconium from 'Sample 1' of zirconia powder by slurry atomisation together with the recoveries from Samples 2,3 and 4.

| Sample | Forward | Carrier gas          | Viewing | Emission Line <sup>(a)</sup> | Recovery <sup>(b)</sup> | Total % Volume | • : |
|--------|---------|----------------------|---------|------------------------------|-------------------------|----------------|-----|
| No.    | power   | flow rate            | Height  | Wavelength                   | /%                      | Below 2 µm     |     |
|        | /kW     | /l min <sup>-l</sup> | /៣៣     | /nm                          |                         |                |     |
| 1      | 1.5     | 1.3                  | 28.5    | II,343.823                   | 76.1                    | 77.7           |     |
| 1      | 1.5     | 1.3                  | 46.0    | I,360.119                    | 78.2                    | 77.7           |     |
| 1      | 1.5     | 1.7                  | 47.0    | I,360.119                    | 74.3                    | 77.7           |     |
| 1      | 1.5     | 2.3                  | 40.0    | II,343.823                   | 70.2                    | 77.7           |     |
| 1      | 1.8     | 1.4                  | 40.0    | II, <b>3</b> 43.823          | 72.6                    | 77.7           |     |
| 1      | 1.5     | 1.35                 | 34.6    | II,343.823                   | 75.9                    | 77.7           |     |
| 2      | 1.5     | 1.35                 | 34.6    | II,343.823                   | 63.4                    | 66.4           |     |
| 3      | 1.5     | 1.35                 | 34.6    | II,343.823                   | 58.1                    | 47.2           |     |
| 4      | 1.5     | 1.35                 | 34.6    | II,343.823                   | 57.5                    | 53.4           |     |

(a) I Atom line, II Ion line

(b) Based upon the ratio of the slurry sample emission signal over the emission signal from the dissolved sample of same concentration (background corrected).

# The particle size distributions of the zirconia

powder samples 1,2,3 and 4.

•

| Size band   |      | %Volume | in band |      |
|-------------|------|---------|---------|------|
| /µm         | (1)  | (2)     | (3)     | (4)  |
| 0.63 - 0.79 | 24.3 | 19.4    | 13.9    | 12.1 |
| 0.79 - 1.0  | 17.2 | 12.8    | 6.6     | 8.7  |
| 1.0 - 1.26  | 15.7 | 13.6    | 8.7     | 10.9 |
| 1.26 - 1.58 | 11.4 | 11.0    | 9.0     | 10.8 |
| 1.58 - 2.0  | 9.1  | 9.6     | 9.0     | 10.9 |
| 2.0 - 2.52  | 6.8  | 6.6     | 7.6     | 10.1 |
| 2.52 - 3.17 | 6.1  | 8.4     | 10.1    | 13.9 |
| 3.17 - 4.0  | 5.5  | 8.4     | 14.3    | 13.0 |
| 4.0 - 5.04  | 2.5  | 8.1     | 13.6    | 7.2  |
| 5.04 - 6.35 | 1.5  | 2.0     | 6.0     | 2.1  |
| 6.35 - 8.0  | 0    | 0       | 1.2     | 0    |

• -

.

4.5.3 The Determination of Boron and Iron in Polyboron nitride

Polyboron nitride is a highly refractory ceramic material which sublimes at 3300 K. It is used in specialist engineering designs for high temperature environments and more recently has been considered suitable as an inert former for the semi-conductor industry. Polyboron nitride is extremely difficult to bring into solution and monitoring of its purity is therefore problematical.

Two samples of polyboron nitride (PBN) were obtained for iron analysis (Ringsdorff Werke GmbH, Ringsdorff, W. Germany). These were ground by a two stage process described in sections 2.3.1.1. to 2.3.1.3. of Chapter 2. Contamination from the first stage dry grinding process (Tema Mill) was kept to a minimum by grinding and discarding two subsamples of the PBN supplied. Both the grinding chamber and elements were left with a fine coating of PBN, from the second sub sample ground, to act as a barrier. The third subsample ground was used for the second stage grinding process but the material adhering was again discarded. The material from this first grinding stage was then wet ground by the bottle and bead method to prepare slurries of 0.1, 1 and 2% m/v concentration in 0.1% m/v SHMP solution. Slurries were introduced into the Plasmakon S-35 ICP with the running conditions shown in Table 4.32. Both boron and iron levels were determined in the slurry samples using simple aqueous standards for calibration.

## 4.5.4 Results and Discussion

The particle size distributions of PBN from the first and second stage grinding processes are shown in Figure 2.4 of Chapter 2. Material up to 25 µm size was present after the second stage wet grind with 76.5%

Plasma conditions used on the Plasmakon S-35 ICP for the determination of boron and iron in 0.1 to 2% m/v slurries of polyboron nitride.

| Torch                              | Greenfield type     |
|------------------------------------|---------------------|
| Forward power/kW                   | 1.5                 |
| Gas flow rates/l min <sup>-l</sup> |                     |
| Coolant                            | 16                  |
| Auxiliary                          | 0.6 - 0.7           |
| Injector                           | 1.7 - 2.3           |
| Injector bore/mm                   | 3                   |
| Nebuliser type                     | Ebdon               |
| Viewing height/mm                  | 20 - 22             |
| Spray chamber                      | Double Pass (Glass) |
| Boron line/nm                      | 208.959 I           |
| Iron line/nm                       | 259.94 II           |

...

(by volume) below 8  $\mu m,~67\%$  below 6.4  $\mu m,~55\%$  below 5  $\mu m$  and 26.5\% below 3 µm sizes. Certainly a smaller median particle size is preferred (below 2.5  $\mu m)$  together with a smaller maximum size (below 5  $\mu$ m). The hardness of PBN (MOH <9) and the possibility of contamination severely restricts the time of milling and type of grinding media used. The defined stoichiometry of PBN ((BN) $_{\rm X}$ ), with boron constituting 43.56% by weight, meant that this element could be used as an intrinsic internal standard to correct for any transportation and atomisation phenomena as has previously been shown by Ebdon and Collier (83) with kaolin slurries using silicon to standardise. The recoveries for boron from the PBN slurries were found to be 67.0% and 52.3% based upon the theoretical stoichiometry. Two boron recovery values were obtained because the two samples gave slightly different particle size distributions; the finer slurry giving the greater recovery. The iron content of the PBN samples was determined using the 1 and 2% m/v slurries and the blank used in this analysis was the 0.1% m/v PBN slurry. As the level of iron in this 1/1000 diluted slurry was below the detection limit of the instrument this served as a blank correction for both the dispersant and for any contamination that may have been incurred using this technique. The iron content of the 2% slurried sample was determined as 9  $\mu$ g g<sup>-1</sup> (<u>+</u>2) when corrected for the transportation/atomisation effects.

The reduced recoveries for boron from the PBN samples are not unexpected considering the temperature required for atomisation of the ceramic (3300 K) and the particle size range obtained from the grinding techniques used. If comparable atomisation with the solutions was experienced by the slurries then the maximum particle size transported would be 5 to 6  $\mu$ m based on the mass distribution of the slurry and the recoveries. The relatively low density of PBN, 2.25 g cm<sup>-3</sup>, should

however be an advantage in transport terms. It is of note that while the 0.1 m/v SHMP solution was adequate as a dispersant, some flocculation effects were seen in some slurries and a more stable system would need to be investigated if finer PBN slurries are to be prepared.

4.5.5. The Determination of Boron in Ceramic Starting Materials.

A series of base materials (borosilicate glass, vitreous enamels, aluminoborosilicates; British Ceramics Research Association, Stoke, UK) used in the preparation of ceramic goods were analysed for boron as part of a feasibility study to assess the use of the slurry atomisation technique for these types of samples.

Slurries of 0.1% m/v concentration were prepared in 0.1% m/v SHMP solution by the bottle and bead method using a 3 hour grinding period. Under similar plasma running conditions to those shown in Table 4.32, except that a carrier gas flow rate of 1.4 l min<sup>-1</sup> and viewing heights between 13 and 16 mm were used, the boron emission from both slurries and simple aqueous standards was monitored (boron atom line 249.678nm).

4.5.6. Results and Discussion.

The results of the boron determinations are shown in Table 4.33. Recovery values are seen to be between 70 and 114%. While as stated a carrier gas flow rate of 1.4 1 min<sup>-1</sup> was employed for the first eight samples, when this was raised to 2.3 1 min<sup>-1</sup> the recovery for the sample 7VE was increased from 81% to 94.5%. Slurry particle size distributions are shown for four of the samples in Table 4.34.

The determination of boron in ceramic starting materials by slurry atomisation using the Plasmakon S-35 ICP.

|                       | % Bo                       | ron                |            |
|-----------------------|----------------------------|--------------------|------------|
| Sample <sup>(1)</sup> | Known value <sup>(3)</sup> | Slurry value       | % Recovery |
|                       | ·                          |                    |            |
| 1 VE -                | 4.66                       | 3.62 <u>+</u> 0.09 | 77.7       |
| 2 LFC                 | 4.19                       | 3.21 <u>+</u> 0.09 | 76.5       |
| 3 TG                  | 2.54                       | 1.88 <u>+</u> 0.04 | 74.0       |
| 4 GP                  | 7.89                       | 6.47 <u>+</u> 0.10 | 82.0       |
| 5 VE                  | 5.68                       | 5.07 <u>+</u> 0.11 | 89.2       |
| 6 F                   | 2.90                       | 3.05 <u>+</u> 0.08 | 105        |
| 7 VE (i)              | 7.83                       | 6.37 <u>+</u> 0.10 | 81.3       |
| 8 AS                  | 1.52                       | 1.75 <u>+</u> 0.04 | 114        |
| 7 VE(ii)(2            | ) 7.83                     | 7.40 <u>+</u> 0.16 | 94.5       |

(1) VE = Vitreous enamel, LFC = Lead free ceramic, TG = T-Glass, GP = Glass powder, F = frit, AS = Aluminoborosilicate.

(2) High gas flow rate used, 2.3 l min<sup>-1</sup> carrier and 15 mm viewing height.

÷

(3) Private communication from G. Oliver, BCRA, Stoke, UK.

••

# Particle size distributions of some ceramic starting materials ground for 3 hours by the bottle and bead method.

| Particle size | icle size <u>% Volume (in band)</u> |                 |        |                   |  |
|---------------|-------------------------------------|-----------------|--------|-------------------|--|
| /μm           |                                     |                 |        |                   |  |
|               | <u>7VE</u> (1)                      | <u>2LFC</u> (1) | 8AS(1) | <u>4GP</u> (1)    |  |
| up to 2.5     | 42.1                                | 48.6            | 58.3   | 50.0              |  |
| 2.52 - 3.17   | 23.7                                | 26.5            | 21.4   | 27.9              |  |
| 3.17 - 4.0    | 12.3                                | 13.2            | 8.2    | 12.4              |  |
| 4.0 - 5.04    | 5.4                                 | 5.9             | 3.2    | 4.9               |  |
| 5.04 - 6.35   | 3.0                                 | 2.1             | 1.2    | 1.6               |  |
| 6.35 - 8.0    | 2.0                                 | 0.8             | 0.5    | 0.5               |  |
| 8.0 - 10.08   | 2.5                                 | 0.6             | 0.4    | 0.6               |  |
| 10.08 - 12.7  | 2.9                                 | 0.8             | 0.4    | 0.4               |  |
| 12.7 - 16.0   | 3.0                                 | 1.1             | 0.9    | 0.2               |  |
| 16.0 - 20.16  | 1.6                                 | 0.4             | 2.2    | 1.0               |  |
| 20.16 - 25.4  | 0.6                                 |                 | 1.2    | 0.7               |  |
| 25.4 - 32.0   | 0.9                                 |                 | 2.3    |                   |  |
| % below 5 µm  | 83.5                                | 94.2            | 91.1   | 95.2              |  |
| % below 8 µm  | 88.5                                | 97.1            | 92.8   | 97.3 <sup>.</sup> |  |

(1) As defined in Table 4.33.

-

The effect of carrier gas flow rate and forward power upon the peak emission signal for boron, from the slurry 2 LFC (42.6  $\mu$ g ml<sup>-1</sup> boron) and a standard 40  $\mu$ g ml<sup>-1</sup> boron solution.

|  | <u>40 μg ml<sup>-1</sup> E</u>              | Boron Solution  | <u>2LFC Slur</u>                          | ry (42.6 µg ml <sup>-1</sup>                                       | Boron)   |                      |
|--|---|---|---|--|--|----------------------|
| Carrier gas<br>flow rate<br>/l min <sup>-l</sup> | Viewing heigh<br>of emission p<br>/mm       | nt <sup>(1)</sup> Peak <sup>(2</sup><br>Deak emissic<br>/counts | 2) Viewing hei<br>on of emission<br>3 /mm | ght <sup>(1)</sup> Peak <sup>(2)</sup><br>peak emission<br>/counts | Recovery at <sup>(</sup><br>peak emission<br>/ % | 2)<br>n <sub>:</sub> |
| 1 4  | <b>10</b> $1$ $10$ $0$                      | 1000  | 1250 W                                    |  |  |                      |
| 1.4  | 10.2 - 0.8                                  | 1535  |   | -  | -  |                      |
| 1./  | $10.2 \pm 0.2$                              | 1965  | $10.4 \pm 0.5$                            | 1678   | 80.2   |                      |
| 1.9  | $10.4 \pm 0.4$                              | 1678  | $11.3 \pm 0.7$                            | 1477   | 82.6   |                      |
| 2.1  | $12.3 \pm 0.4$                              | 1224  | $11.7 \pm 0.4$                            | 1128   | 86.5   |                      |
| 2.3  | 12.8 <del>+</del> 2.1                       | 793   | 11.9 ± 1.5                                | 793  | 93.9   |                      |
|  |   |   | 1500 W                                    |  |  |                      |
| 1.4  | $10.8 \pm 0.2$                              | 2410  | $10.6 \pm 0.5$                            | 1989   | 77.5   |                      |
| 1.9  | $11.7 \pm 0.2$                              | 2970  | $11.3 \pm 0.8$                            | 2539   | 80.2   |                      |
| 2.3  | $12.3 \pm 0.8$                              | 2147  | $12.3 \pm 0.3$                            | 2264   | 99.0   |                      |
| 2.6  | $12.3 \pm 0.85$                             | 1343  | $14.2 \pm 1.1$                            | 1358   | 94.9   |                      |
|  |   |   | 1800 W                                    | 2000   |  |                      |
| 1.7  | •   |   | $11.1 \pm 0.21$                           | 2707   |  |                      |
| 1.9  |   |   | $11.9 \pm 0.4$                            | 2826   |  | •                    |
| 2.1  |   |   | $13.4 \pm 0.4$                            | 2625   |  |                      |
| 2.3  | $15.5 \pm 0.6$                              | 2778  | $14.5 \pm 0.8$                            | 2515   | 85 0   |                      |
| 2.6  | $15.3 \pm 0.8$                              | 2420  | $14.3 \pm 0.6$                            | 2142   | 02.0   |                      |
| 2.9  | 14.9±13                                     | 1525  |   | 1650   | 05.1   |                      |
| 3 0  |   | 1201  |   | 1007   | 77.4   |                      |
| (1) The $+$ f                                    | $1 \mathbf{J} \cdot \mathbf{J} = 1 \cdot 0$ | 1201  | 13.8 - 2.3                                | 11/6   | 86.2   |                      |
| $(\mathbf{I})$ me $-\mathbf{T}$                  | igure gives an i                            | naication of  | the spread of the                         | emission profile   | at its peak.                                     | All figures          |

reported as height above the load coil.

.

(2) Background corrected.

.

The effect of carrier gas flow rate and forward power upon the viewing height emission profile coincidence points from a boron<sup>(1)</sup> containing slurry and solution.

| Carrier gas                   | 1250 W    |             | 1500 W    |                  | 1800 W    |           |            |
|-------------------------------|-----------|-------------|-----------|------------------|-----------|-----------|------------|
| flow rate 1 min <sup>-1</sup> | 2.1       | 2.3         | 2.3       | 2.6              | 2.3       | 2.9       | 3.0        |
| Profile height                | 0 up to   | complete    | 0 up to   | 13 to 15 mm      | 0 up to   | 0 up to   | From 21 mm |
| Coincidence                   | 9.5 mm    | coincidence | 14.5 mm   | near coincidence | 11 mm     | 20 mm     | upwards    |
|                               | not above | over entire | not above | over entire      | not above | not above | not below  |
|                               |           | range       |           | range            |           |           |            |

l = see text and Table 4.35 for solution and slurry details.

Using the 0.1% m/v slurry 2LFC (boron concentration 42.6  $\mu$ g ml<sup>-1</sup>) and a 40  $\mu$ g ml<sup>-1</sup> standard boron solution, viewing height emission profiles were recorded at carrier gas flow rates 1.4 to 3.0 1  $min^{-1}$  and forward powers 1250 W to 1800 W. From the profiles the effects of the atomisation/transportation mechanisms on both slurries and solutions can be followed, and regions of coincidence may be ascertained and interpreted accordingly. Table 4.35 shows the effects of carrier gas flow rate and power upon the peak emission signal for boron (background corrected), as both counts per second and height above the load coil, from the slurry 2LFC and the standard solution. It can be seen that in most cases the trends are the same for solution and slurry. However the magnitude of the change differs between them and is reflected in the changing percentage recovery. Therefore as the carrier gas flow rate is increased ()2.3 l min<sup>-1</sup>) the mass transport and atomisation efficiencies for both are altered but to different degrees. Both show a peak response with flow rate but the rate of change of emission signal from the solution appears to be greater than that from the slurry. Hence coincidence points occur between the profiles at particular flow rates which are dependent upon the forward power (see Table 4.36). At 1250 W and 2.3 1 min<sup>-1</sup> complete coincidence occurs between the slurry and solution profiles over the entire viewing height range. At 1500 W this coincidence, or near coincidence, occurs at 2.6  $1 \text{ min}^{-1}$ .

4.6. TRANSPORT AND ATOMISATION EFFICIENCIES FROM EMISSION DATA.4.6.1. Experimental.

A series of experiments were undertaken to determine relative transport and atomisation efficiencies directly from emission data. Known

amounts of magnesium (100  $\mu$ g) were adsorbed at pH 3.5 to 4.0 onto surface-bonded, silica-based cation exchange materials (0.2 g) of known, narrow size distributions (partisil, 10 SCX and 5 SCX, 10 and 5  $\mu$ m size respectively, Whatman labsales Ltd, Maidstone, Kent, UK) and were made up to 100 ml in a volumetric flask. The silica slurries were aspirated into the Plasmakon S-35 ICP held at 1500 W forward power, through an Ebdon nebuliser, glass double pass spray chamber and 3 mm injector. The emission signals (Mg II: 279.553 nm; Si I: 251.612 nm) were compared with solutions containing an equivalent amount of the analyte of interest.

4.6.2. Results and Discussion.

The particle size of the silica exchange slurries was determined both microscopically and using a Coulter Counter TA II. The latter showed the 10 SCX material to have a distribution ranging from 4 µm up to 12 µm size with a peak at 6 to 8 µm and the 5 SCX material from 2 µm up to 8  $\mu$ m size with a peak at 4  $\mu$ m size. Optically the slurries showed the majority of particles to be of the size stated <u>i.e.</u> 5 and 10  $\mu$ m, along a major axis. The particles were not spherical and aspect ratios have to be taken into account. Analysis of the supernatent liquids (after centrifugation of the slurries) for magnesium and silicon showed that 98.4  $\pm$  0.2% of the magnesium had been adsorbed and that between 0.8 and 2.5%, as silicon, of the exchange material was present in the solution (sol, solution, colloid). These factors were taken into account in the subsequent calculations. Table 4.37 shows the recovery of the magnesium (slurry over solution) at carrier gas flow rates 1.4 to 2.3 l min<sup>-1</sup> together with the peak emission height used. As the magnesium is bonded to the anionic end of an organic chain, which is surface bonded to the silica base material, atomisation of the analyte

might be expected before the particle matrix. Thus it may model, more accurately, atomisation from solution. The magnesium recovery may therefore be an indicative measure of the transport efficiency of the slurry compared with solution. If these experiments do indeed model transport effects only 3% transport efficiency was obtained for the 10  $\mu m$  size particles and 14% for the 5  $\mu m$  . This is consistent with the previously determined cut-off of 5 to 6  $\mu$ m for solid particles under the conditions used. It is also of note that the recovery for magnesium increased with an increase in the carrier gas flow rate and may be attributed to an increase in transport efficiency for the silica particles. The recovery for the silicon was less than that for the magnesium. When corrected for the magnesium recovery (assumed transport efficiency) this may give a measure of the atomisation efficiency of the silica particles compared with solution. These results are shown in Table 4.38; the conditions used were 1500  ${\tt W}$ forward power, 1.7 l min<sup>-1</sup> carrier gas flow rate and 20 mm viewing height. It is seen that neither the 10 nor the 5 µm silica particles model solution atomisation. This would indicate that if slurry particles of this size were able to reach the plasma and if they were of a refractory nature (SiO $_2$  boiling point 2500 K) then full recoveries are unlikely to be obtained under the plasma conditions used. Work by Saba et al. (68) has shown similar transportation and atomisation effects for iron powder in oil when aspirated into the ICP. While absolute atomisation and transport efficiencies for these slurries would best be determined by comparison with monodisperse aerosols of the same particle size, these results serve to outline the practical problems of slurry transport and atomisation when calibrating with solutions of broad aerosol size distribution.

The recovery for magnesium adsorbed onto silica-based cation exchange slurries of 5 and 10  $\mu$ m sizes, at various carrier gas flow rates compared with solution of equal magnesium concentration.

.

| Carrier gas flow rate | Emission height | Reco  | overy |
|-----------------------|-----------------|-------|-------|
| /l min <sup>-l</sup>  | /mm             |       | /%    |
|                       |                 | 10SCX | 5SCX  |
| 1.4                   | 1.7             | 1.3   | 11.4  |
| 1.7                   | 1.7             | 2.8   | 13.5  |
| 2.0                   | 2.0             | 2.9   | 14.0  |
| 2.3                   | 1.9             | 3.2   | 14.3  |

#### **TABLE 4.38**

Ratio of the magnesium signal for the SCX particles to that of an aqueous solution of the same magnesium concentration (Recovery values) and also for silicon (Recovery) and silicon corrected for magnesium recovery.

| Sample                | Recovery Mg(%)        | Recovery Si(%)       | Atomisation Si(%)      |
|-----------------------|-----------------------|----------------------|------------------------|
| l μg ml <sup>-l</sup> |                       |                      |                        |
| standard              |                       |                      |                        |
| solution              | 100                   | 100                  | 100                    |
| 10 μm SCX             | 2.8                   | $0.6 - 0.7^{(1)}$    | 20 - 25 <sup>(2)</sup> |
| 5 μm SCX              | 13.5                  | 8 - 9 <sup>(1)</sup> | 60 - 70 <sup>(2)</sup> |
| (1) Range of r        | ecovery found for s   | ilicon in experiment | <b>c</b>               |
| (2) Range of a        | itomisation found for | r silicon in experim | nent                   |

#### 4.7. CONCLUSIONS.

While good elemental recoveries can be obtained from fine, light and readily vaporised solid materials by the slurry technique some hard, dense refractory samples can be problematical. The particle size of the material is the most critical parameter as this will influence both the transport and atomisation efficiencies of the slurry. When the solids distribution of a ground slurry is essentially below 5 µm size it is possible to create plasma running conditions under which full analyte recoveries can be obtained particularly if an atom emission line is used. Decreasing the carrier gas flow rate to increase particle residence time in the plasma is seen to be of benefit. Matrix effects, however, must be taken into account if high carrier gas flow rates are employed with low viewing heights above the load coil; as a result of the initial radiation zone invading the viewing region.

Ultrafine slurries (below 2  $\mu$ m solid size) of monodensitic materials show comparable transport and atomisation efficiencies to those of solutions and there is evidence to suggest that these phenomena mechanistically model those of solutions. When the particle size is increased, however, the magnitude of the atomisation and transportation effects for solutions and slurries are different and recoveries are dependent upon the carrier gas flow rate and viewing height. Refractory particles above 5  $\mu$ m size are limited in their transport efficiency through the double pass spray chamber (14% at 5  $\mu$ m and 3% at 10  $\mu$ m) and there are experimental indications that the relative atomisation efficiency of slurries, to that of simple aqueous solutions, is also reduced. Correction for incomplete recoveries may be realised for monodensitic solids of large particle size (above 8  $\mu$ m)

if an intrinsic internal standard is present in the material which allows a correction factor to be employed.

..

Polydensitic materials, such as ores, are more complex and can show segregation effects due to the individual mineral distributions (dependent upon the resistance to grinding) and densities. Thermodynamic effects may also contribute to reduced recoveries for some elements under certain plasma running conditions.

#### CHAPTER 5

# ROTATIONAL TEMPERATURE MEASUREMENTS IN THE INDUCTIVELY COUPLED PLASMA

### 5.1 INTRODUCTION

When an analyte, in aerosol form, enters the central channel of the inductively coupled plasma (ICP) a number of processes occur. The sample desolvates, the matrix decomposes and the resulting analyte and solvent vapour undergoes excitation to produce molecular, atomic and ionic species in various energy states. Some of this energy is released in the form of electromagnetic radiation of a wavelength that is characteristic of the emitting species and it is this property of the plasma that is utilised for analytical purposes.

Although the ICP has been studied for over 25 years the fundamental mechanisms which govern its production and properties are not fully understood. This also applies to the energy transfer process between the body of the plasma and the analyte channel. Many diagnostic approaches have been taken to clarify the situation but with varying degrees of success (131, 132). The measurement of both 'temperature', be it rotation, excitation, ionisation or electron temperature, and electron density has proved of benefit when investigating the effect of a plasma on an analyte or matrix (133, 134, 135, Chapter 11 of 62).

A study by Ramsey and Thompson (119) of the effect of matrix elements upon analyte emission in the ICP has resulted in a predictive model which centres on the hypothesis that the matrix cools the plasma. While

these effects can be accounted for in an analysis by matrix matching of the solutions and samples the implications are further reaching when simple solution standards are used for calibration in the slurry atomisation technique. However of equal if not greater importance, when using this technique, is the 'atomisation temperature' experienced by an analyte. For high melting and boiling point solids in slurry form the 'atomisation temperature' must be sufficient to bring about complete decomposition of the matrix (or at least to the same degree as the solution standards). Also the larger solid particle size of the slurry compared with that from the desolvated solution (Chapter 4, Section 4.4.2) may demand more energy for complete or comparable atomisation of the matrix and hence perturb the energy transfer processes within the central channel.

This chapter deals with the measurement of rotational temperature and temperature mapping within the ICP together with the recoveries for certain high melting and boiling point solids in order to elucidate the importance of the arguments stated when using the slurry technique.

# 5.2 TEMPERATURE AND THE INDUCTIVELY COUPLED PLASMA

From Planks function (Chapter 10 of 62) the temperature of a black body radiator, within a closed system, is termed  $T_{rad}$ . Under the conditions of 'thermal equilibrium' (TE) the energy terms used to describe the state of a system <u>i.e.</u> E translational, E rotational, E vibrational, E electronic, can be characterised by the one temperature  $T_{rad}$ . A laboratory IC plasma discharge however is optically thin (radiation trapping is many orders of magnitude less than that of a black body), spatially inhomogenous and hence shows wide temperature and concentration gradiants as the plasma gas travels away from the power source

(dynamic system). As a result a marked deviation from Planks law is encountered with analytical plasmas. However if the exchange of energy from such species as the fast moving electrons is sufficiently rapid and their population density  $(n_e)$  is large enough  $(>10^{17}m^{-3})$ , plasmas in which equilibrium is maintained for all distributions (with the exception of the Plank function) at any point are said to be in local thermal equilibrium (LTE). An indication of which is given by measurement of the temperatures  $T_k$  (gas kinetic),  $T_{exc}$  (electronic excitation of neutral atoms),  $T_{ion}$  (the degree of ionisation of atomic species) and  $T_e$  (free electron) using a statistical thermodynamic distribution function.

The analytical plasma is not considered to be in LTE by many workers studying plasma mechanisms (Chapter 11 of 62 and references therein) but the extent to which a plasma deviates from LTE is very much in debate (136, 137).

It is considered that the plasma is 'thermal' at very low viewing heights and 'non thermal' higher up where the classical LTE concept of 'norm temperature' loses its significance (138). If this is so then the plasma environment through which the analyte first passes is 'thermal' and the 'atomisation temperature' experienced by the analyte will be governed by a thermal/kinetic collisional process.

# 5.2.1 The Gas Kinetic/Rotational Temperature

The rotational temperature, that deduced from the quantised rotational spectra of molecular species in the plasma, is generally accepted to be numerically similar to the gas kinetic temperature. This is due to the low energies involved in the rotational process and the rapid exchange
between the rotational and kinetic energy of the molecular species (62, 134). This also applies when the excitation is not thermal and can be understood theoretically if it is considered that excitation by electron impact changes only the electron configuration of a molecule whereas the angular momentum of the rotation is practically unaffected (139).

A transition between rotational levels gives rise to a rotational line. If the level belongs to one (<u>i.e.</u> the same) electronic state the line is seen in the infra-red, if the transition between rotational levels also involves a transition between electronic states the line is seen in the visible or ultra violet range of the spectrum (139). It is this transition which is of major importance when estimating gas temperatures.

If the absolute intensity  $I_{qp}$  of a (spontaneous) emission line from state q to state p is related to the transition probability  $A_{qp}$  (s<sup>-1</sup>) by the equation:

$$I_{qp} = \frac{d}{4 \pi} A_{qp} h \vartheta_{qp} N_{q}$$
(5.1)

where d = depth of source (cm), h is Planks constant  $(Js^{-1})$ ,  $V_{qp}$  is the frequency of the transition  $(s^{-1})$  and  $N_q$  the number of excited level species, and the Boltzmann distribution law is used to calculate  $N_q$  at temperature T from the total number of atoms as shown in equation 5.2

$$N_{q} = \frac{N g_{q}}{Z} \exp(-E_{q}/kT)$$
(5.2)

where  $g_q$  is the statistical weight of the q state,  $E_q$  is the energy state for level q (from a ground state = 0), k is the Boltzmann constant (JK<sup>-1</sup>) and Z is the partition function given by equation 5.3

$$Z = \sum_{m=0}^{m=j} g_m \exp(-E_m/kT)$$
(5.3)

for energy levels 1,2,3...J

then substituting (5.2) into (5.1)

$$I_{qp} = \frac{d}{4 \pi} \frac{A_{qp} h \tilde{v}_{qp}}{Z} N g_q \exp(-E_q/kT)$$
(5.4)

and taking logarithms, rearranging and substituting  $I_{qp}$  and  $A_{qp}$  with relative intensity  $I'_{qp}$  and relative transition probability  $A'_{qp}$  we obtain

$$\ln \left[ \frac{I'_{qp} \mathbf{A}_{qp}}{g_{q} \mathbf{A}'_{qp}} \right] = \ln \left[ \frac{N}{Z} \right] - \frac{E_{q}}{kT} + \text{constant}$$
(5.5)

If equation 5.5 is applied to a series of spectral lines emitted by a particular type (single group) of atom, ion or molecule, then a plot of ln ( $I'A_{qp}/A'$ ) against the corresponding excitation energy  $E_q$  will result in a straight line of slope proportional to 1/T (provided self absorption is negligible).

### 5.3 EXPERIMENTAL AND RESULTS

5.3.1 The Measurement of the Rotational Temperature of the OH Radical

The presence of water, carried as the aerosol, in the central channel of the plasma provides a naturally occurring molecular species which can be exploited for rotational temperature measurement, namely the OH radical. The comprehensive study of this molecule by Dieke and Crosswhite (140) provides line assignments and transition probabilities for the major transition  $A^2 \sum_{i=1}^{+} x^2 \Pi x^i$  which has five main branches (0,P,Q,R and S). The most intense (0-0) vibrational band of OH was chosen (band head 306.4 nm) of which the  $Q_1$  and  $R_2$  branches were recorded. The assignments (K), wavelengths ( $\mathbf{A}$ ,nm), energies (E,cm<sup>-1</sup>) and transition probabilities (A,s<sup>-1</sup>) for these branches are shown in Table 5.1

The OH band spectra were recorded between 306 and 310 nm (an example with assignments is shown in Figure 5.1) using the ICP spectrometer (Plasmakon S-35, Kontron, Spektralanalytik, Eching, W.Germany) described in Chapter 4. The conditions used are given in Table 5.2.

Spectra were recorded at various carrier gas flow rates (1.4 to 2.6 l min<sup>-1</sup>) at a constant viewing height above the load coil (1.9cm) and also at various viewing heights (1.0 to 3.7 cm) at a constant flow rate of 1.4 l min<sup>-1</sup>. Pure water aerosols were produced for measurement and the water fed to the Ebdon nebuliser at a flow rate of 0.9 ml min<sup>-1</sup>.

The relative intensities of the assigned  $Q_1$  (and  $R_2$ ) lines were measured and rotational temperatures were determined from the slope of the graph Log(I'**A**/ A') against E which is given by -0.625/T. Typical plots are shown in Figures 5.2 and 5.3 (2.3 l min<sup>-1</sup>, l.9cm height;

1.4  $1 \text{ min}^{-1}$ , 1.9 cm height respectively). The rotational temperatures determined for gas flow rates 1.4 to 2.6  $1 \text{ min}^{-1}$  are shown in Figure 5.4 and Table 5.3 and those determined for viewing heights 1.0 to 3.7 cm are shown in Figure 5.5 and Table 5.4.

Rotational spectra were also recorded when various solutions and slurries were admitted to the plasma in order to study the effect of various analyte forms and concentrations on the rotational temperature. These experiments are outlined in Table 5.5 together with the rotational temperature determined from each experiment.

### 5.4 DISCUSSION

The rotational temperature values show a dependence upon the plasma conditions (viewing height, carrier gas flow rate, water-loading) and cover the range 2200 to 3600 K. Direct comparisons are therefore difficult to make, however, these values are of the same order as those found for  $T_{rot}$  for solutions and water vapour by other workers. Fleitz and Seliskar (141) found a range of values between 3700 and 4500 K for  $T_{rot}$  using the OH radical from water vapour while Hasegawa and Winefordner (142) found a value of 2000 K from the OH radical, 3200 to 4000 K from the N<sub>2</sub> rotational spectra, 3300 to 4500 K from the N<sub>2</sub><sup>+</sup> rotational spectra. Seliskar <u>et al.</u> (143) however found lower rotational temperatures than Hasegawa from the N<sub>2</sub> and N<sub>2</sub><sup>+</sup> spectra, being in the region 1600-1700 K and 1650-1850 K respectively.

Fleitz (141) shows that the  $Q_1$  branch plot from the (0-0)OH spectra is not a simple Boltzmann distribution and presents evidence to show it to be the sum of two separate Boltzmann distributions. This deviation is

known and apparent (see Figure 5.2, and 5.3, the first two points  $Q_1^2$ , and  $Q_1^4$ ) and all branch plots were drawn with no weight from the first two points  $Q_1^2$  , and  $Q_1^4$  , which in all cases for  $Q_1^2$  and most cases for  ${\mathbb Q}_1^4$  , show curvature away from the main line. Extrapolation of this main line to where  $Q_1^2$ , would be if it followed a simple distribution, on 10 of the plots, showed the deviation to be the result of a constant factor. As only a change in  $A'(Q_1^2)$ , the relative transition probability, can account for this, a revised value was calculated, being  $22.1\pm 1 \times 10^8 \text{ s}^{-1}$ . Originally the value was 17.0 x  $10^8 \text{ s}^{-1}$ . Dieke and Crosswhite (140) table the rotational transition probabilities for the  $Q_1$  series using two different coupling constants (designated (a)) <u>i.e.</u> the degree of coupling between the electron spin and rotational axis. While generally the coupling constant of a = -7.55 is taken by most workers for the 12 branches of the  ${}^{2}\Sigma \rightarrow {}^{2}\Pi$  transition, a scrutiny of the decoupled system (a = 0, (140)), shows the  $Q_{1}^{2}$  transition probability to be 22.4 x  $10^8$  s<sup>-1</sup>. It is therefore suggested that the deviation from the Boltzmann distribution, for the low K transitions of the  $Q_1^k$  series, is due to a change in the degree of coupling within the rotronic system i.e. 0 to -7.55. The consistency of the deviation in the plot would also suggest that the line chosen to represent the slope of the temperature was acceptable.

Figures 5.4 and 5.5 show how the rotational temperature varies with the conditions of carrier gas flow rate and viewing height in the plasma. The indication is that the higher gas flow rates, 2 to 2.3 1 min<sup>-1</sup> and viewing heights of about 3 cm would favour the atomisation process. The rise in rotational temperature with flow rate may be attributed to a thermalising effect due to an increase in water loading (high up in the non-thermal region) however the effect may also be a result of the increased efficiency of the energy transfer process from the plasma

body to the central channel (thermal conductivity). The role of water in the central channel of the ICP has been investigated by a number of workers. Caughlin and Blades (144), Long et al. (145) and Alder et al. (146) have shown that the presence of water increases the electron density,  $T_{exc}$  and  $T_{ion}$ . Tang and Trassy (135) also observed an increase in T<sub>exc</sub> when water vapour was present (compared to a dry aerosol) and attributed the difference to the presence of atomic hydrogen. At 3000 K the thermal conductivity of hydrogen is 88 times greater than that of argon (135). Certainly a small quantity of hydrogen does have a significant effect on the electron density (144, 147), excitation temperature (135) and ionisation temperature (147). The effect on the rotational temperature, seen in experiments 12 to 15 (Table 5.5), where humidified argon was admitted to the central channel, compared with water, may be explained in much the same way. While little or no difference is seen at 10 mm above the load coil (2180 and 2210 K with and without water) at 15 mm the temperatures diverge slightly (2950 and 2550 K with and without water).

It is interesting to note that some species (FeI and ZrII) show peak emissions(371.993 and 343.823 nm) in the region 3 to 4 cm above the load coil which coincide with the peak of the  $T_{rot}$  versus viewing height graph (Figure 5.5, Table 5.4). Improved recoveries have been found at these heights for certain slurries where the results have indicated that an atomisation rather than transportation effect was responsible for the reduced recoveries (<u>e.g.</u> Determination of iron in Dolomite; Chapter 4, section 4.3.3.) or that both effects were present (<u>e.g.</u> determination of zirconium in zirconia; Chapter 4, section 4.5.1.)

The value of 3500 K for  $T_{rot}$  found from the separate  $R_2$  branch spectra (Experiment 1, Table 5.5, Figures 5.1 and 5.6) for a water sample

compared well with the values of 3400 to 3600 K found from the  $Q_1$  branch spectra under the same conditions. When a sample, other than water, is introduced, be it a simple surfactant solution, simple analyte solution or a slurry, a slight reduction in  $T_{rot}$  is apparent <u>i.e.</u> water 3400 to 3600 K; samples 2850 to 3150 K). The variation between samples, other than water appears to be even less under the same conditions. This may in part be due to a difference in the efficiency with which water is transported to the plasma.

No difference is seen in the rotational temperatures from adding 0.1 and 1.0% m/v aluminium in solution to the plasma (experiments 4 and 5, 2980, 2970) at a gas flow rate of 1.4 l min<sup>-1</sup>. At 1.7 l min<sup>-1</sup> however a slight rise in  $T_{rot}$  is noticed (experiments 16 and 17, 2970, and 3250).

When coarse and fine alumina slurries (0.2% m/v  $\equiv$  concentration of aluminium in solution) were admitted to the plasma little difference in  $T_{rot}$  was observed and these values compare well with those from the aluminium solutions (Experiments 7,8,4 and 5; 3150, 2900, 2980, 2970 K respectively). It is of note that the presence of aluminium interferes with some of the line spectra in the Q<sub>1</sub> branch hence the intensity of the Q<sup>8</sup><sub>1</sub> line cannot be used.

The presence of boron as a 500  $\mu$ g ml<sup>-1</sup> solution, as a 1000  $\mu$ g ml<sup>-1</sup> slurry matrix of polyboron nitride or as a 10,000  $\mu$ g ml<sup>-1</sup> slurry matrix of polyboron nitride also shows no significant differences in rotational temperatures and also compares with the value from the 0.1% m/v sodium hexametaphosphate (SHMP) solution which was used as a dispersant for the slurries (experiments 9,10,11,3; 3070,3130,3040,3120 K respectively). A graph of log(I'**Å** A') versus E for the boron slurries is shown in Figure 5.7 and illustrates how close the Q<sub>1</sub> values are.

۰.

Assignment, Wavelengths, Energies and Transition probabilities for the  $Q_1$  and  $R_2$  Branches of the OH (0-0) Band

| К  | . <b>λ</b> (nm) | E(cm <sup>-1</sup> )  | A(10 <sup>8</sup> s <sup>-1</sup> ) |
|----|-----------------|-----------------------|-------------------------------------|
|    |                 | R <sub>2</sub> BRANCH |                                     |
| 1  | 308.405         | 32,542                | 2.7                                 |
| 2  | 308.023         | 32,643                | 5.7                                 |
| 3  | 307.703         | 32,778                | 8.9                                 |
| 4  | 307.437         | 32,947                | 12.8                                |
| 7  | 306.918         | 33,650                | 24.8                                |
| 13 | 306.967         | 35,912                | 49.1                                |
| 14 | 307.114         | 36,393                | 53.2                                |
| 15 | 307.303         | · 36,903              | 57.2                                |
|    |                 | Q1 BRANCH             |                                     |
| 1  | 307.844         | 32,475                | 0.0                                 |
| 2  | 307.995         | 32,543                | 17.0                                |
| 4  | 308.328         | 32,779                | 33.7                                |
| 5  | 308.520         | 32,948                | 42.2                                |
| 6  | 308.734         | 33,150                | 50.6                                |
| 8  | 309.239         | 33,652                | 67.5                                |
| 9  | 309.534         | 33,952                | 75.8                                |

FIGURE 5.1

.

Spectral scan of the (0-0) band emission from OH showing Q and R branches.



264

.

FIGURE 5.2

Plot of  $Q_1$  branch line emission intensities against energy level from the OH (0-0) band measured at 2.3 l min<sup>-1</sup> injector gas flow rate and 19mm viewing height from a 1500W plasma.



.



Plot of  $Q_1$  branch line emission intensities against energy level from the  $\overline{OH}$  (0-0) band measured at 1.4 l min<sup>-1</sup> injector gas flow rate and 19mm viewing height from a 1500W plasma.



Plasma running conditions used for the recording of OH spectra

| Torch type                            | Greenfield Size            |
|---------------------------------------|----------------------------|
| Forward power/kW                      | 1.5                        |
| Gas flow rates/1 min <sup>-1</sup>    |                            |
| Coolant                               | 16                         |
| Auxiliary                             | 0.6                        |
| Carrier                               | 1.4 to 2.6                 |
| Liquid flow rate/ml min <sup>-1</sup> | 0.9                        |
| Injector bore/mm                      | 3                          |
| Nebuliser type                        | Ebdon (300 µm gas orifice) |
| Scan rate/nm s <sup>-1</sup>          | 0.005                      |
| Viewing height/mm                     | 10 to 37                   |
| Scan range/nm                         | 306 to 310                 |

### TABLE 5.3

OH rotational temperatures ( $T_{rot}$ ) determined at a constant viewing height of 1.9 cm with carrier gas flow rates of 1.4 to 2.6 l min<sup>-1</sup>

| Carrier gas flow rate | T <sub>rot</sub> |
|-----------------------|------------------|
| l min <sup>-1</sup>   | · K              |
| 1.4                   | 2840             |
| 1.7                   | 3190             |
| 2.3                   | 3430             |
| 2.6                   | 3410             |

FIGURE 5.4

Graph showing the change in rotational temperature, K, with injector gas flow rate for a constant viewing height of 19mm in a 1500W plasma.

1



OH rotational temperatures ( $T_{rot}$ ) determined at a constant gas flow rate of 1.4 l min<sup>-1</sup> for viewing heights of 1.0 to

3.7cm (above load coil)

| Viewing height | T <sub>rot</sub> |
|----------------|------------------|
| СП             | К                |
| 1.05           | 2180             |
| 1.52           | 2940.            |
| 2.20           | 3170             |
| 3.00           | 3370             |
| 3.70           | 3170             |

Graph showing the change in rotational temperature, K, with viewing height for a constant injector gas flow rate 1.4 l min<sup>-1</sup> in a 1500W plasma.



.

| TA | BL        | E | 5 |   | 5 |
|----|-----------|---|---|---|---|
|    | <b>WL</b> | _ | _ | ٠ | - |

| Table | of | experim | ents  | performe   | d to  | determine  | the   | effect   | of   | various |
|-------|----|---------|-------|------------|-------|------------|-------|----------|------|---------|
|       | 50 | lutions | and s | slurries d | on tl | ne rotatio | nal ( | temperat | ture | e.      |

| Experi- | Branch | Gas | flow             | Height | Sample t | type/Analyte            | Temperature           |
|---------|--------|-----|------------------|--------|----------|-------------------------|-----------------------|
| ment No | •      | r   | ate .            |        |          | concentratio            | n (T <sub>rot</sub> ) |
|         |        | 1 m | in <sup>-1</sup> | CM     |          | µg ml <sup>-1</sup>     | ĸ                     |
|         |        |     |                  |        |          |                         |                       |
| 1       | R      | 1.4 | 4                | 3      | Water    | -                       | 3500                  |
| 2       | Q      | 1.4 | 4                | 3      | Water    | -                       | 3640                  |
| 3       | Q      | 1.4 | 4                | 3      | Surfact  | ant 0.1%m/v (5          | ) 3120                |
|         |        |     |                  |        | solutio  | on SHMP                 |                       |
| 4       | Q      | 1.4 | 4                | 3      | Alumini  | um 1000 Al              | 2980                  |
|         |        |     |                  |        | solutio  | n                       |                       |
| 5       | Q      | 1.4 | +                | 3      | Alumini  | um 10,000 A1            | 2970                  |
|         |        |     |                  |        | solutio  | n                       |                       |
| 6       | Q      | 1.4 | +                | 3      | Alumini  | um 1000 Al              | 2850                  |
|         |        |     |                  |        | solutio  | n                       |                       |
| 7       | Q      | 1.4 | ÷                | 3      | Coarse   | 2000 Al <sub>2</sub> 03 | 3150                  |
|         |        |     |                  |        | alumina  | ı (1)                   |                       |
|         |        |     |                  |        | slurry   |                         |                       |
| 8       | Q      | 1.4 | ł                | 3      | Fine     | 2000 Al <sub>2</sub> 03 | 2900                  |
|         |        |     |                  |        | alumina  | · (2)                   |                       |
|         |        |     |                  |        | slurry   |                         |                       |
| 9       | Q      | 1.4 | ł                | 3      | Boron    | 500 B                   | 3070                  |
|         |        |     |                  |        | solutio  | 'n                      |                       |
| 10      | Q      | 1.4 | ł                | 3      | Coarse   | PBN 1000 PBN            | 3130                  |
|         |        |     |                  |        | slurry   | (3)                     |                       |
| 11      | Q.     | 1.4 | F                | 3      | Coarse   | PBN 10,000 PBN          | 3040                  |
|         |        |     |                  |        | slurry   | (4)                     |                       |
|         |        |     |                  |        |          |                         |                       |
| 12      | Q      | 1.4 | ł                | 1.5    | Humidif  | ied -                   | 2550                  |
|         |        |     |                  |        | argon    |                         |                       |
| 13      | Q      | 1.4 |                  | 1.5    | Water    | -                       | 2940                  |
| 14      | Q      | 1.4 |                  | 1.05   | Humidif  | ied -                   | 2210                  |
|         |        |     |                  |        | argon    |                         |                       |
| 15      | Q      | 1.4 |                  | 1.05   | Water    | - ·                     | 2180                  |
| 16      | Q      | 1.4 |                  | 3      | Alumini  | um 10,000 A1            | 2970                  |
|         |        |     |                  |        | solutio  | n ·                     |                       |
| 17      | Q      | 1.7 |                  | 3      | Alumini  | um 10,000 Al            | 3250                  |
|         |        |     |                  |        | solutio  | n                       |                       |

(1) coarse alumina slurry, 0.2% m/v in 0.1% m/v SHMP = 1000  $\mu$ g ml<sup>-1</sup> Al (2) ultra fine alumina slurry, 0.2% m/v in 0.1% m/v SHMP = 1000  $\mu$ g ml<sup>-1</sup> Al

(3) coarse polyboron nitride, 0.1% m/v in 0.1% m/v SHMP

(4) coarse polyboron nitride, 1% m/v in 0.1% m/v SHMP

(5) 0.1% m/v sodium hexametaphosphate solution, dispersing agent.

FIGURE 5.6

Plot of  $R_2$  branch line emission intensities against energy level from the OH (0-0) band measured at 1.4 1 min<sup>-1</sup> injector gas flow rate and 30mm viewing height from a 1500W plasma.



#### FIGURE 5.7

Plot of  $Q_1$  branch line emission intensities against energy level from the OH (0-0) band measured at 1.4 1 min<sup>-1</sup> injector gas flow rate and 30mm viewing height while aspirating a 500µg ml<sup>-1</sup> boron solution and slurries containing 0.1 and 1% m/V polyboron nitride.



Few workers have studied the variation of temperatures ( $T_{rot}$ ,  $T_{exc}$ ,  $T_{ion}$ ) and election density ( $n_e$ ) in a plasma while aspirating slurries. Sparkes and Ebdon (43) observed little change in  $T_{ion}$  and  $T_{exc}$  when 5% m/v slurries and less were introduced into the direct current plasma. A slight variation in electron density however was observed. At high matrix concentrations a 'thermalising effect' was seen. Rotational temperatures were not reported. Parry (100) found no significant change within a temperature series when up to 25% of light, easily atomised coal slurries were admitted to the ICP.

It is important to note that lateral information from the plasma could not be obtained from the instrument used in the temperature determinations. Hence it was not possible to perform an Abel inversion technique on the data in order to correct for the contribution from the plasma body to the emission spectra recorded.

5.5 THE TEMPERATURE RANGE AND ATOMISATION OF HIGH BOILING POINT SOLIDS

The rotational temperatures measured in the experiments covered the range 2200 up to 3600 K depending upon the plasma conditions used. Ceneral running conditions narrow this range down to 2800 K to 3200 K at 1.4 to 1.7 1 min<sup>-1</sup> gas flow rate and 1.5 to 2 cm viewing height. As  $T_{rot}$  is accepted as comparable to the gas kinetic temperature  $(T_g)$  which is itself considered to be the atomisation temperature for matrix breakdown (collisional exchange from argon atoms) then certain high melting and boiling point materials, if of large solid size <u>e.g.</u> 5 µm, may not experience a sufficiently high temperature to produce complete breakdown. As the rotational temperature appears to decrease as it approaches the load coil (2200 k at 10 mm) the highest thermal

temperature a solid particle may encounter could be as low as 3000 K. It is this and the other important factors such as particle size, particle residence time, thermal conductivity of the matrix and optimum position for excitation which need to be considered if slurries are to model solutions. A paper by Hieftje et al. (148) considers the arguments for solute particle vaporisation in flames and plasmas on a theoretical basis. That slurry solids can pass through the thermal environment without breakdown is suggested in the transportation/ atomisation results for magnesium adsorbed onto silica ion exchange materials discussed in Chapter 4 (section 4.6). Some 60 to 70% atomisation occurred for 5 µm silica particles. Indeed there is evidence that certain solution aerosol particles, those that can form refractory species in the plasma( <u>e.g.</u>  $A1^{3+} \rightarrow A1_20_3$ ), can pass through the plasma IRZ with incomplete vaporisation (128). The presence of a refractory matrix can also delay the atomisation of a non-volatile concomitant element (e.g. Eu in aluminium solution (128).

Table 5.6 shows a list of refractory materials likely to be encountered in a plasma which have melting or boiling points comparable to T<sub>rot</sub> (99).

An investigation of the recoveries for some high boiling point solids (>3200 K) in slurry form was therefore undertaken.

5.6 EXPERIMENTAL AND RESULTS

5.6.1 Slurry Atomisation of High Boiling Point Solids.

Three compounds were chosen for this study (i) chromium III oxide which melts at 2538 K and boils at 4273 K, (ii) magnesium oxide which melts at 3125 K and boils at 3873 K and (iii) aluminium oxide which melts at 2345 K and boils at 3253 K. Aluminium slurries have already been

examined in Chapter 4, section 4.4 and will therefore only be included in the discussion section (5.7.) of this Chapter.

Samples of AnalaR chromium III oxide and magnesium oxide were prepared as 0.1% m/v slurries by the bottle and bead method detailed in Chapter 2 section 2.3.1.3. Dispersions were maintained in 0.1% m/v sodium hexametaphosphate (SHMP) solution after a 3 hour grinding period was employed. The particle size of the resultant slurries was determined by optical microscopy. The chromium oxide slurry was found to be 100% less than 2.5 µm and the magnesium oxide 100% less than 1 µm.

The slurries were analysed using the Plasmakon S-35 ICP (Kontron, Spektralanalytik, Eching, W. Germany) under the conditions shown in Table 5.7. The recoveries were determined against standards containing the equivalent amounts of analyte under investigation in 1% nitric acid and matched for dispersant. The results from these determinations are shown in Table 5.8.

#### 5.7 DISCUSSION

The values of 98% recovery for the magnesium and 100% recovery for the chromium (which change only very slightly when the conditions are varied) shows that the slurries are modelling the solution standards in both transportation and atomisation. This result is identical to the 0.1% m/v ultrafine alumina slurries ( $100\% < 2.5 \mu m$ ) studied in Chapter 4 where the recovery obtained was 99%. The results do not imply that full atomisation has occurred but that the fine slurries show the same degree of atomisation as the solution standards. Coarser slurries can show transportation losses as described in the alumina study and hence the point where the degree of atomisation deviates from that of a

standard solution may be a fine one. As 5  $\mu$ m particles of silica have been shown to give 15% transport efficiency but experience 60 to 70% atomisation (boiling point of SiO<sub>2</sub> = 2503 K) the atomisation deviation point may lie within this transport boundary. Again this will be dependent upon the melting/boiling point and thermal conductivity of the matrix. Hence it is suggested that the thermochemical properties of the matrix within the plasma environment be considered in more detail (phase equilibria, eutectics) in order to clarify the atomisation process.

5.8 CONCLUSIONS

Rotational temperatures within the central channel of the ICP show a range of values, 2200 to 3600 K, which are dependent upon the carrier gas flow rate and viewing height. Under general running conditions this range decreases to between 2800 and 3200 K. Little or no difference is seen in the rotational temperatures from solutions and slurries, up to 1% m/v solids loading, introduced into the plasma. The presence of water, from the aerosol, in the central channel does appear to raise the rotational temperature compared with humidified argon. Fine slurries of pure single compounds that have melting points in excesss of  $T_{rot}$  give near to full recoveries for the major element. This shows that the transportation and atomisation efficiencies of the slurries model those of solutions.

Some refractory materials likely to be encountered for analysis in a plasma with melting or boiling/decomposition points comparable to  $T_{\rm rot}$ 

| Compound                       | Melting point   | Boiling point |
|--------------------------------|-----------------|---------------|
|                                | к               | К             |
| A1203                          | 2345            | 3253          |
| Be0                            | 2823            | 4173          |
| CaO                            | 2887            | 3123          |
| Cr <sub>2</sub> 0 <sub>3</sub> | 2538            | 4273          |
| CaF <sub>2</sub>               | 1696            | 2773          |
| MgO                            | 3125            | 3873          |
| Si0 <sub>2</sub>               | 2000            | 2503          |
| Sr0                            | 2703            | 3273          |
| WC                             | 3143            | 6273          |
| Zr0 <sub>2</sub>               | 3000            | 5000          |
| vo <sub>2</sub>                | 3151            | -             |
| SiC                            | 2973            | -             |
| BN                             | 3300 (sublimes) | -             |

Running conditions used on the Plasmakon S-35 ICP for the determination

of Cr and Mg recoveries in  $\text{Cr}_2\text{O}_3$  and MgO Slurries (0.1% m/v)

,

| Torch type                         | Greenfield |
|------------------------------------|------------|
| Forward power/kW                   | 1.5        |
| Gas flow rates/l min <sup>-l</sup> |            |
| Coolant                            | 16         |
| Auxiliary                          | 0.6        |
| Carrier                            | 1.4 - 2.0  |
| Injector bore/mm                   | 3          |
| Nebuliser type                     | Ebdon      |
| Viewing height/mm                  | 11-20      |
| Wavelengths used/nm                |            |
| Cr                                 | 276.259    |
| Mg                                 | 279.079    |

Recoveries for Cr and Mg from 0.1% m/v slurries of  $Cr_2O_3$  and MgO

| Element | Viewing height | Carrier gas flow       | Recovery |
|---------|----------------|------------------------|----------|
|         | (mm)           | (1 min <sup>-1</sup> ) | %        |
| Cr      | 11.3           | 1.4                    | 98.3     |
|         | 15.0           | 1.7                    | 102.3    |
|         | 20.2           | 2.0                    | 98.7     |
|         |                |                        |          |
| Mg      | 12.6           | 1.4                    | 96.6     |
|         | 15.5           | 1.7                    | 97.6     |

#### CHAPTER 6

### THE LAMINAR FLOW TORCH

6.1 INTRODUCTION

6.1.1 Plasma Torches

The inductively coupled plasma torch generally consists of three concentrically mounted silica tubes (Figure 4.2), the functions of which can be basically divided into two separate sections: (i) plasma formation and containment and (ii) analyte injection.

- (i) The outer (coolant) and intermediate (auxiliary) tubes channel the gas required for plasma formation. The former passes through the RF coil of the generator and extends a short distance above it while the latter terminates a short distance below the coil. The relative dimensions and positions of the tubes are necessary to maintain the velocity profile of the gas that issues from the annulus and stabilise the flame-like shape of the plasma formed above the auxiliary tube.
- (ii) The injection system comprises a small bore tube concentrically mounted within the auxiliary tube. A supply of gas from the nebuliser/spray chamber assembly passes up the injector tube and exits with a velocity necessary to 'punch' a hole through the centre of the plasma. During analysis the analyte is transported by the gas from the nebuliser to the injector which guides the aerosol to the channel formed in the plasma.

Plasma torches, whether of the large 'Greenfield' type or small 'Fassel' type, are generally based on the tangential-turbulent design, <u>i.e.</u> the gas enters tangentially to the coolant and auxiliary tubes and at such a rate as to be in turbulent flow within the coolant annulus.

Work by Belchamber and Horlick (149) and Davies and Snook (150,151) has shown that the rotation of plasma matter, which is a consequence of the tangential flow, is a major contributor of noise to the power spectra from an ICP (in the frequency range 100 - 500 Hz). Vortex stabilisation is not, however, necessary for the stabilisation of a plasma discharge (152) and a few workers (150, 152, 153, 154) have described the design and successful use of a small (Fassel size) laminar flow torch (LFT). The reduction in noise and superior detection limits are advantages attributed to the use of a laminar flow torch but it is conjectured that greatly reduced coolant gas flows can be used and larger injector bore diameters employed with the LFT. Because of the possible advantage when running the large Greenfield-type plasma torch for the analysis of slurries a preliminary investigation into the design, construction and use of large 'Greenfield size' laminar flow torches was undertaken.

#### 6.2 EXPERIMENTAL

#### 6.2.1 Laminar Flow Torches

Two large 'Greenfield' size laminar flow torches were designed and constructed for the study and these are shown in Figures 6.1 and 6.2. One was of an all brass body construction (Figure 6.1) while the other was of a composite PTFE/glass fibre (Figure 6.2). Both torches were constructed with extended coolant tubes to reduce entrainment of atmospheric gases and increase plasma stability (154).

FIGURE 6.1

Diagram of brass body Greenfield-size laminar flow torch.



FIGURE 6.2

Diagram of PTFE/Glass fibre body Greenfield-size laminar flow torch.



The conventional LFT retains the three concentric tube configuration of the tangential flow torch but the coolant and auxiliary gases enter normal to the base rather than tangentially. The coolant gas flows into and around a gallery within the base and traverses axially up the torch base through a series of small holes arranged circumferentially around the torch base. The gas entering the coolant annulus is in streamline/laminar flow which is dependent upon the flow rate and cross sectional area of the annulus.

The criterion for the maintenance of laminar flow for a gas or liquid is that the Reynolds number,  $R_e$ , is less than 2300 (155). On a more practical basis  $R_e$  values of less than 2000 are considered 'laminar' and those over 2500 are considered 'turbulent'. The Reynolds number is a dimensionless quantity and for an annulus, the  $R_e$  of a gas is given by the relationship (156).

$$R_e = V.2 (1 - K) r_0$$
 (6.1)

and for a tube (155).

$$Re = \underline{V.1} \qquad \text{where } a = \pi/p \qquad (6.2)$$

where V = gas velocity in ms<sup>-1</sup>, a = kinematic viscosity of gas (argon = 1.25 x  $10^{-5}$  m<sup>2</sup> s<sup>-1</sup>),  $\eta$  = dynamic viscosity of gas (kg m<sup>-1</sup> s<sup>-1</sup>), P = density of gas (kg m<sup>-3</sup>) K =  $r_i/r_o$ ,  $r_i$  = radius of inner tube (m),  $r_o$  = radius of outer tube (m) and 1 = diameter of tube (m). The allbrass LFT body (Figure 6.1) was designed with a gallery and axial series of holes (1 mm diameter) for both the coolant and auxiliary gases. The LFT constructed for use with the Kontron S-35 ICP (Figure 6.2) was made of a loaded PTFE (40% glass fibre, 60% PTFE). A laminar flow insert was used instead of a fixed gallery.

The same tube dimensions were used for both laminar flow torches and a configuration factor (the ratio of the auxiliary tube radius to that of the coolant tube radius which together produce the coolant annulus) of 0.94 was achieved by use of a flared 'tulip design' auxiliary. Table 6.1 lists the values of maximum allowable gas flow rates for the annuli of the LF torches based on a Reynolds number of 2000.

Table 6.2 lists the values of maximum allowable gas flow rates for the axial holes of the LF torches based on a Reynolds number of 2000.

As typical gas flow rates for running a plasma torch <u>i.e.</u> coolant 16 l min<sup>-1</sup>, auxiliary l l min<sup>-1</sup>, are well below the maxima listed in Tables 6.1 and 6.2 then laminar flow is expected.

The brass-base LFT was used in the preliminary investigation with a Radyne R50P ICP (Radyne Co. Wokingham, Berks, Uk; 5 kW maximum, 27 MHz free running R.F. generator). The ICP was optically coupled to a 1 metre Czerny-Turner scanning monochromator (Bentham M1000, Bentham Instruments, Reading, Berks, UK) which was controlled by a Bentham SMD 10S controller. Radiation was focussed on to an end window photomultiplier (EMI, 9558QB) the output from which was amplified by a Bentham 210 current amplifier and fed to a chart recorder (Linseis E40, West Germany).

••

•

. Gas flow rates for the laminar flow torch annuli based on a Reynolds number of 2000.

-

| Parameter                            | Flared I                | Part                    | Non-Flared Part                |                        |  |
|--------------------------------------|-------------------------|-------------------------|--------------------------------|------------------------|--|
|                                      | Coolant<br>annuli       | Auxiliary<br>annuli     | Coolant <sup>·</sup><br>annuli | Auxiliary<br>annuli    |  |
| R <sub>e</sub>                       | 2000                    | 2000                    | 2000                           | 2000                   |  |
| r <sub>o</sub> (m)                   | $1.3 \times 10^{-2}$    | $1.07 \times 10^{-2}$   | $1.3 \times 10^{-2}$           | 7.5 x 10 <sup>-3</sup> |  |
| r <sub>i</sub> (m) .                 | $1.225 \times 10^{-2}$  | 3.75 x 10 <sup>-3</sup> | 9 x 10 <sup>-3</sup>           | $3.75 \times 10^{-3}$  |  |
| ĸ                                    | 0.942                   | 0.349                   | 0.692                          | 0.5                    |  |
| Area of<br>annulus (m <sup>2</sup> ) | 5.95 x 10 <sup>-5</sup> | 3.19 x 10- <sup>4</sup> | 2.76 x 10 <sup>-4</sup>        | 1.3 x 10 <sup>-4</sup> |  |
| Argon                                |                         |                         |                                |                        |  |
| flow rate<br>(l min <sup>-l</sup> )  | 60                      | 342                     | 52                             | 26                     |  |

# TABLE 6.2

. .

# Gas flow rates for axial holes of laminar flow torches based on a Reynolds number of 2000

|  | Brass LFT              |                         | PTFE LFT                |
|--|------------------------|-------------------------|-------------------------|
| Parameter                              | Coolant<br>holes       | Auxiliary<br>holes      | Coolant<br>holes        |
| Number of holes                        | 94                     | 48                      | 27                      |
| Diameter of holes (m)                  | $1 \times 10^{-3}$     | $1 \times 10^{-3}$      | $2 \times 10^{-3}$      |
| Total area of holes (m <sup>2</sup> )  | 7.4 x 10 <sup>-5</sup> | 3.77 x 10 <sup>-5</sup> | 8.48 x 10 <sup>-5</sup> |
| R <sub>e</sub>                         | 2000                   | 2000                    | 2000                    |
| Argon flow rate (1 min <sup>-1</sup> ) | 111                    | 56                      | 64                      |

The experiments with the all brass body LFT centred on establishing the conditions for running a stable laminar flow plasma with a 3 mm bore injector and comparing them with those conditions employed with a conventional tangential flow torch of identical tube dimensions except that the coolant tube length was not extended. A univariate search procedure was used to estimate the boundary conditions of the LFT and a simplex program (71,124) was used to optimise the running conditions based on the criterion of signal to background ratio. Standard solutions containing 100  $\mu$ g ml<sup>-1</sup> of iron and 1  $\mu$ g ml<sup>-1</sup> of magnesium were prepared for the experiments and the Fe II 259.939 nm, and Mg II 279.553 nm emission lines were monitored. Samples were introduced to the plasma via an Ebdon nebuliser/single pass spray chamber arrangement at a liquid flow rate of 1.5 ml min<sup>-1</sup> from a peristaltic pump.

6.2.3 The PTFE/GF-base LFT

All the experiments using the PTFE/glass fibre-base LFT were performed with the Kontron S-35 ICP described in Chapter 4.

6.2.3.1 Simplex optimisation experiments

The performance of the PTFE/glass fibre-base extended laminar flow torch was evaluated using a simplex optimisation program (124) and a 0.1% m/v slurry of the ground mineral ore SAl/Cl20 stabilised in 0.1% m/v sodium hexametaphosphate solution. The criterion of signal to background ratio of the iron emission line (259.939 nm) from the slurry (present at a concentration of 189  $\mu$ g ml<sup>-1</sup> in the slurry) was used to monitor the performance. Experiments were first performed by varying

the five parameters of coolant, auxiliary and carrier gas flows, viewing height and forward power. The second series of experiments centred on varying the forward power, viewing height and carrier gas flow while keeping the coolant and auxiliary gas flows constant at 21 1 min<sup>-1</sup> and 2 1 min<sup>-1</sup> respectivey.

6.2.3.2 Rotational temperature measurements using the PTFE/GF-base LFT.

Rotational temperature measurements were made using the PTFE/GF-base laminar flow torch in order to estimate the thermal environment through which a solution or slurry would pass and then gauge if any benefit in atomisation efficiency would be gained from using the LFT compared with . the TFT employed in the experiments described in Chapters 4 and 5.

The intense (0-0) vibrational band of the OH radical was chosen (band head 306.4 nm) of which the  $Q_1$  branch was recorded. The criteria for use of this system, the theory behind the measurement technique and the practical handling of the data are covered in detail in Chapter 5. Line assignments, wavelengths, energies and transition probabilities for the  $Q_1$  branch are shown in Table 5.1 of Chapter 5. One extra line was included in the measurements, that of  $Q_1^{10}$  which occurs at 309.859 nm, involves the energy level 34,283 cm<sup>-1</sup> and has a transition probability of 84.1 x  $10^8$  s<sup>-1</sup> (140).

The OH band spectra were recorded between 307 and 310 nm using the conditions shown in Table 6.3. Spectra were recorded at various carrier gas flow rates (1.4 to 2.6  $1 \text{ min}^{-1}$ ) at a constant viewing height of 19 mm above the load coil and also at various viewing heights (5 to 50 mm) at a constant carrier flow rate of 1.4 1 min<sup>-1</sup>. Pure water aerosols were used for the measurement and the water was fed to

### TABLE 6.3

..

Conditions used for the measurement of the OH (0-0) band spectra with the PTFE/GF-base extended laminar flow torch (LFT) on the Kontron S-35 ICP.

.

| Torch                              | extended LFT 'Greenfield size' |
|------------------------------------|--------------------------------|
| Forward power/kW                   | 1.5                            |
| Gas flow rates/l min <sup>-l</sup> |                                |
| Coolant                            | 16.2                           |
| Auxiliary                          | 1.1                            |
| Carrier                            | 1.1 to 2.3                     |
| Viewing height/mm                  | 5 to 50                        |
| Injector size/mm                   | 3                              |
| Nebuliser type                     | Ebdon                          |
| Spectral scan range/nm             | 307 to 310                     |
| Scan rate/nm min <sup>-1</sup>     | 0.3                            |
an Ebdon nebuliser and double pass spray chamber sample introduction system at a flow rate of 0.9 ml min<sup>-1</sup>.

6.3 RESULTS AND DISCUSSION.

6.3.1 Brass-base Laminar Flow Torch.

A stable plasma was readily attained using the conditions listed in Table 6.4.

Less perturbation of the LF plasma was noted during the formation of an analyte channel by the injector gas compared with the tangential flow plasma. This effect is attributed to the absence of a vortex above the injector which results in a slightly flattened base to the LF plasma.

The plasma was also noted to be stable over a wide range of forward power settings and gas flows. The change in emission of the Fe II 259.939 nm line obtained from a 100  $\mu$ g ml<sup>-1</sup> iron solution was monitored for the power range 0.8 to 1.6 kW, coolant gas flows of 3.5 to 8 l min<sup>-1</sup>, auxiliary flows up to 1 l min<sup>-1</sup> and injector flows of 0.6 to 1.3 l min<sup>-1</sup>. The best signal to noise response was obtained with the conditions shown in Table 6.5. The conditions used to obtain a similar response from a 100  $\mu$ g ml<sup>-1</sup> iron solution using a TFT are included for comparison.

The change in emission of the magnesium II 279.553 nm line obtained from 1  $\mu$ g ml<sup>-1</sup> magnesium solutions was also monitored with variations of power and gas flow. The peak signal to noise ratio was obtained with very similar conitions to those listed in Table 6.5 for the LFT.

# TABLE 6.4

Operating conditions for stable laminar flow plasma formation with an injector flow using the brass laminar flow torch.

Gas flows/l min  $^{-1}$ 

| Forward power | Coolant | Auxiliary | Injector |  |  |
|---------------|---------|-----------|----------|--|--|
| 1.5 kW        | 6       | 0.4       | 0.7      |  |  |

..

# TABLE 6.5

Operating conditions for the best signal to noise ratio obtained from 100 µg ml<sup>-1</sup> iron solution (Fe II 259.939nm) using the brass-base laminar flow torch together with the conditions necessary to produce an equivalent signal to noise ratio using the turbulent flow torch.

| Parameter                     | LFT  | TFT. |
|-------------------------------|------|------|
| Forward power/kW              | 1.5  | 1.5  |
| Gas flows/l min <sup>-l</sup> |      |      |
| Coolant                       | 6    | 4    |
| Auxiliary                     | 0.5  | 9.5  |
| Injector                      | 0.76 | 0.76 |
|                               |      |      |

..

Max<sup>m</sup> Emission

| Viewing | Height/mm | 8 | 23 |
|---------|-----------|---|----|
|---------|-----------|---|----|

The laminar flow torch forms a stable plasma with gas flows that are considerably reduced compared with the TFT. This effect was investigated further with a view to determining the low power and low flow operating conditions necessary to produce a similar signal to noise response from a 100  $\mu$ g ml<sup>-1</sup> iron solution using the LFT conditions in Table 6.5. The results are shown in Table 6.6.

A simplex program (124) was used to optimise the LFT conditions. Noise and drift from the Radyne R50P ICP limited the efficiency of the experiments however the optimum response, based on the criterion of signal to background ratio was found with the operating conditions shown in Table 6.7.

Two mineral slurries were analysed for their iron content using the LFT but apart from the result that the reduced percentage recoveries were similar to previously obtained results on the same slurries no further deductions could be made. This was mainly due to the increasing instability of the Radyne R50P used at the time.

All the experiments show that a considerable saving in gas results from the use of a LFT compared with the TFT and with little or no loss in sensitivity. The ability to run a stable LF plasma in a 'Greenfield size' torch at under 4 l min<sup>-1</sup> argon coolant, 0.9 kW forward power and still employ a 3 mm bore injector is encouraging, especially when the analytical utility of the system is retained.

It is interesting that under the same forward power conditions and, in some cases, similar injector gas flow rates, the viewing height of maximum emission for an analyte is considerably lower in the LFT than in the TFT. A similar effect is seen in the 'Fassel size' laminar flow

# TABLE 6.6

Low laminar flow, low power operating conditions for comparable signal to noise ratio from 100  $\mu$ g ml<sup>-1</sup> Fe solution (Fe II 259.939 nm) using the conditions from Table 6.5.

Gas flows / l min<sup>-1</sup> Max<sup>m</sup> Emission Forward power (kW) Coolant Auxiliary Injector Viewing Height (mm)

0.9 3.5 0 0.65 4

# TABLE 6.7

# Operating conditions for the brass-base LFT optimised on signal to background ratio using a simplex program.

|                  | Gas fl  | Max <sup>m</sup> Emission |          |           |
|------------------|---------|---------------------------|----------|-----------|
| Forward power/kW | Coolant | Auxiliary                 | Injector | Viewing   |
|                  |         |                           |          | Height/mm |

.

6

1.15

..

0.5

0.9

torch compared with a TFT of similar dimensions (150) and it is noted that excitation and ionisation temperatures in the small laminar flow torch were found to be higher than those found from the small TFT over the viewing height range 2 to 17mm (150).

It has been suggested that the well defined base of the laminar flow plasma would facilitate the introduction of carrier gas from an injector of larger than 3 mm bore. Experiments with a 5 mm bore injector were unsuccessful in punching the plasma to form an analyte channel.

Instabilities with the Radyne R50P ICP system terminated the experimental work with the all brass-base laminar flow torch.

6.3.2 The PTFE/Glass fibre-base Laminar Flow Torch.
6.3.2.1 Simplex optimisation experiments.

The conditions obtained for maximum signal to background ratio of the Fe II 259.939 nm emission line from the slurry SA1/C120 using a simplex optimisation program (where five parameters were varied) are shown in Table 6.8. The high values of forward power (1.9 to 2.4 kW) together with the low coolant gas flow rates requested by the simplex program (down to 13.6 l min<sup>-1</sup>) had a detrimental effect upon the extended LFT coolant tube while the SHMP stabilised slurry was being monitored. A progressive devitrification of the tube and hence degredation of the viewing zone, due to the accompanying progressive opacity, was noted. In order to facilitate realisation of the simplex optimisation a three parameter simplex was used where the coolant gas flow at 2 l min<sup>-1</sup>. The results of this simplex are shown in Table 6.9. Again, high values of

# TABLE 6.8

Conditions found for maximum signal to background ratio from a simplex program (5 parameters) for the Fe II 259.939 nm line from a 0.1% m/v slurry of SA1/C120 using the PTFE/GF-base laminar flow torch on the Kontron S-35 ICP.

Gas flows/l min  $^{-1}$ 

• •

| Coolant | Auxiliary | Carrier | Forward power | Height | Response |
|---------|-----------|---------|---------------|--------|----------|
|         |           |         | /k₩           | /mm    | (SBR)    |
| 21.9    | 3.2       | 1.8     | 2.0           | 16     | 19.4     |
| 13.6    | 2.6       | 1.5     | 1.9           | 13     | 25.2     |
| 17.2    | 2.7       | 2.1     | 1.9           | 16     | 19.6     |
| 16.2    | 2.2       | 1.8     | 2.4           | 16     | 20.6     |

# TABLE 6.9

Conditions found for maximum signal to background ratio from a simplex program (3 parameters) for the Fe II 259.939 nm line from a 0.1% m/v slurry of SA1/Cl20 using the PTFE/GF-base laminar flow torch on the Kontron S-35 ICP.

Gas Flows/l min  $^{-1}$ 

..

| Coolant | Auxiliary | Carrier | Forward power | Height | Response |
|---------|-----------|---------|---------------|--------|----------|
|         |           |         | / <b>k</b> ₩  | /mm    | (SBR)    |
| 21      | 2         | 1.4     | 2.5           | 14     | 25.7     |
| 21      | 2         | 1.9     | 1.6           | 15     | 30.0     |
| 21      | 2         | 2.2     | 2.5           | 32     | 30.5     |
| 21      | 2         | 1.6     | 1.9           | 24     | 28.6     |

forward power were requested by the program (up to 2.5 kW) with medium to high carrier gas flow rates (1.4 to 2.2  $1 \text{ min}^{-1}$ ) which may be the result of using a high auxiliary gas flow (2  $1 \text{ min}^{-1}$ ) which has the effect of lifting the plasma. Viewing heights cover the range 14 to 32 mm. While a high response factor at 14 to 15 mm using a carrier gas flow rate of 1.9  $1 \text{ min}^{-1}$  may be a result of matrix effects (where the tip of the injector bullet encroaches on the viewing zone) this is most unlikely in the case of the greatest response (30.5). In this case a high power (2.5 kW) and carrier gas flow of 2.2  $1 \text{ min}^{-1}$  are present but the viewing height is high at 32 mm.

6.3.2.2 Rotational temperature measurements in the LFT.

Temperature measurements from the Q<sub>1</sub> branch of the (0-0) OH band spectra were calculated from the slope of a graph of log (I' $\lambda$ /A') against E for the series Q<sub>1</sub><sup>2</sup> to Q<sub>1</sub><sup>10</sup> as described in Chapter 5. A typical plot is shown in Figure 6.3 for the Q<sub>1</sub> series obtained at a viewing height of 19 mm and 1.7 1 min<sup>-1</sup> carrier gas flow rate (other conditions shown in Table 6.3). The revised figure of 22.1 x 10<sup>8</sup> s<sup>-1</sup> for the relative transition probability of the Q<sub>1</sub><sup>2</sup> line was also used and as previously discussed in Chapter 5, produced a value for log (I' $\lambda$ /A') which shows near coincidence with the line.

This coincidence was noted in 80% of the graphical plots.

The change in rotational temperature with carrier gas flow rate (constant height) and viewing height (constant flow rate) is shown in Table 6.10 (Figure 6.4) and Table 6.11 (Figure 6.5) respectively.

FIGURE 6.3

Plot of  $Q_1$  branch line emission intensities against energy level from the OH (0-0) band measured at 1.7 l min<sup>-1</sup> injector gas flow

•



## TABLE 6.10

The change in rotational temperature (T<sub>rot</sub>) with carrier gas flow rate at a constant viewing height (19mm) using the PTFE/GF-base laminar flow torch calculated from the OH (0-0) band spectrum, Q<sub>1</sub> series.

Carrier gas flow rate Trot 1 min<sup>-1</sup> K 1.1 2180 1.4 2580 1.7 2600 2.0 3150 2.3 2910

FIGURE 6.4

Graph showing the change in rotational temperature, K, with injector gas flow rate for a constant viewing height of 19 mm in a 1500W laminar flow plasma.



The change in rotational temperature  $(T_{rot})$  with viewing height at a constant carrier gas flow rate (1.4 l min<sup>-1</sup>) using the PTFE/CF-base laminar flow torch calculated from the OH (0-0) band Spectrum, Q<sub>1</sub> series.

| Viewing Height | T <sub>rot</sub>         |
|----------------|--------------------------|
| mm             | к                        |
|                |                          |
| - 5            | 2140                     |
| 10             | 2380 (1400) <sup>1</sup> |
| . 15           | 2500                     |
| 20             | 2580                     |
| 25             | 2590                     |
| 30             | 2780                     |
| 35             | 2770                     |
| 40             | 2690                     |
| 50             | 2630 (2620) <sup>2</sup> |

l No water aerosol, water vapour only.

2 Example of duplicate run.

FIGURE 6.5

Graph showing the change in rotational temperature, K, with viewing height for a constant injector gas flow rate of 1.4 l min<sup>-1</sup> in a 1500W laminar flow plasma.



As previously found with the turbulent flow 'Greenfield size' torch described in Chapter 5 the rotational temperature within the LFT plasma shows a progressive increase with carrier gas flow rate, up to a maximum (3150 K at 2 l min<sup>-1</sup>) and with viewing height up to a maximum (2780 K at 30 to 35 mm). Compared with the rotational temperatures obtained from the TFT however, the laminar flow temperatures are lower, under the same running conditions, at the maxima by up to 20%. The maxima do occur at very nearly the same positions of viewing height and carrier gas flow conditions for the two torches. If these values are a true reflection of the 'Kinetic temperature' through which a sample would pass, it may be conjectured that little benefit would be gained from using a LFT of the design shown for a slurry where atomisation problems are encountered.

Rotational temperatures, measured by Davies and Du (154), in a 'Fassel size' laminar flow torch from the  $R_2$  branch of the OH (0-0) band spectra show values in the range 3500 to 3900 K over a wide range of viewing heights (2 to 25 mm). These temperatures are comparable to the maximum  $T_{rot}$  values obtained from the TFT in Chapter 5. The difference in rotational temperatures measured between the two LF torches may be a reflection of the different plasma types <u>i.e</u> compact Fassel size and large Greenfield size, and the conditions used for plasma formation and loading.

It is of note that when no water loading is present, the rotational temperature, measured from vapour in the system, drops to 1400 K. This value is very much lower than that seen in the TFT under the same conditions (2200 K). Whether the laminar flow torch is more dependent upon the water loading for the energy transfer process is unknown but such an inference is indicated.

Two large 'Greenfield size' laminar flow torches have been designed and constructed. The all brass-base LFT has shown advantages of greatly reduced gas consumption while retaining comparable plasma stability to that of a TFT and increased signal to noise values. While a plasma formed with this torch shows less Perturbation when an analyte channel is punched (3 to 3.5 mm bore injector) experiments with large (<u>i.e</u> 5 mm) bore injectors proved unsuccessful.

The PTFE/GF-base laminar flow torch which employed a laminar flow insert produced stable plasmas over a wide range of operating conditions. Simplex optimisation of this torch indicated that a high forward power (2kW range) and medium to high values of both carrier gas flow (1.5 to 2.2 l min<sup>-1</sup>) and viewing height (15 to 32 mm) are necessary for high signal to background ratios from emission signals.

Rotational temperature measurements from the PTFE/GF laminar flow torch show a dependence upon water loading, carrier gas flow rate and viewing height. Maximum values of  $T_{rot}$  are lower than those found from a comparable sized TFT under the same running conditions. No benefit to resolving atomisation problems which occur with some refractory slurries is therefore indicated from using a LFT under the conditions used in the experiments.

#### CHAPTER 7

#### SLURRY ATOMISATION - PLASMA SOURCE MASS SPECTROMETRY

#### 7.1 INTRODUCTION

The technique of plasma-source mass spectrometry (MS) was pioneered by Gray (157, 158) using a direct current capillary arc plasma to demonstrate its potential as an analytical tool. The inherent, interelement and matrix effects encountered with the relatively cool dc arc plasma source forced a change to the higher temperature and more stable inductively coupled plasma (ICP) as an ion-source. Two groups developed early ICP mass spectrometry (ICP-MS), that under the direction of Fassel at the Ames laboratory, Iowa, USA (159) and that under Gray at the University of Surrey, UK (160); a microwave plasma source mass spectrometer was also described by Douglas and French (161) at around the same time.

It was not until the advent of the more sophisticated forms of quadrupole mass filter, originally developed for coupling with gas chromatographs, together with the use of continuum ion sampling that the higher resolution and mass range (162, 163) attributed to modern ICP-MS was realised. A schematic layout of an ICP mass spectrometer and the plasma-sampling zone are shown in Figures 7.1 and 7.2 respectively (164). The ICP mass spectrometer produces simpler spectra compared with an optical emission system (just over 200 usable mass lines from most of the periodic table, compared with the many thousands of complex optical emission lines) and generally lower detection limits (in many cases lower by a factor of 10 but is dependent upon the element under investigation and the matrix). The advantage of the

simpler spectra presented by the mass spectrometer is no better demonstrated than in the determination of rare earths. The complex optical spectra of the lanthanides are difficult to resolve and interpret. This problem does not arise with ICP-MS and the series is readily quantified (163, 165, 166)

The ICP mass spectrometer can, like its optical emission counterpart accept a variety of sample types, provided that they can be introduced into the injector flow. While the majority of samples are presented in solution form, there are advantages to introducing solid samples in slurry-form to the ICP mass spectrometer. The removal of a time consuming, error prone and sometimes hazardous dissolution stage is beneficial especially with rock and mineral analyses which invariably result in a high dissolved solids matrix from a fusion step. High dissolved solids can cause nebuliser and cone blockage in ICP-MS. Also a number of acids can cause polyatomic ion interferences (167) <u>e.g.</u>  $40_{Ar}^{35}C1^+$  on  $75_{As}^{32}S0_2^+$  on  $64_{Zn}$  from HCl and H<sub>2</sub>S0<sub>4</sub>, and, together with the possible loss of volatile elements during preparation of a solution, clearly indicates the advantages to be gained from a solid sampling technique. To date few workers have used the slurry atomisation technique with ICP-MS (40, 41) but its use has proved successful.

#### 7.1.1 Semi-Quantitative Analysis using ICP-MS

This section describes the use of slurry atomisation with an inductively coupled plasma mass spectrometer to analyse 10 certified reference materials (coals, ash and soils) in the semi-quantitative mode. This was performed in order to determine the applicability of using both the slurry technique and a single standard in the estimation

of nearly 70 elements in a sample. The ability to use a rapid, semiquantitative technique to analyse materials, would be a distinct advantage when only threshold information (less than limits) is required or an estimate of the composition prior to a full quantitative analysis. The efficacy of the technique is dependent upon the mass response curve. The mass response curve is a measure of the response of the elements, with respect to their increasing mass, in the periodic table , for a simple matrix. This response curve can be updated by using suitable standards and retained in the instrument software. The curve is then used to estimate the concentration of elements in a sample which contains a single internal standard for reference.

#### 7.2 EXPERIMENTAL

The ICP-MS instrument used in the experiments was the commercially available VG Plasmaquad (VG Elemental, Winsford, Cheshire, UK). The instrumental details have recently been reported (41) and are given in Table 7.1. The slurry samples were peristaltically pumped at 1 ml min<sup>-1</sup> (Gilson Minipuls 2, Anachem, Luton, Beds, UK) to an Ebdon nebuliser (PS Analytical, Sevenoaks, Kent, UK) constructed from Kel-F, passed as an aerosol through a Scott-type double pass spray chamber (of similar design to that shown in Figure 3.6 but water cooled) to a Fassel size torch with a 1.8 mm injector. The plasma running conditions used are shown in Table 7.2.

Ten certified reference materials (CRM) were analysed by the semiquantitative method. The samples were i) a low rank bituminous coal (SARM 18, South African Bureau of Standards, Private bag X191, Pretoria 0001, South Africa), ii) a low rank sub-bituminous coal (SARM 19), iii) a low rank sub-bituminous coal (SARM 20), iv) a bituminous

FIGURE 7.1

Schematic diagram of inductively coupled plasma mass spectrometer instrumentation.



FIGURE 7.2

Diagram illustrating the plasma sampling interface.



# TABLE 7.1

.

| Instr  | umental details for the VG Elemental Plasmaquad<br>ICP-MS Plasma system.   |
|--|--|
| RF generator                                   | - 27.12MHz,0-1500W RMS carrier-wave power (Henry Radio,<br>California, USA).   |
| Torch system                                   | <ul> <li>Three turn water - cooled coil, inductively coupled<br/>with a Fassel size quartz torch.</li> </ul>   |
| Gas controls                                   | <ul> <li>Mass flow controller regulating the carrier gas.</li> <li>Precision rotameters regulate the coolant and</li> <li>auxiliary gas flows</li> </ul>   |
| Nebuliser                                      | <ul> <li>Ebdon high-solids Kel-F nebuliser ( PS Analytical,<br/>Sevenoaks, Kent). Fed with sample at 1 cm<sup>3</sup>min<sup>-1</sup> from</li> </ul>  |
| Spray chamber                                  | <ul> <li>Scott-type double pass water-cooled spray chamber<br/>constructed from glass.</li> </ul>  |
| Ion sampling.                                  |  |
| Sampling cone<br>Skimmer cone<br>Vacuum system | <ul> <li>Nicone (1.0 mm dia. orifice)</li> <li>Nicone (0.7 mm dia. orifice)</li> <li>Three stage system- <ul> <li>(i) expansion stage pumped by rotary EIM/18 pump.</li> <li>(Edwards high vacuum, Crawley, Sussex UK) 333 l min<sup>-1</sup></li> <li>to working pressure of 2 mbar;</li> <li>(ii) intermediate stage pumped by Balzers 200</li> <li>diffusion pump, 2000 l min<sup>-1</sup> to working pressure of 10<sup>-4</sup> mbar;</li> <li>(iii) analyser stage pumped by Balzers Diffset 063</li> <li>diffusion pump at 180 l s<sup>-1</sup> to working pressure of 2.5x10<sup>-6</sup> mbar. Both diffusion pumps backed by an E2M/18 rotary pump.</li> </ul> </li> </ul> |
| Pressure                                       |  |
| detectors                                      | <ul> <li>Pirani PRM 10 and PRL 10 pressure detectors for the<br/>expansion and intermediate stages respectively.</li> <li>Penning gauge detector used for analyser stage. All<br/>three detectors operated by Edwards 1108 controller.</li> </ul>  |
| Mass   |  |
| spectrometer                                   | - VG Masslab 12-12 quadrupole analyser, mass range 1 to<br>300 u. Fitted with Channeltron pulse counter<br>electron multiplier   |
| Multi channel<br>analyser                      | - VG MCA 100 MHz, 4096 channels, 2x10 <sup>9</sup> counts per channel.   |
| Data collectior                                | n system   |
| System   | <ul> <li>IBM PC/XT with 8087 co-processor, with 640K RAM, 10M<br/>hard disk, 360K floppy disks.</li> <li>Graphics from a Sigma dazzler card with a 7210<br/>processor.</li> </ul>  |

.

TABLE 7.2

Instrument running conditions for the VG Plasmaquad ICP-MS.

| Forward power/kW                   | 1.4                      |
|------------------------------------|--------------------------|
| Gas flow rates/l min <sup>-l</sup> |                          |
| Coolant                            | 12                       |
| Auxiliary                          | 0.5                      |
| Carrier                            | 0.8                      |
| Ion lens set.                      | Optimum setting for mass |
|                                    | calibration and counts.  |
|                                    |                          |
| Mass range /u                      | 4-255                    |
| Sweeps                             | 120                      |
| Channels                           | 2048                     |
| Dwell time/µs                      | 250                      |

Total run time/s

coal (NBS SRM 1632a, National Bureau of Standards, Washington DC, USA), v) a bituminous coal (NBS SRM 1632b), vi) a coal fly ash (NBS SRM 1633a), vii) a coal (BCR No. 40, Community Bureau of Reference, Brussels, Belgium), viii) a light sandy soil (BCR No 142), ix) a weathered clay soil (CANMET CRM SO-1, Canadian Centre for Mineral and Energy Technology, Ottawa, Ontario, Canada) and x) a sandy soil (CANMET CRM S0-2). The slurries were prepared as aqueous suspensions of the finely ground samples. The grinding method employed was the 'bottle and bead' method described in Chapter 2. In summary 0.1 or 1g of the samples were weighed into a 30 ml Nalgene bottle together with 10g of 2.5 mm zirconia spheres (beads, Glen Creston, Stanmore, Middx, UK). An aqueous solution of 0.1% m/v Aerosol OT (an anionic surfactant, sodium salt of an octyl-sulphosuccinate ester, BDH, Poole, Dorset, UK) was added until the beads were just covered, this being typically 3 to 4ml, in order to stabilise the suspension. The sealed bottle was shaken using a laboratory shaker (Gallenkamp, Loughborough, UK) for an ll hour period (overnight for convenience) to bring the particle size down to below 8µm. The slurries were then washed into a calibrated flask though a Buchner funnel which seperated out the grinding media. A suitable quantity of a rhodium internal standard was added to the flask (to produce 100 ng ml<sup>-1</sup> final concentration) and the slurry was then made up to the mark with 0.1% m/v Aerosol OT.

Particle size analysis was then performed on the slurries using both optical microscopy and a Coulter Counter TA II particle size analyser.

In order to gauge the contamination from the grinding media (zirconia beads) blank solutions were prepared under the same conditions and shaken with the beads for the same period as the samples. The blank solutions were then seperated from the beads, the rhodium internal

standard was added (to produce 100 ng ml<sup>-1</sup> final concentration) and the solution was then made up to the mark in a 100ml calibrated flask with 0.1% m/v Aerosol OT in an identical fashion to the samples.

The slurries and blank solutions were analysed in the undiluted state (0.1 and 1% m/v) and each contained 100 ng ml<sup>-1</sup> of a rhodium internal standard (103 Rh) in order to estimate the concentrations of 68 elements via the mass response curve. This curve was generated by a recalibration technique which employed a multielement standard solution. The solution contained 6 elements, in equal concentration (100 ng ml<sup>-1</sup>), whose masses covered the range Lithium to Uranium. The response for each element was determined under the conditions set down in Table 7.2 and stored in the operating software of the instrument. The relative sensitivity to this wide range of elements was therefore taken partly into account.

# 7.3. RESULTS AND DISCUSSION.

Optical microscopy showed that in most cases the primary particle size was below 8  $\mu$ m, however, some loose flocculates were present. The particle size analyses for six of the certified reference materials, (two soils, three coals and one ash) performed on the Coulter Counter TA II, are shown in Table 7.3 and illustrate the grinding efficiency of the technique and suitability of the dispersant. Over 90% by volume in each of the samples, is below 8  $\mu$ m in size and for SARM 20 over 98% by volume is less than 6  $\mu$ m. With the exception of the coal 1632(b) the distributions indicate that the majority of the samples are below 2.5  $\mu$ m in size and that only the shoulder of the larger fraction of the distribution is seen.

# TABLE 7.3

.

...

% volume particle size distributions for the CRM coals (SARM 18, 20;

NBS 1632b), fly ash (NBS 1633a), and soils (SO-1 and SO-2)

determined using the Coulter Counter TAII.

|         |        |         |         |                  | SAMPLE    |             |             |  |  |
|---------|--------|---------|---------|------------------|-----------|-------------|-------------|--|--|
| Partic  | le siz | e       |         | % VOLUME IN BAND |           |             |             |  |  |
| range ( | (µm)   | SARM 18 | SARM 20 | NBS 1632b        | NBS 1633a | CANMET SO-1 | CANMET SO-2 |  |  |
| up to   | 2.5    | 33.4    | 70.7    | 20.8             | 33.6      | 50.9        | 52.9        |  |  |
| 2.5 -   | 3.17   | 24.7    | 21.7    | 24.3             | 16.9      | 18.9        | 12.0        |  |  |
| 3.17-   | 4.0    | 17.4    | 4.8     | 23.0             | 18.9      | 9.6         | 11.2        |  |  |
| 4.0 -   | 5.0    | 10.5    | 1.0     | 12.3             | 14.9      | 5.4         | 10.2        |  |  |
| 5.0 -   | 6.35   | 6.5     | 0.6     | 6.7              | 8.8       | 4.8         | 6.9         |  |  |
| 6.35-   | 8.0    | 3.3     | 0.5     | 4.2              | 4.0       | 2.8         | 2.7         |  |  |
| 8.0 -   | 10.1   | 2.7     | 0.3     | 3.9              | 1.9       | 3.6         | 1.6         |  |  |
| 10.1 -  | 12.7   | 1.2     | 0.3     | 2.3              | 0.8       | 3.0         | 1.3         |  |  |
| 12.7 -  | 16.0   | 0.3     | 0.1     | 1.9              | 0.3       | 1.2         | 0.9         |  |  |
| 16.0 -  | 20.2   | 0       | 0       | 0.5              | 0         | 0           | 0.4         |  |  |

In the semi-quantitative mode the analysis time for the slurries was approximately one minute for 68 elements. Based on the 100 ng ml<sup>-1</sup> rhodium internal standard and corrected using the mass response curve, values of within a factor of two to three of the certified and indicated values were obtained for most elements. In many instances closer agreement with the known value was found. These results are shown in Tables 7.4 and 7.5 (corrected for the 0.1% m/v Aerosol 0T solution). Marked deviations from certified values were seen for a few elements. The major causes of this appear to be i) when saturation of the detector occured for an element which is present at percentage levels in the concentrated slurries which results in low values, ii) coincidence between the ion of interest and a polyatomic interfering ion and iii) when some contamination may have been introduced during the grinding operation.

The level of contamination from the zirconia grinding media was estimated by measurement of grinding blanks which had undergone the same procedure as the slurries. These results are shown in Table 7.6 (corrected for the Aerosol OT solution). With the exception of zirconium, hafnium, aluminium, titanium and iron the other 63 elements are present at levels of less than 100 ng ml<sup>-1</sup> and in many cases (over 80% of the elements) less than 10 ng ml<sup>-1</sup>. This indicates that the method is acceptable for slurry preparation, especially for samples with a measure of hardness of less than 7 and when shorter grinding periods are used. Deviation from the certified values are seen for hafnium and zirconium which can be accounted for by contamination during the grinding operation. The low sodium values may be a result of overcorrection but is more likely due to saturation effects because of the presence of a sodium containing surfactant (Aerosol 0T, 1000  $\mu$ g ml<sup>-1</sup>). Under the conditions used no evidence was found for the

polyatomic ions  $ArNa^+$  or  $PO_2^+$  which can interfere with  $^{63}Cu$ . An examination of the  $^{65}Cu$  isotope results showed the same values as  $^{63}Cu$ . The aluminium results are all low which may in part be due to saturation of the analyser, a result of high concentrations of that element being present (0.9 to 14% in the samples). However it has been noted that determining aluminium by ICP-MS using the slurry technique can give low results (40, 41): the explanation being that aluminium forms a refractory oxide that does not break down easily in the plasma environment. The high value for cadmium is disappointing and may be due to a combination of using the low abundance isotope  $^{111}Cd$  (12.86%) and possibly polyatomic ion interference e.g.  $^{94}Zr$  OH<sup>+</sup>, when measuring trace levels of cadmium in the 1% m/v slurries (down to 0.05 µg g<sup>-1</sup>)

Both arsenic and selenium can suffer polyatomic ion interferences when determined by ICP-MS. This is most pronounced when those elements are in low concentrations. The arsenic signal at 75 atomic mass units (AMU) is affected by the presence of  $^{40}$ Ar  $^{35}$ Cl<sup>+</sup> (167) and because there is only one naturally occuring isotope of arsenic, 75 As, the determination of this element in samples which contain a high level of concomitant chloride (natural, biological systems) can pose a problem. The presence of chloride may in part account for the high values obtained for arsenic in the semi- quantitative determination (generally 3.5 to 5 times higher than certified value).

The six isotopes of selenium of masses 74,76,77,78,80 and 82 AMU have relative abundances of 0.96, 9.12, 7.50, 23.61, 49.96 and 8.84% respectively. The most abundant isotopes,  $^{80}$ Se and  $^{78}$ Se, suffer polyatomic ion interferences from  $^{40}$ Ar<sub>2</sub><sup>+</sup> (157, 159, 168) and  $^{38}$ Ar  $^{40}$ Ar<sup>+</sup> respectively. The ions  $^{40}$ Ar  $^{37}$ Cl<sup>+</sup> and  $^{40}$ Ar  $^{36}$ Ar interfere with the isotope responses of  $^{77}$ Se and  $^{76}$ Se leaving  $^{82}$ Se as the highest abundant

| T | ΆB | LE | 7 | .4 |  |
|---|----|----|---|----|--|
|   |    |    |   |    |  |

# Results for rapid semi-quantitative (S-Q) analysis of seven CRM coals using slurry atomisation.

Coal sample/µg g<sup>-1</sup>

:

|            | SARM 18 |                      | M 18                   | SARM 19              |                        | SARM 20              |                        | NBS SRM     | NBS SRM 1632a          |                      | NBS SRM 16326          |                      | NBS SRM 1633a          |                      | BCR 40                 |  |
|------------|---------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|-------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|--|
| Elemen     |         | Certificate<br>value | Sturry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate | Slurry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Sturry<br>S-Q analysis | Certificate<br>value | Sturry<br>S•Q analysis |  |
| Li         |         | (1)                  | 46                     | (37)                 | 160                    | (90)                 | 350                    | (36)        | 56                     | (10)                 | 42                     | _                    | 570                    | _                    | 170                    |  |
| Be         |         | 4.1                  | 9.3                    | 2.8                  | 7.8                    | 2.5                  | 6.4                    | _           | 1.9                    | _                    | 1.5                    | (12)                 | 23                     | -                    | 3.6                    |  |
| В          |         | (30)                 | 90                     | (90)                 | 280                    | (90)                 | 240                    | (53)        | 87                     | _                    | 150                    | (39.2)               | 100                    |                      | 52                     |  |
| Na         |         | (130)                | 61                     | 2150                 | 78                     | 2003                 | 83                     | (760)       | 140                    | 515                  | 38                     | 1700                 | 39                     | _                    | 65                     |  |
| Mg         |         | 0.066%               | 0,07%                  | 0.121%               | 0.092%                 | 0.259%               | 0.089%                 | (600)       | 470                    | 0.038%               | 0.05%                  | 4550                 | 380                    | _                    | 0.09%                  |  |
| AĽ         |         | 1.36%                | 0.01%                  | 4.24%                | 0,014%                 | 5.96%                | 0.018%                 | 30 700      | 220                    | 0.855%               | 0.009%                 | (14%)                | 0.014%                 | _                    | 0.012%                 |  |
| Р          |         | 30                   | 75                     | 130                  | 290                    | 0.061%               | 0.15%                  | (280)       | 244                    | -                    | 150                    | (1.5%)               | 0.3%                   | _                    | 0.019%                 |  |
| Sc         |         | 4.3                  | 63                     | 7.6                  | 130                    | 10                   | 160                    | 6.3         | 34                     | (1.9)                | 33                     | (4U)                 | 220                    | _                    | 93                     |  |
| Ti         | • •     | 0.0683%              | 0,17%                  | 0.204%               | 0,44%                  | 0.378%               | 0.70%                  | (0.175%)    | 0.16%                  | 0.045%               | 0.052%                 | (0.8%)               | 0.84%                  | _                    | 0.27%                  |  |
| v          | • •     | 23                   | 38                     | 35                   | 65                     | 47                   | 87                     | 44          | 39                     | (14)                 | 24                     | (300)                | 360                    | -                    | 110                    |  |
| Cr         | • •     | 16                   | 34                     | 50                   | 110                    | (67)                 | 130                    | 34,4        | 32                     | (1)<br>(1)           | 26                     | 196                  | 290                    | 31.3                 | 62                     |  |
| Mn         |         | 22                   | 38                     | 157                  | 262                    | 80                   | 140                    | 28          | 40                     | 12.4                 | 73                     | (190)                | 340                    | 139                  | 300                    |  |
| Fe         | ••      | 0.203%               | 0.33%                  | 1.22%                | 1.5%                   | 0.818%               | 1.2%                   | 1.11%       | 0.96%                  | 0.76%                | 1.0%                   | 9.4%                 | 0.50%                  | _                    | 1.5%                   |  |
| Co ·       |         | 6.7                  | 9.7                    | 5.6                  | 9.5                    | 8.3                  | 13                     | (6.8)       | 7.9                    | 2.29                 | 3.6                    | (46)                 | 76                     | 7.8                  | 11                     |  |
| Ni         |         | 10.8                 | 15                     | 16                   | 23                     | 25                   | 37                     | 19.4        | 21                     | 6. I                 | 11                     | 127                  | 190                    | 25.4                 | 33                     |  |
| Cu         | • •     | 5.9 ·                | 8.6                    | 13                   | 18                     | 18                   | 27                     | 16.5        | 14                     | 6.28                 | 9.6                    | 118                  | 170                    | -                    | 48                     |  |
| Zn         |         | 5.5                  | 29                     | 12                   | 26                     | 17                   | 33                     | 28          | 41                     | 11.89                | 22                     | 220                  | 420                    | 30.2                 | 60                     |  |
| Ga         |         | (8)                  | 26                     | 14                   | 76                     | 16                   | 88                     | (8.49)      | 18                     | —                    | 14                     | (58)                 | 250                    |                      | 45                     |  |
| Ge         | • •     | (8)                  | 12                     | 13                   | 22                     | _                    | 5.1                    |             | 3.4                    | —                    | 5.2                    | _                    | 75                     | -                    | 4.8                    |  |
| As         | • •     | -                    | 31                     | 7                    | 82                     | 4.7                  | 22                     | 9.3         | 37                     | 3.72                 | 18                     | 145                  | 510                    | 13.2                 | 64                     |  |
| Se .       | ••      | -                    | 0.41                   | (1)                  | 3.0                    | 0.8                  | 3.0                    | 2.6         | 1.2                    | 1.29                 | 1.4                    | 10,3                 | 8.1                    |                      | 2.9                    |  |
| Br         | ••      | (3)                  | 6.5                    | (2)                  | 7.7                    | (2)                  | 8.2                    | (43)        | \$7                    | (17)                 | 25                     | _                    | 4.4                    | -                    | 10                     |  |
| RD .       | ••      | 8.1                  | 16                     | 9                    | 17                     | 10                   | 17                     | (31)        | 36                     | 5.05                 | 8.5                    | 131                  | 240                    | -                    | 69                     |  |
| Sr         | ••      | 44                   | .73                    | 126                  | 220                    | 330                  | 460                    | (88)        | 120                    | (102)                | 140                    | 830                  | 560                    | -                    | 80                     |  |
| Y .        | ••      | (12)                 | Z9                     | (20)                 | 66                     | 29                   | 84                     | . (5.8)     | 29                     | -                    | 12                     | —                    | 100                    | -                    | 29                     |  |
| Zr         | ••      | 67                   | 400                    | 351                  | 150                    | (180)                | 220                    | (53)        | 330                    | -                    | 480                    | *                    | 120                    | -                    | 180.                   |  |
| ND .       | ••      | (6)                  | 7.4                    | (10)                 | 15                     | (16)                 | 22                     | . —         | 7.1                    |                      | 2.2                    |                      | 48                     | _                    | 5.2                    |  |
| Mo .       | ••      | (1)                  | 1.0                    | (2)                  | 3.9                    | _                    | 2.2                    | (<4)        | 2.2                    | (0.9)                | 1.4                    | (29)                 | 59                     | -                    | 5.5                    |  |
| KU .       | • •     | -                    | ND                     | _                    | ND                     | -                    | ND                     | _           | ND                     | —                    | ND                     | -                    | ND                     | _                    | ND                     |  |
| KD .       | •••     |                      | 10-                    | -                    | 10-                    | —                    | 10-                    | -           | 104                    | -                    | 10-                    | -                    | 10"                    |                      | 10"                    |  |
| Pa .       | ••      | -                    | 10                     |                      | / <u>5</u> .           |                      | 80                     |             | 26                     | -                    | .11                    | -                    | 160                    | -                    | 41                     |  |
| Ag .       | • •     | -                    | 0.52                   | _                    | 2.2                    | _                    | 3.5                    | (0.3)       | 0.62                   |                      | 0.5                    |                      | 3.7                    |                      | 1.3                    |  |
|            | • •     | -                    | 2.0                    | -                    | 0.17                   | _                    |                        | (0.04)      | 3.1                    | 0.057                | 1.5                    | 1.0                  | 22                     | 0.11                 | 4,8                    |  |
| 10 .<br>Sa | ••      |                      | 0.1                    |                      | 0.13                   |                      | 0.2                    | (0.04)      | 0.08                   |                      | 0.04                   |                      | 0,34                   |                      | 0.09                   |  |
| 56         | •••     | (1)                  | 0.61                   | (03)                 | 4.0                    | (4)                  | 0.2                    | (0.58)      | 2.1                    | (0.20)               | 0.00                   | ~                    | 12                     | _                    | 2.0                    |  |
|            | •••     | (0.5)                | 1.4                    | (0.5)                | 0.73                   | (0.4)                | 1.0                    | (0.58)      | 1.5                    | (0.24)               | 1.7                    | (7)                  | 0.36                   |                      | 2.3                    |  |
| Te         | ••      | _                    | 0.01                   | _                    | 0.75                   | _                    | <0.1                   | (1.0)       | 1.7                    | -                    | 1.7                    | -                    | 0.30                   | _                    | 0.09                   |  |
| Ġ.         | ••      | ā                    | 13                     | 14                   | 1.6                    | (2)                  | 27                     | (2.4)       | 2 4                    | (0.44)               | 0.03                   | ~~~                  | 14                     | _                    | 6.8                    |  |
| Ra .       | ••      | 78                   | 00                     | 304                  | 324                    | 172                  | 410                    | (130)       | 130                    | 67 5                 | 77                     | (1500)               | 440                    | _                    | 260                    |  |
| la .       | •••     | 10                   | 14                     | 27                   | 47                     | 47                   | 77                     | (150)       | 22                     | (5.1)                |                        | (1300)               | 67                     | _                    | 17                     |  |
| c.         | ••      | 22                   | 29                     | 56                   | 80                     | 87                   | 130                    | (30)        | 47                     | (0)                  | 11                     | (180)                | 180                    | _                    | ii                     |  |
| Pr         |         |                      | 29                     | ~_                   | 81                     | <i></i>              | 12                     | (50)        | 4.8.                   | ()                   | 16                     | ()                   | 18                     | _                    | 3.7                    |  |
| Nd         |         | _                    | 12                     | _                    | 29                     |                      | 42                     | (12.0)      | 17                     | _                    | 47                     | (66)                 | 59                     | _                    | 14                     |  |
| Sm .       |         | 2.0                  | 2.3                    | 4,9                  | 6.3                    | 6.3                  | 9.0                    | (2.3)       | 3.8                    | (0.87)               | 1.1                    | (16)                 | 13                     | _                    | 3.2                    |  |

·

• '

|         | SARM 18              |                        | SARM 19              |                        | SARM 20              |                        | NBS SRM 1632a        |                        | NBS SRM 1632b        |                        | NBS SRM 1633a        |                        | BCR 40               |                        |
|---------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|----------------------|------------------------|
| Element | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Sturry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis | Certificate<br>value | Sturry<br>S-Q analysis | Certificate<br>value | Slurry<br>S-Q analysis |
| Eu .    | . (0.3)              | 0.43                   | (0.7)                | 1.2                    | (1)                  | 1.6                    | (0.54)               | 0.94                   | (0.17)               | 0.26                   | (4)                  | 3.8                    | _                    | 0,78                   |
| Gal.    | . –                  | 2.7                    | ·                    | 7,0                    |                      | 9.0                    | (1.95)               | 4.6                    | —                    | 1.14                   | (15.3)               | 14                     | _                    | 3.3                    |
| тъ.     | , (0.3)              | 0.34                   | (0.7)                | 0.84                   | (0.9)                | 1.1                    | (0,34)               | 0.58                   |                      | 0.15                   |                      | 1.6                    | _                    | 0.41                   |
| Dy .    | . –                  | 3.3                    | ·                    | 7.5                    |                      | 9.8                    | (2.2)                | 5.5                    | _ ·                  | 1.3                    |                      | 13                     | _                    | 3.3                    |
| Ho .    | . –                  | 0.71                   | -                    | 1.7                    | _                    | 2.2                    | _                    | 1.2                    | · —                  | 0.35                   | _                    | 3.2                    | -                    | 0.88                   |
| Er.     | . –                  | 2.4                    | -                    | 6.3                    | _                    | 7.9                    | _                    | 4.6                    | _                    | 1.1                    | _                    | 10                     | _                    | 3.3                    |
| Tm.     | . —                  | 0.40                   | _                    | 1.1                    | -                    | 1.4                    | -                    | 0.86                   | _                    | 0.18                   | —                    | 2.0                    | — ·                  | 0.59                   |
| Yb .    | . –                  | 3.1                    | (2)                  | 8.8                    | (2)                  | П                      | (1.1)                | 6.9                    | -                    | 1.4                    | _                    | 18                     |                      | 4,4                    |
| Lu .    | . —                  | 0.50                   | _                    | 1.5                    | _                    | 1.8                    | (0.2)                | 1.2                    | -                    | 0.22                   | _                    | 2.4                    |                      | 0.78                   |
| Hſ.     | . 1.7                | 66                     | 5.4                  | 300                    | 4.8                  | 360                    | (1.6)                | 260                    | (0.43)               | 34                     | (7.6)                | 570                    |                      | 160                    |
| Ta.     | . (0.3)              | 0.31                   | (0.8)                | 1.0                    | 1.2                  | 1.5                    | (0,4)                | 0.63                   | -                    | 0.12                   |                      | 1.9                    | -                    | 0.3                    |
| w .     | . (2)                | 1.7                    | (2)                  | 2.6                    | (3)                  | 3.6                    | (0.8)                | 1.4                    | (0.48)               | 0.32                   | _                    | 8.0                    |                      | 1.1                    |
| Re ,    | . –                  | <0.01                  | -                    | <0.01                  | -                    | ND                     | -                    | ND                     | _                    | <0.02                  | -                    | <0.01                  | -                    | 0.01                   |
| Os .    |                      | 0.016                  | -                    | ND                     | _                    | ND                     | -                    | 0.04                   | —                    | 0.03                   | -                    | 0.02                   | -                    | ND                     |
| Ir .    | . –                  | 0.1                    |                      | 0.47                   | _                    | 0.57                   |                      | 0.2                    | -                    | 0.06                   | <del></del>          | 1.0                    |                      | 0.3                    |
| Pt .    | . –                  | 0.39                   | _                    | 1.6                    | _                    | 1.9                    |                      | 0.78                   | —                    | 0.41                   | _                    | 3.3                    | -                    | 0.99                   |
| Au .    | . –                  | 0.085                  | _                    | 0.37                   | -                    | 0.47                   | (<0.05)              | 0.24                   | -                    | 0.05                   | -                    | 0.8                    | -                    | 0.21                   |
| Hg .    | . (0.04)             | 0.034                  | (0.2)                | 0.26                   | 0.25                 | 0.47                   | 0.13                 | 0.16                   | _                    | 0,06                   | 0.16                 | 0.3                    | 0.35                 | 0.43                   |
| Π.      | . —                  | 0.11                   | <u> </u>             | 0.64                   | -                    | 0,36                   | -                    | 0.77                   | _                    | 0.16                   | 5.7                  | 7.2                    | -                    | 0.7                    |
| Pb.     | . (5)                | 6.6                    | 20                   | 28                     | 26                   | 33                     | 12.4                 | 24                     | 3.67                 | 4.5                    | 72.4                 | 100                    | 24.2                 | 41                     |
| Bi .    | . –                  | 0.23                   | -                    | 0.84                   | -                    | 0,99                   | _                    | 0.44                   | -                    | 0.08                   | _                    | 1.2                    | _                    | 0,36                   |
| Th.     | . 3.4                | 7.0                    | 12                   | 25                     | 18                   | 34                     | 4.5                  | 17                     | 1.34                 | 2.9                    | 24.7                 | 28                     | _                    | 8.0                    |
| υ.      | . 1.5                | 2.9                    | 5                    | 9.3                    | 4                    | 10                     | 1.28                 | 5.2                    | 0.436                | 0.93                   | 10.2                 | 28                     | -                    | 4.3                    |
| • ND =  | not detected         |                        |                      |                        |                      |                        |                      |                        |                      |                        |                      |                        |                      |                        |

-

•

-

.

:

.

·

#### TABLE 7.5

Results for rapid semi-quantitative (S-Q) analysis of three CRM soils using slurry atomisation (the values in parentheses are uncertified thus are indicative values only) Major elements expressed as percentages.

| - 1     | CANME   | <u>T SO-1</u> | CANME | <u>T SO-2</u> | BCR 1    | 42        |
|---------|---------|---------------|-------|---------------|----------|-----------|
| Element | t Cert. | Slurry        | Cert. | Slurry        | Cert.    | Slurry    |
|         | value   | S-Q anal.     | value | S-Q anal.     | value    | S-Q anal. |
| Li      |         | 190           |       | 50            |          | 100       |
| Be      |         | 5.8           |       | 5.            |          | 1.7       |
| В       |         | 38            |       | ND            |          | 120       |
| Na      | 1.97%   | 0.066%        | 1.9%  | 0.06%         |          | 0.82%     |
| Mg      | 2.31%   | 0.80%         | 0.54% | 0.62%         | (0.66%)  | 0.67%     |
| A1      | 9.38%   | 0.16%         | 8.07% | 0.20%         |          | 0.24%     |
| Р       | 0.062%  | 0.13%         | 0.3   | 0.66%         | (0.096%) | 0.17%     |
| Sc      |         | 360           |       | 365           |          | 390       |
| Ti      | 0.53%   | 0.71%         | 0.86% | 0.73%         | (0.37%)  | 0.46%     |
| V       | 139     | 260           | 64    | 98            |          | 95        |
| Cr      | 160     | 320           | 16    | 15            |          | 120       |
| Mn      | 0.089%  | 0.16%         | 0.72% | 1.26%         |          | 0.10%     |
| Fe      | 6.00%   | 9.29%         | 5.56% | 8.4%          | (1.96%)  | 3.4%      |
| Со      | 32      | 47            | 9     | 12            |          | 16        |
| Ni      | 94      | 127           | 8     | 13            | 29.2     | 45        |
| Cu      | 61      | 114           | 7     | 51            | 27.5     | 38        |
| Zn      | 146     | 430           | 124   | 400           | 92.4     | 137       |
| Ga      |         | 139           |       | 148           |          | 63        |
| Ge      |         | 18            | ·     | 15            |          | 7.1       |
| As      |         | 9.0           |       | 100           | •        | 44        |
| Se      |         | ND*           |       | 1.7           |          | ND        |
| Br      |         | 1.4           |       | 30 .          |          | 14        |
| Rb      | 139     | 250           | 78    | 135           |          | 170       |
| Sr      | 328     | 580           | 340   | 530           |          | 280       |
| Y       |         | 56            |       | 130           |          | 140       |
| Zr      |         | 0.87%         |       | 0.48%         |          | 0.32%     |
| Nb      |         | 18            |       | 41            |          | 25        |
| Мо      |         | 1.2           |       | 19            |          | 0.8       |
| Ru      |         | ND            |       | ND            |          | ND        |
| Rh(Int. | Std)    | -             |       | -             |          | -         |
| Pd ·    |         | 69            |       | 220           |          | 270       |
| Ag      |         | 4.5           |       | 6.1           |          | 7.6       |
| Cd      |         | 15            |       | 32            | 0.25     | 33        |
| In      |         | 0.23          |       | 1.7           |          | 0.13      |
| Sn      |         | 68            |       | 130           |          | 16        |
| Sb      |         | 1.1           |       | 0.60          |          | 3.5       |
| I       |         | 6.9           |       | 17            |          | 4.7       |

Soil sample/µg g-l

\* N.D. = not detected.

# TABLE 7.5 continued

..

| Soil | sample/ | ′μg | g-1 |
|------|---------|-----|-----|
|------|---------|-----|-----|

|         | CANMET SO-1 |           | CANMET | S0-2      | BCR 1 | BCR 142   |  |  |
|---------|-------------|-----------|--------|-----------|-------|-----------|--|--|
| Element | Cert.       | Slurry    | Cert.  | Slurry    | Cert. | Slurry    |  |  |
|         | value       | S-Q anal. | value  | S-Q anal. | value | S-Q anal. |  |  |
| Te      |             | ND*       |        | ND        |       | 0.08      |  |  |
| Cs      |             | 6.8       |        | 0.47      |       | 7.2       |  |  |
| Ba      | 0.879%      | 1.24%     | 0.966% | 1.3%      |       | 650       |  |  |
| La      |             | 82        | (46)   | 63        |       | 49        |  |  |
| Ce      |             | 168       | (111)  | 174       |       | 91        |  |  |
| Pr      |             | 17        | (13.4) | 18        |       | 12        |  |  |
| Nd      |             | 67        | (57)   | 71        |       | 36        |  |  |
| Sm      |             | 11        | (12.2) | 15        |       | 9.1       |  |  |
| Eu      |             | 2.8       | (3.43) | 5.1       |       | 2.1       |  |  |
| Gd      |             | 12        | (10.3) | 16        |       | 10        |  |  |
| ТЬ      |             | 1.0       | (1.3)  | 1.9       |       | 1.6       |  |  |
| Dy      |             | 7.1       | (8.6)  | 16        |       | 17        |  |  |
| Но      |             | 1.8       | (1.7)  | 3.8       |       | 4.1       |  |  |
| Er      |             | 6.2       | (4.1)  | 15        |       | 15        |  |  |
| Tm      |             | 1.0       | (0.5)  | 2.6       |       | 3.2       |  |  |
| Yb      |             | 9.2       | (3.4)  | 24        |       | 27        |  |  |
| Lu      |             | 1.3       | (0.47) | 3.4       |       | 4.4       |  |  |
| Hf      |             | 300       |        | 950       |       | 0.12%     |  |  |
| Ta      |             | 1.4       |        | 2.3       |       | 1.8       |  |  |
| W       |             | 1.3       |        | 4.2       |       | 3.1       |  |  |
| Re      |             | ND        |        | ND        |       | ND        |  |  |
| 0s      |             | <0.1      |        | ND        |       | 0.09      |  |  |
| Ir      |             | 0.6       |        | 1.6       |       | 1.9       |  |  |
| Pe      |             | 1.5       |        | 5.6       |       | 6.9       |  |  |
| Au      |             | 0.4       |        | 1.3       |       | 1.7       |  |  |
| Hg      | 0.022       | ND        | 0.082  | ND        | 0.104 | ND        |  |  |
| T1      |             | 0.74      |        | 0.58      |       | 0.76      |  |  |
| РЬ      |             | 36        | 21     | 41        | 37.8  | 47        |  |  |
| Bi      |             | 0.41      |        | 0.14      |       | 0.22      |  |  |
| Th      |             | 23        |        | 20        |       | 32        |  |  |
| U       |             | 7.7       |        | 12        |       | 22        |  |  |

.

•

\*ND = not detected.

.

.

.

| Element      |      |       | Concentration<br>/ng ml- <sup>l</sup> | Element |     |     | Concentration<br>/ng ml <sup>-1</sup> |  |
|--------------|------|-------|---------------------------------------|---------|-----|-----|---------------------------------------|--|
| Li           | ••   | ••    | 1.4                                   | Sn      | ••  | ••  | 0.24                                  |  |
| Be           | ••   |       | 0.22                                  | Sb      | ••  | ••  | 0.12                                  |  |
| В            | ••   | ••    | ND*                                   | I       |     | ••  | ND                                    |  |
| Na           | ••   | • •   | 50                                    | Te      | ••  | ••  | ND                                    |  |
| Mg           | ••   | ••    | 25                                    | Cs      | ••  | ••  | ND                                    |  |
| Al           | ••   | ••    | 400                                   | Ba      | ••  |     | ND                                    |  |
| Ρ            | ••   | • •   | ND                                    | La      | ••  | • • | 0.95                                  |  |
| Sc           | ••   | ••    | 22                                    | Ce      | ••  | ••  | 2.3                                   |  |
| Ti           | ••   | ••    | 150                                   | Pr      | ••  | ••  | 0.22                                  |  |
| ۷            | ••   | ••    | 0.17                                  | Nd      | ••  | ••  | 0.66                                  |  |
| Cr           | ••   | ••    | 15                                    | Sm      | • • | ••  | 0.31                                  |  |
| Mn           | ••   | ••    | 3.1                                   | Eu      | ••  | ••  | 0.15                                  |  |
| Fe           | ••   | ••    | 100                                   | Gd      | ••  | ••  | 0.92                                  |  |
| Со           | • •  | ••    | 0.24                                  | Tb      | ••  |     | 0.17                                  |  |
| Ni           | • •  | ••    | 9.4                                   | Dy      | ••  | ••  | 1.9                                   |  |
| Cu           | ••   | ••    | 2.5                                   | Но      | ••  | ••  | 0.57                                  |  |
| Zn           | ••   | ••    | 11                                    | Er      | ••  | ••  | 2.8                                   |  |
| Ga           | ••   | ••    | 0.28                                  | Tm      | ••  | ••  | 0.46                                  |  |
| Ge           | ••   | ••    | ND                                    | Yb      | ••  | ••  | 4.0                                   |  |
| As           | ••   | ••    | 7.4                                   | Lu      | ••  | ••  | 0.58                                  |  |
| Se           | ••   | ••    | 0.71                                  | Hf      | ••  | ••  | 200                                   |  |
| Br           | ••   | ••    | 2.3                                   | Ta      | ••  |     | 0.15                                  |  |
| Rb           | ••   | ••    | 0.1                                   | W       | ••  | ••  | 2.3                                   |  |
| Sr           | • •  | ••    | 0.3                                   | Re      | ••  | ••  | ND                                    |  |
| Y            | ••   | ••    | 22                                    | 0s      | ••  | ••  | ND                                    |  |
| Zr           | ••   | ••    | 4.4µg ml-1                            | Ir      | ••  | ••  | 0.33                                  |  |
| Nb           | ••   | ••    | 0.46                                  | Pt      | ••  | ••  | 1.2                                   |  |
| Мо           | ••   | ••    | 1.0                                   | Au      | ••  | ••  | 0.22                                  |  |
| Ru           | ••   | ••    | ND                                    | Hg      | ••  | ••  | 0.18                                  |  |
| Rh (internal |      | rnal  |                                       | T1      | ••  | ••  | 0.05                                  |  |
|              | stan | dard) | 100                                   | Pb      | ••  | ••  | 1.2                                   |  |
| Pd           | ••   | ••    | 47                                    | Bi      | ••  | ••  | ND                                    |  |
| Ag           | ••   | ••    | 1.3                                   | Th      | ••  | ••  | 11                                    |  |
| Cd           | ••   | ••    | 5.2                                   | U       | ••  |     | 1.6                                   |  |
| In           | ••   | • •   | 0.03                                  |         |     |     |                                       |  |

Semi-quantitative analysis of blank elements in 100 ml of solution after zirconia grinding.

TABLE 7.6

\*ND = not detected.

isotope that is free (8.84%). The results in this study show most values for the selenium content of samples to be within a factor of 2 to 3 of the known value.

The contribution from polyatomic chloride ions to the response at certain mass units can be accounted for by use of a correction factor (167) and is applicable to both slurries and solutions. For samples in solution chloride itself may be removed from the system by means of a chromatographic separation prior to sample injection (169).

It is interesting to compare the few semi-quantitative results presented in the slurry feasibility paper using ICP-MS by Williams et al. with those in this study. Values for the rare earths (La to Lu), determined by slurry atomisation are given in the paper for the CANMET soils SO-1 and SO-2 together with the values of the lanthanides in SO-2 determined by Crock and Lichte (170) using a fully quantitative dissolution technique. If the values for the Lanthanides in SO-2, determined by slurry atomisation in the Williams et al. paper are taken as a ratio to those in SO-2 determined by the dissolution technique of Crock and Lichte a trend in seen (Table 7.7) i.e. from lanthanum to holmium the ratio increases to 2.2 and from erbium to lutetium the ratio rises rapidly from 2.9 to 7.9. If the values for the lanthanides determined by slurry atomisation in this study are taken as a ratio to those of Crock and Lichte the same trend is seen (Table 7.7). These results indicate that from terbium to lutetium the deviation of the slurry value from that of the solution value in the series is due either to contamination (bottle and bead method used in all slurry work including that by Williams <u>et al.</u>) or to a polyatomic species arising from a concomitant element in the sample SO-2.

TABLE 7.7

A comparison of the lanthanide group elemental concentrations ( $\mu g g^{-1}$ ) in the soils SO-1 and SO-2 determined by semi-quantitative slurry atomisation ICP-MS and by a quantitative dissolution technique.

|         | Dissolution        | Slurry    | Slurry    | Slurry    | Slurry    |
|---------|--------------------|-----------|-----------|-----------|-----------|
| Element | technique          | technique | technique | technique | technique |
|         | SO-2 (1)           | SO-2 (2)  | SO-2 (3)  | SO-1 (2)  | SO-1 (3)  |
|         |                    |           |           |           |           |
| La      | 46 <u>+</u> 1      | 39        | 63        | 34        | 82        |
| Ce      | 111 <u>+</u> 3     | 124       | 174       | 83        | 168       |
| Pr      | 13.4 <u>+</u> 0.4  | 15        | 18        | 9.5       | 17        |
| Nd      | 57 <u>+</u> 1      | 66        | 71        | 41        | 67        |
| Sm      | 12.2 <u>+</u> 0.1  | 13 .      | 15.7      | 6.8       | 11        |
| Eu      | 3.4 <u>+</u> 0.02  | 3.7       | 5.1       | 1.5       | 2.8       |
| Gd      | 10.3 <u>+</u> 0.2  | 11        | 16.7      | 5.9       | 12.4      |
| ТЬ      | 1.3 <u>+</u> 0.2   | 2.4       | 1.9       | 0.88      | 1.0       |
| Dy      | 8.6 <u>+</u> 0.1   | 17        | 16.5      | 4.6       | 7.1       |
| Но      | 1.7 <u>+</u> 0.05  | 3.8       | 3.8       | 1.5       | 1.8       |
| Er      | 4.1 <u>+</u> 0.1   | 12        | 14.8      | 5.6       | 6.2       |
| Tm      | 0.54 <u>+</u> 0.02 | 2.5       | 2.6       | 0.56      | 1.0       |
| Yb      | 3.39 <u>+</u> 0.01 | 15        | 23.7      | 6.5       | 9.2       |
| Lu      | 0.47 <u>+</u> 0.4  | 3.7       | 3.4       | 1.2       | 1.3 ·     |

l Results taken from reference (170), Crock and Lichte.

2 Results taken from reference (40), Williams, Norman, Gray and Ebdon.
3 This study (41).
A comparison of the lanthanide results for the soil SO-1 determined by slurry atomisation from Wiliams <u>et al.</u> paper with those of SO-1 from this study show that although the Williams results are numerically lower for a number of elements the same trend is seen, when ascending the series, from both sets of results (Table 7.7).

It is of note that both 0.1 and 1% m/y slurries were used over a four hour period with little or no effect on the sampling interface of the mass spectrometer.

# 7.4 CONCLUSION

Slurry atomisation ICP-MS offers the potential of a rapid screening technique, as well as that for a full quantitative analysis, for the major, minor and trace elemental components in coals and soils with minimal sample pretreatment. Information obtained in the semi-quantitative mode can be used to assess rapidly the concentration range of an element in a sample, prior to any full quantitative analysis which may not be required if threshold or semi-quantitative data (<u>i.e.</u> values within a factor of two or three) are sufficient thereby reducing analysis time.

The fact that slurries of up to 1% m/v failed to show any effects of cone blockage during the analyses, under the operating conditions used, suggests that the tolerance of the ICP-MS instrumentation to high solids is greater than previously thought. This may allow, if only for short periods, the use of flow injection techniques and the analysis of slurries of higher concentration for ultra trace elemental constituents.

### CHAPTER 8

## CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

### 8.1. CONCLUSION.

The work described in this thesis has illustrated the use of slurry atomisation (SA) for the determination of major, minor and trace elements in numerous mineral and refractory samples using plasma spectrochemical techniques. Fundamental questions concerning the preparation and stability of slurries, transportation phenomena within the sample introduction system (SIS) and atomisation effects within a plasma, in comparison with aqueous calibrants, have been addressed. The information gained in these studies has been successfully applied to the analysis of slurried samples using the techniques of inductively coupled plasma atomic emission spectrometry (ICP-AES), direct current plasma atomic emission spectrometry (DCP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS).

The preparation of the slurry has been shown to be a critical step in the SA technique. Factors such as the chemical form and hardness of the sample, the grinding media to use and the lyophilic nature of the material need to be considered for the successful application of a slurry procedure. The hardness of a sample limits the efficiency of a grinding technique, for a given time period, and the selection of the grinding medium, in the comminution step. The bottle and bead and microniser grinding methods possess the ability to reduce rapidly the particle size of a solid sample to less than 6  $\mu$ m, with little contamination, provided that the measure of hardness (MOH) is less than that of the grinding medium. In the grinding trials dissociated

zircon/zirconia grinding beads (MOH 7 - 7.5) were employed in the bottle and bead method and agate grinding media (MOH 7) were used in the microniser method. Soft minerals such as galena (MOH 2.5 - 2.8) and graphite (MOH 1 - 2) and semi-hard minerals such as chalcopyrite and sphalerite (MOH 3.5 - 4.0) ground efficiently while a hard mineral such as pyrite (MOH 6 - 6.5) ground less efficiently. For soft and semi-hard minerals the microniser grinding technique has been found to be more efficient than the bottle and bead method, reducing a sulphide ore to the 6  $\mu$ m particle size range in 20 to 25 minutes. For harder materials the bottle and bead method was preferred due to the high collision frequency of the technique. Reduction to the size required may, however, take several hours.

Both the microniser and bottle and bead methods are wet grinding techniques which produce a slurry directly from the sample. The lyophilic nature of the sample is known to affect the dispersion of the solid particles in the liquid medium. Many ores and minerals are hydrophilic and inclusion of a wetting agent in the grinding step did not significantly improve the grinding efficiency. A dispersant does, however, improve the stability of the slurry by reducing flocculation and cementation effects (thereby maintaining particulate segregation) and allows redispersion of the particles after settlement. Ostwald ripening effects are also reduced.

Aerosol transportation studies, using laser measuring techniques, have shown that the mechanisms of droplet formation, transportation and loss, within a nebuliser-spray chamber-injector assembly, are similar for both solutions (0.1% m/v sodium hexametaphosphate) and slurries (1% m/v solids) and the effects upon the two types of aerosol, throughout the sample introduction system, are of comparable magnitude.

Aerosols measured from a single pass spray chamber (SPSC) alone show that particle coagulation is a major modification process. The large particles produced are subsequently removed when an injector is fitted. An aerosol population distribution above an injector covers a size range of 18 µm down to below 1 µm and shows a frequency maximum in the region of 6 to 9  $\mu m$  size. In terms of volume this region becomes 7 to ll µm size. The bore of the injector affects the aerosol distribution; the 3 mm injector allowing a greater fraction of the larger droplets to pass to the plasma (8 to 9  $\mu$ m mean diameter) than the 2 mm injector (6 to 8 µm mean diameter). As a consequence the aerosol volume flux from the 3 mm injector is approximately twice that from the 2 mm injector at a gas flow rate of 0.75 l min<sup>-1</sup>. The aerosol mean particle size exiting both injectors decreases when the gas flow rate is increased suggesting ballistic/turbulent loss mechanisms are operative. The double pass spray chamber (DPSC) study showed that the volume flux of an aerosol that exits from the inner pass is greatly reduced from that of the primary aerosol from the nebuliser. This indicates that the inner pass is a major area of loss in droplet mass terms. As seen previously with the SPSC, the presence of an injector modifies the aerosol distribution exiting the DPSC. It has also been shown that aerosols exiting from a 2 and 3 mm injector, on a population-diameter basis mainly cover the size range 14 µm down to below 1 µm. The frequency maximum being in the region 5 to 7  $\mu$ m, which transforms to 6 to 10  $\mu\text{m}$  size in terms of volume. Mechanistically the 2 and 3 mm injectors act differently. Aerosols that exit the 3 mm injector show an increase in population mean and mode particle sizes with a decrease in gas flow rate, while those from the 2 mm injector show the reverse trend. The latter case may be explained in terms of an increase in residence time for aerosol particles along the outer pass and below the DPSC exit allowing settling-type forces to become operative. Theory

predicts that laminar flow is present in this region and the settling diameters calculated in this thesis are consistent with the size of aerosol particles seen to be removed.

When a broad particle size sample (0.6 to 40  $\mu$ m) was dispersed and the aerosol transported solids collected (bottle collection technique) after passing through a DPSC system using various gas flow rates and injector bores marked differences were noted between the starting and final distributions. In most cases the effective particle size range of the post-injector material was from 7 µm down to below 0.63 µm and showed a gain in the fraction of smaller sized particles,  $\boldsymbol{\zeta}$  0.63 to 5 µm, compared with those from the slurry before nebulisation. The position of the distribution maxima (mode) was not significantly changed by the gas flow rate or injector bore (with the exception of very small bore injectors i.e. l.l mm) and in most cases the mode of the distribution from the post-nebulised material was the same as that of the starting slurry. For a constant bore size an increase in gas flow rate increased the contribution from the larger size fraction. For a constant gas flow rate the change in contribution from larger sized particles with increase in injector bore was more complex and may be dependent upon the degree of turbulence of the gas flow within the spray chamber-injector assembly. The volume mean and mode solids diameters generally fell within the region 1.3 to 4 µm under the conditions used.

Total isokinetic sampling of ground slurries (2.5 to 5% m/v loading) using a cascade impactor provided both mass transfer information and solids distribution from aerosols exiting an injector-spray chamber assembly. When a slurry with a distribution covering the size range 0.7 to 12  $\mu$ m and a mode of 3 to 4  $\mu$ m was collected after passing

through a DPSC and 3 mm injector the resulting size distribution range contracted to 0.7 to 5  $\mu$ m with a mode of 1 to 2  $\mu$ m. This is consistent with the results from the bottle collection technique. When a finer particle size slurry was conveyed to the impactor, 0.7 to 6  $\mu$ m size with mode 1 to 2  $\mu$ m, representative transportation occurred; the range and mode being very close in both distributions. The mass transfer efficiency of a slurry aerosol was found to increase with gas flow rate in the same manner as a solution aerosol and was of comparable magnitude when the particle size was very fine. Hence, slurry aerosols will model solution aerosols, in terms of mass transfer efficiency, and will also representatively sample and transport to a plasma solids from the suspension, when the solid particle size is below 5  $\mu$ m and the mode of the distribution is below 3  $\mu$ m size.

Hard, dense, refractory samples may show reduced elemental recoveries if mass transportation and atomisation efficiencies are less than those of the solutions used for calibration. The particle size of the material is the most critical parameter as this will influence both sample transport and atomisation. When the solids distribution of a slurry is essentially below 5  $\mu$ m size plasma running conditions may be found under which near to full recoveries can be obtained. When atomisation effects are suspected as the cause of reduced recoveries from a slurry sample, use of low carrier flow rates and an atom line which shows acceptable emission sensitivity high up in the plasma (30 mm) is sometimes beneficial. It is conjectured that the increase in residence time within the plasma allows differences in the atomisation profiles, between slurry particles and solution salts, to be reduced thereby increasing the relative atomisation efficiency and recovery for the slurry. Very high carrier gas flow rates may also improve recoveries but this often results in decreased sensitivity due to the reduced

residence time of particles in the plasma and the accompanying 'spreading out' of the emission profile; relative transport efficiencies may also be affected. Matrix effects must be taken into account if high carrier gas flow rates and low viewing heights are employed; this is a result of the initial radiation zone invading the viewing position. Buffering agents (easily ionised elements) have been shown to reduce these matrix effects.

Ultrafine slurries (below 2  $\mu$ m size) of refractory materials, <u>e.g.</u> alumina, show comparable transport and atomisation efficiencies to those of solutions and yield full recoveries. When the particle size is increased the magnitude of the atomisation and transportation effects are different and recoveries are dependent upon the carrier gas flow and viewing height. Refractory particles above 4 to 5  $\mu$ m size are limited in their transport efficiency through a DPSC (14% for 5  $\mu$ m and 3% for 10  $\mu$ m) and it is indicated from experiments that their relative atomisation efficiency, to that of simple aqueous solutions, is also reduced (60 - 70% for 5  $\mu$ m and 20 - 25% for 10  $\mu$ m). Use of an intrinsic internal standard (concomitant major element of known concentration in a sample) may, when the particle size range extends beyond 5  $\mu$ m, afford a correction factor for the reduced transport and atomisation efficiencies.

Polydensitic materials, such as ores, can show segregation effects due to the individual mineral distributions (dependent upon their resistance to grinding) and their densities. Thermodynamic effects may also contribute to the reduced recoveries found for some elements using the slurry atomisation technique under certain plasma running conditions.

Measurement of the rotational temperature (that considered to be numerically similar to the gas kinetic temperature) in the central channel of a plasma, using the OH molecule, has shown the value of  $T_{rot}$ to be dependent upon the plasma running conditions <u>i.e.</u> carrier gas flow rate, viewing height and water loading. The temperature range covered was 2200 to 3600 K and is comparable to that found by other workers. High carrier gas flow rates, 2 to 2.3 l min<sup>-1</sup> through a 3 mm injector, and viewing heights in the region of 30 mm, would appear to favour the atomisation process. The high viewing height for peak temperature,  $T_{rot}$ , is consistent with the viewing position used to observe near to full recoveries from slurry samples suspected of reduced atomisation efficiency.

When pure water was admitted to the plasma a rotational temperature of 3400 to 3600 K was observed. When a sample, other than water was introduced, be it surfactant solution, simple analyte solution or slurry, a slight reduction in  $T_{rot}$  was observed (range covered 2850 to 3150 K). The variation in  $T_{rot}$  between samples, under the same conditions, appeared to be less, and little to no difference was seen in the rotational temperature values measured from solutions and slurries up to 1% m/v solids loading.

Fine slurries (less than 2.5  $\mu$ m particle size) of pure single compounds that have melting points comparable to the rotational temperatures measured and boiling points in excess of T<sub>rot</sub> gave near to full recoveries for major elements. This shows that the atomisation efficiencies for both the high melting point refractory slurry particles analysed and the calibration solution salts (which may decompose to give similar oxide species to the slurry solids used in the experiments) are comparable, as are their transport efficiencies.

Rotational temperatures measured from the 'OH' emission within the analyte channel of a laminar flow plasma (Greenfield sized torch) ranged from 2600 to 3200 K and showed a similar dependence upon carrier gas flow and viewing height as seen with the conventional tangential flow plasma. These slightly lower values of  $T_{rot}$  suggest that no advantage would be gained in the use of the laminar flow torch (LFT) for materials which manifest reduced atomisation efficiencies. The all brass body (double laminar flow) in-house designed and constructed LFT does, however, show the advantages of reduced gas consumption and improved signal to noise ratios while retaining comparable plasma stability to that from the tangential flow torch. While a laminar flow plasma shows less perturbation when punched with the gas flow from a 3 mm injector, attempts to produce a central channel with a large bore, 5 mm, injector were unsuccessful.

Simplex optimisation experiments using the PTFE/glass fibre base LFT (in-house design) indicated that high forward power (2 kW), medium to high carrier gas flow rates (1.5 to 2.2 l min<sup>-1</sup>), through a 3 mm injector, and raised viewing heights (15 to 32 mm) are required to observe increased signal to background ratios from emission signals.

Slurry atomisation ICP-MS has been shown to offer the potential of a rapid screening technique, for the analysis of major, minor and trace elemental components in coals and soils with minimal sample pretreatment. The information obtained in the semi-quantitative (S-Q) mode can be used to assess, rapidly, the concentration range of an element in a sample prior to a full quantitative analysis which can itself be performed by the slurry atomisation technique. Concentration values within a factor of two or three of the known values were generally obtained using the rapid S-Q mode and if threshold values are

all that is required further analysis may not be necessary. The use of rhodium as an internal standard has proved to be a suitable choice for the analysis of coals and soils by slurry atomisation ICP-MS and it is of note that its natural abundance is normally restricted to the low and sub ng  $g^{-1}$  range.

It is suggested, from a semi-quantitative measure of the contamination from the zirconia grinding medium used in the bottle and bead technique that, with the exception of zirconium, silicon and hafnium, there is unlikely to be significant contamination for major, minor and very minor elements. Trace levels of aluminium, iron and titanium contamination may occur.

8.2. FUTURE WORK

Further improvements upon the grinding efficiency of the techniques used would be an advantage. The reduction of the maximum particle size of a hard, refractory material to below 5  $\mu$ m, with grinding times of less than 20 minutes, and with little or no contamination has yet to be realised. Some benefit may be gained from using the microniser and bottle and bead methods with tungsten carbide grinding media of the same physical form and size as those already employed <u>i.e.</u> cylinders and beads. Tungsten carbide (WC) is harder (MOH 9+) and denser (15.6 g cm<sup>-3</sup>) than zirconia and agate. A reduction in the grinding time for a hard sample would therefore be expected using WC media due to the increased momentum from each cylinder and bead, while maintaining a comparable collision frequency to that seen with the present grinding media.

The measurement of aerosol population and volume distributions by laser techniques may help in the design and production of efficient sample introduction systems for particular applications in ICP-AES and ICP-MS. The information gained may be used in the construction of small volume spray chamber/nebuliser systems for flow injection techniques (171, 172), including the analysis of slurries (173), and for coupled HPLC systems. Flow injection techniques should be of benefit with ICP-MS as they may allow the introduction of high solids loading slurries without the problems of cone blockage.

While it has been shown that ultrafine slurries (less than 2 µm size), of up to 1% m/v solids loading, exhibit comparable mass transfer efficiencies (MTE) to those of solutions, the effect of increasing the slurry concentration upon the MTE is poorly understood. This applies to some fine (less than 6  $\mu m$  size) slurries where transportation differences may be seen even at relatively low (3% m/v and above) concentrations depending upon the ability of the slurry aerosol to representatively sample from the bulk. Further cascade impactor experiments may help to clarify the boundary conditions (slurry loading, gas flow rates, particle size, density) to which the slurry technique using solution calibrants may be used. Near to full recoveries are frequently obtained for many elements using the technique of slurry atomisation - DCP-AES. This may be attributed to the sample introduction system (SPSC) and high dissolved solids content of the samples (due to buffer solution). The effect of a high dissolved salt content (e.g. 3% m/v), in the calibration solutions and slurry to be analysed (  $\langle 1\% m/v \rangle$ , upon the recovery of an analyte determined by SA-ICP-AES requires investigation. By near matching of the viscosity, surface tension, density and mass flux the transport properties of slurries are less likely to be influenced by the presence

of particulate matter at low concentration and would compare with the solution calibrants. By also near matching of the heat capacities of the solution and slurry aerosols differences in atomisation efficiency may be reduced. The possibility of using releasing agents <u>i.e.</u> dissolved materials which improve the volatility of species in a thermal environment by chemical modification, should also be investigated with regard to the analysis of refractory materials by the slurry atomisation technique.

Due to the accompanying transport phenomena, the estimation of the relative (to solution) efficiency of atomisation for a slurry particle, directly from emission data is a difficult task. An alternative to using ion-exchange/adsorption techniques may be found from using molecular emission spectra. Internal standardisation, using a dissolved salt, with a low concentration (not greater than 1% m/v) slurry of fine (below 6 µm) particle size should allow any major transportation differences between the slurry and calibration solution to be quantified. The measurement of the concentration of a diatomic molecular species (from the emission band head) produced by one element in the slurry solid and another from solution compared with the same molecular species formed from solution only may indicate the relative degree of atomisation of the slurry solids, <u>e.g.</u>  $Al_20_3$  (solid) +  $S0_4^{2-}$ (solution) to give AlS (427.54 nm band head (0-0)). Such an examination may also help to identify the particle size region where, for a particular type of material, the atomisation efficiency and/or transport efficiency is the dominant cause of reduced recoveries using the slurry technique. This may also be applied to slurry materials whose boiling points are in excess of the value of  $T_{rot}$ , determined in this thesis, but whose particle size range exceeds 2.5  $\mu m.$ 

Removal of reduced atomisation effects, seen with some materials, may be brought about if the kinetic temperature of the plasma is raised. While there is evidence from the literature to suggest that mixed coolant gas plasmas do not significantly improve the analytical capability of ICP-AES (174), the same cannot be said when the gas mixture is added to the carrier flow. An evaluation is therefore needed of the effects of adding gases such as hydrogen, oxygen, nitrogen and certain fluorocarbons, upon the relative atomisation and excitation mechanisms of slurry and solution aerosols within the analyte channel of the ICP. Of particular interest will be the results from hydrogen addition as this gas should increase the thermal conductivity of the central channel and may, therefore, thermalise the analyte plasma.

# REFERENCES

| 1  | Mondadori, A., "Rocks and Minerals", Macdonald and Co., London          |
|----|---|
|    | . <sup>1983.</sup>  |
| 2  | Van Loon, J.C., Anal. Chem., 1980, <u>52</u> , 955A.                    |
| 3  | Greenfield, S., Hieftje, G.M., Omenetto, N., Scheeline, A. and          |
|    | . Slavin, W., Anal. Chim. Acta, 1986, <u>180</u> , 69.                  |
| 4  | Adams, F., Gijbels, R. and Van Grieken, R., "Inorganic Mass             |
|    | Spectrometry", John Wiley and Sons, New York, 1988.                     |
| 5  | Bacon, J.R. and Ure, A.M., Analyst, 1984, <u>109</u> , 1229.            |
| 6  | Jenkins, R., Gould, R.W. and Gedcke, D., "Quantitative X-Ray            |
|    | Spectrometry", Marcel Decker Inc., New York, 1981.                      |
| 7  | Schwenke, H., Adv. X-Ray Anal., 1984, <u>28</u> , 79.                   |
| 8  | Iida, A., Nucl. Inst. Methods Phys. Res., 1986, A246, 736.              |
| 9  | Langmyhr, F.J., Analyst, 1979, <u>104</u> , 993.                        |
| 10 | Mohamed, N. and Fry, R.C., Anal. Chem., 1981, <u>53</u> , 450.          |
| 11 | Fry, R.C. and Denton, M.B., Anal. Chem., 1977, <u>49</u> , 1413.        |
| 12 | Fuller, C.W., Analyst, 1976, <u>101</u> , 961.                          |
| 13 | Ebdon, L. and Pearce, W.C., Analyst, 1982, <u>107</u> , 942.            |
| 14 | Ebdon, L. and Parry, H.G.M., J. Anal. At. Spectrom., 1987, <u>2</u> ,   |
|    | 131.  |
| 15 | Ebdon, L., "An Introduction to Atomic Absorption Spectroscopy",         |
|    | Heyden, London, 1982.   |
| 16 | Brackett, J.M. and Vickers, T.J., Spectrochim. Acta, 1982, <u>37B</u> , |
|    | 841.  |
| 17 | Harrison, W.W., Hess, K.R., Marcus, R.K. and King, F.L., Anal.          |
|    | Chem., 1986, <u>58</u> , 341.   |
| 18 | Grimm, W., Spectrochim. Acta, 1968, <u>23B</u> , 443.                   |
| 19 | McDonald, D.C., Spectrochim. Acta, 1982, 37B, 747.                      |

| 20              | Aston, F.W., "Mass Spectra and Isotopes", Longmans, Green, New            |
|-----------------|---|
|                 | York, 1942.   |
| 21              | Slevin, P.J. and Harrison, W.W., Appl. Spectrosc. Rev., 1975, <u>10</u> , |
|                 | 201.  |
| 22              | Harrison, W.W. and Bentz, B.L., Prog. At. Spectrosc., 1988, <u>11</u> ,   |
|                 | 53.   |
| 23              | Harrison, W.W., J. Anal. At. Spectrom. 1988, <u>3</u> , 867.              |
| 24              | Mai, H. and Scholze, H., Spectrochim. Acta, 1987, <u>42B</u> , 1187.      |
| 25 <sup>°</sup> | Thompson, M. and Walsh, J.N. "A Handbook of Inductively Coupled           |
|                 | Plasma Spectrometry", Blackie, Glasgow, 1983.                             |
| 26              | Greenfield, S., McGeachin, H. McD. and Smith, P.B., Talanta,              |
|                 | 1976, <u>23</u> , 1.  |
| 27              | Dagnell, R.M., Smith, D.J., West, T.S. and Greenfield, S., Anal.          |
|                 | Chim. Acta, 1971, <u>54</u> , 397.  |
| 28              | Hoare, W.C. and Mostyn, R.A., Anal. Chem., 1967, <u>39</u> , 1153.        |
| 29              | Ng, K.C., Zerezghi, M. and Caruso, J.A., Anal. Chem. 1984, <u>56</u> ,    |
|                 | 417.  |
| 30              | Allen, M.G. and Coleman, D.M., Appl. Spectrosc., 1987, <u>41</u> , 381.   |
| 31              | Meyer, G.A. and Barnes, R.M., Spectrochim. Acta, 1985, <u>40B</u> , 893,  |
| 32              | Kantor, T., Spectrochim. Acta, 1983, <u>38B</u> , 1483.                   |
| 33              | Matusiewicz, H., J. Anal. At. Spectrom., 1986, <u>1</u> , 171.            |
| 34              | McLeod, C.W., Clarke, P.A. and Mowthorpe, D.J., Spectrochim.              |
|                 | Acta, 1986, <u>41B</u> , 63.  |
| 35              | Thompson, M., Chenery, S. and Brett, L, J. Anal. At. Spectrom.,           |
|                 | 1989, <u>4</u> . 11.  |
| 36              | Su, G. and Lin, S., J. Anal. At. Spectrom., 1988, <u>3</u> , 841.         |
| 37              | Date, A.R. and Gray, A.L., "Applications of Inductively Coupled           |
|                 | Plasma-Mass Spectrometry", Blackie, Glasgow, 1989.                        |
| 38              | Hall, G.E.M., Park, C.J. and Pelchat, J.C., J. Anal. At.                  |
|                 | Spectrom., 1987, <u>2</u> , 189.  |

•

.

.

- 39 Gray, A.L., Analyst, 1985, 110, 551.
- 40 Williams, J.G., Gray, A.L., Norman, P. and Ebdon, L, J. Anal. At. Spectrom., 1987, <u>2</u>, 469.
- 41 Ebdon, L., Foulkes, M.E., Parry, H.G.M. and Tye, C., J. Anal. At. Spectrom., 1988, <u>3</u>, 753.
- 42 Decker, R.J., Spectrochim. Acta, 1980, 35B, 19.
- 43 Sparkes, S.T. and Ebdon, L., J. Anal. At. Spectrom., 1988, <u>3</u>,
   563.
- 44 Sparkes, S.T. and Ebdon, L., Anal. Proc., 1986, 23, 410.
- 45 Gilbert, P.J., Anal. Chem. 1962, <u>34</u>, 1025.
- 46 Schrenk, W.G., Appl. Spectrosc., 1986, <u>40</u>, xix.
- 47 Willis, J.B., Anal. Chem., 1975, 47, 1752.
- 48 Fuller, C.W., Hutton, R .C. and Preston, B., Analyst, 1981, <u>106</u>,
  913.
- 49 Stupar, J. and Ajlec, R., Analyst, 1982, <u>107</u>, 144.
- 50 Wichman, M.D., Fietkau, R. and Fry, R.C., Appl. Spectrosc., 1986, <u>40</u>, 233.
- Mohamed, N., McCurdy, D.L, Wichman, M.D., Fry, R.C. and O'Reilly,
   J.E., Appl. Spectrosc., 1985, <u>39</u>, 979.
- 52 Ebdon, L. and Parry, H.G.M., J. Anal. At. Spectrom., 1988, <u>3</u>, 131.
- 53 Ebdon, L. and Lechotycki, A., Microchem. J., 1986, 34, 340.
- 54 Ebdon, L. and Lechotycki, A., Microchem. J., 1987, <u>36</u>, 207.
- 55 Mohamed, N., Brown, R.M. and Fry, R.C., Appl. Spectrosc., 1981, 35, 153.
- 56 McCurdy, D.L., Wichman, M.D. and Fry, R.C., Appl. Spectrosc., 1985, <u>39</u>, 984.
- 57 Vien, S.H. and Fry, R.C., Appl. Spectrosc., 1988, <u>42</u>, 381.
- 58 Ebdon, L. and Cave, M.R., Analyst, 1982, <u>107</u>, 172.

- 59 Bittencourt, J.A., "Fundamentals of Plasma Physics", Pergamon Press, Oxford, 1986.
- 60 Criem, H.R., "Plasma Spectroscopy" McGraw Hill, New York, 1964.
- 61 Sharp, B.L., Selected Annual Reviews of the Analytical Sciences, 1976, 4, 37 (Chem. Soc., London).
- 62 Boumans, P.W.J.M. "Inductively Coupled Plasma Emission Spectroscopy" Part 2 - Applications and Fundamentals, J. Wiley and Sons, New York, 1987.
- 63 Reed, T.B., J. Appl. Phys., 1961, <u>32</u>, 821.
- 64 Reed, T.B., J. Appl. Phys., 1961, <u>32</u>, 2534.
- 65 Reed, T.B., International Science and Technology, June 1962, 42.
- 66 Greenfield, S., Jones, I., and Berry, C.T., Analyst, 1964, <u>89</u>, 713.
- 67 Wolcott, J.F. and Sobel, C.B., Appl. Spectrosc., 1978, 32, 591.
- 68 Saba, C.S., Rhine, W.E. and Eisentraut, K.J., Anal. Chem., 1981, 53, 1099.
- 69 Wilkinson, J.R., Ebdon, L. and Jackson, K.W., Anal. Proc., 1982, 19, 305.
- 70 Babington, R.S., Pop. Sci., 1973, May, 102.
- 71 Ebdon, L., Cave, M.R. and Mowthorpe, D.J., Anal. Chim. Acta, 1980, <u>115</u>, 179.
- 72 Sugimae, A. and Mizoguchi, T., Anal. Chim. Acta, 1982, 144, 205.
- 73 Spiers, G.A., Dudas, M.J. and Hodgins, L.W., Clays Clay Miner., 1983, <u>31</u>, 397.
  - 74 Watson, A.E. and Moore, G.L., S. Afri. J. Chem., 1984, <u>37</u>, 81.
  - 75 Mackey, J.R. and Murphy, W.J., Zeolites, 1985, 5, 233.
  - 76 Algeo, J.D., Heine, D.R., Phillips, H.A., Hoek, F.B.G., Schneider, M.R., Freelin, J.M. and Denton, M.B., Spectrochim. Acta, 1985, <u>40B</u>, 1447.
  - 77 Watson, A.E., S. Afri. J. Chem., 1986, <u>39</u>, 147.

- 78 Moore, G.L., Humphries-Cuff, P.J. and Watson, A.E., Spectrochim. Acta, 1984, <u>39B</u>, 915.
- 79 McCurdy, D.L. and Fry, R.C., Anal. Chem., 1986, <u>58</u>, 3126.
- 80 Ebdon, L. and Wilkinson, J.R., J. Anal. At. Spectrom., 1987, <u>2</u>, 39.
- 81 Ebdon, L. and Wilkinson, J.R., J. Anal. At. Spectrom., 1987, <u>2</u>, 325.
- 82 Ebdon, L. and Collier, A., Spectrochim. Acta, 1988, 43B, 355.
- 83 Ebdon, L. and Collier, A., J. Anal. At. Spectrom., 1988, 3, 557.
- 84 Halicz, L. and Brenner, I.B., Spectrochim. Acta, 1987, 428, 207.
- 85 Verbeek, A.D. and Brenner, I.B., J. Anal. At. Spectrom, 1989, <u>4</u>,
   23.
- 86 Foulkes, M.E., Ebdon, L. and Hill, S., Anal. Proc., 1988, 25, 92.
- 87 Broekaert, J.A.C., Leis, F., Raeymaekers, B. and Zaray, G.Y., Spectrochim. Acta, 1988, <u>43B</u>, 339.
- 88 Raeymaekers, B., Graule, T., Broekaert, J.A.C., Adams, F. and Tschopel, P., Spectrochim, Acta, 1988, 43B, 923.
- 89 Browner, R.F. and Boorn, A.W., Anal. Chem., 1984, 56, 786A.
- 90 Matthews, G.P., 'Experimental Physical Chemistry', Clarendon Press, Oxford, 1985.
- 91 Wood, C.W. and Holliday, A.K. 'Physical Chemistry', Butterworths, London, 1971, 3rd Edition, 327.
- 92 Levitt, B.P., 'Findlays Practical Physical Chemistry', Longman, London, 1981, 9th Edition, 370.
- 93 Parfitt, G.D., 'Dispersion of Powders in Liquids', Halsted Press (J Wiley Inc), New York, 1973.
- 94 Allen, T., 'Particle Size Measurement', Chapman and Hall, London, 1981.
- 95 Coulter, W. H., Proc. Natl. Elec. Conf. Chicago, 1956,12, 1034.
- 96 Norman, P., PhD. Thesis (Plymouth Polytechnic), CNAA, 1987.

- 97 Perry, J.H., and Chilton, C.H., 'Chemical Engineers Handbook' McGraw-Hill, New York, 1984.
- 98 Obenauf, R.H.and Bostwick, R., 'SPEX, Handbook of Sample Preparation and Handling' SPEX Ind., New Jersey, USA, 1985.
- 99 Weast R.C., 'Handbook of Chemistry and Physics', CRC Press, Cleveland, OH, 1979.
- 100 Parry, H.G.M., PhD. Thesis (Plymouth Polytechnic), CNAA, 1987.
- 101 Routh, M.W., Spectrochim. Acta, 1986, 41B, 39.
- 102 Cull, K.B., and Carnahan, J.W., Spectrochim. Acta, 1987, <u>42B</u>, 629.
- 103 Browner, R.F., and Novak, J.W., Anal. Chem., 1980, 52, 287.
- 104 Olsen, S.D., and Strasheim, A., Spectrochim. Acta, 1983, <u>38B</u>, 973.
- 105 Sharp, B.L., J. Anal. At. Spectrom, 1988, <u>3</u>, 613.
- 106 Layman, L.R., and Lichte, F.E., Anal. Chem., 1982, <u>54</u>, 638.
- 107 Fassel, V.A., and Bear, B.R., Spectrochim, Acta, 1986, 41B, 1089.
- 108 Vermeiren, K.A., Taylor, P.D.P., and Dams, R., J. Anal. At. Spectrom, 1988, 3, 571.
- 109 Sharp, B.L., J. Anal. At. Spectrom., 1988, <u>3</u>, 939.
- 110 Browner, R.F., Boorn, A.W., and Smith, D.D., Anal. Chem., 1982, 54, 1411.
- 111 Gustavsson, A., Spectrochim. Acta, 1984, 39B, 85.
- 112 Davies, C.N., Proc. Inst. Mech. Eng. Part B, 1952, <u>1B</u>, 185.
- 113 Talbot, J.H., J. Min. Vent. Soc. SA., 1974, 27, 11, 161.
- 114 Bachalo, W.D., Houser, M.J., and Smith, J.N., Atomisation-Spray Technol., 1987, <u>3</u>, 53.
- 115 Willis, J.B., Spectrochim. Acta, 1967, <u>23A</u>, 811.
- 116 Browner, R.F., and Boorn, A., Anal. Chem., 1982, <u>54</u>, 1402.
- 117 Kato, K., Fresenius Z. Anal. Chem., 1988, <u>329</u>, 861.
- 118 Sparkes, S.T., PhD Thesis (Plymouth Polytechnic), CNAA 1986.

- 119 Thompson, M and Ramsey, M.H., J. Anal. At. Spectrom., 1986, <u>1</u>, 185
- 120 Kovacic, N., Budic, B. and Hudnik, V., J. Anal, At. Spectrom., 1989, <u>4</u>, 33
- 121 Spendley, W., Hext, G.R. and Himsworth, F.R., Technometrics, 1962, <u>4</u>, 441.
- 122 Nelder, J.A. and Mead, R., Comput. J., 1965, 7, 308.
- 123 Deming, S.N. and Morgan, S.L., Anal Chim. Acta, 1983, 150, 183.
- 124 Ebdon, L., Norman, P. and Sparkes, S.T., Spectrochim. Acta, 1987, 42B, 619.
- 125 Ebdon, L., and Carpenter, R.C., Anal. Chim. Acta, 1987, 200, 551.
- 126 Belchamber, R.M., Betteridge, D., Wade, A.P., Cruickshank, A.J. and Davison, P., Spectrochim. Acta, 1986, 418, 503.
- 127 Allemand, C.D. and Barnes, R.M., Appl. Spectrosc, 1977, 31, 434.
- 128 Monnig, C. and Koirtyohann, S.R., Anal. Chem. 1985, <u>57</u>, 2533.
- 129 Pearse, R.W. and Gaydon, A.G., "The Identification of Molecular spectra", Chapman and Hall, 4th Edition, London, 1976, 41.
- 130 Reeves, R.D., Nikdel, S. and Winefordner, J.D., Appl. Spectrosc., 1980, <u>34</u>, 477.
- 131 Davies, J. and Snook, R.D., J. Anal. At. Spectrom, 1986, 1, 325
- 132 Murillo, M. and Mermet, J.M., Spectrochim. Acta, 1987, <u>42B</u>, 1151
- 133 Walker, Z. and Blades, M.W., Spectrochim. Acta, 1986, <u>41B</u>, 761
- 134 Kornblum, G.R. and de Galan, L., Spectrochim. Acta, 1977, 328, 71
- 135 Tang, Y.Q. and Trassy, C., Spectrochim. Acta, 1986, <u>41B</u>, 143
- Hasegawa, T. and Haraguchi, H., Spectrochim. Acta, 1985, <u>40B</u>, 1067
- Van Der Mullen, J.A.M., Raaijmakers, I.J.M.M., Van Lammeren,
   A.C.A.P., Schram, D.C., Van Der Sijde, B. and Schenkelaars,
   H.J.W., Spectrochim. Acta, 1987, <u>42B</u>, 1039
- 138 Boumans, P.W.J.M., Spectrochim. Acta, 1982, <u>37B</u>, 75

- 139 Boumans, P.W.J.M., "Theory of Spectrochemical Excitation", Hilger and Watts Ltd, Plenum press, New York, 1966
- 140 Dieke, G.H. and Crosswhite, H.M., J. Quant. Spectrosc. Radiat. Transfer, 1962, <u>2</u>, 97
- 141 Fleitz, P.A. and Seliskar, C.J., Appl. Spectrosc., 1987, 41, 679
- Hasegawa, T. and Winefordner, J.D., Spectrochim. Acta, 1987, <u>42B</u>,
  637
- 143 Seliskar, C.J., Miller, D.C. and Fleitz, P.A., Appl. Spectrosc., 1987, <u>41</u>, 658
- 144 Caughlin, B.L., and Blades, M.W., Spectrochim. Acta, 1987, <u>42B</u>, 353
- Long, S.E., Snook, R.D. and Browner, R.F., Spectrochim. Acta, 1985, <u>40B</u>, 553
- 146 Alder, J.F., Bombelka, R.M. and Kirkbright, G.F., Spectrochim. Acta, 1980, <u>35B</u>, 163
- Walters, P.E. and Barnardt C.A., Spectrochim. Acta, 1988, <u>43B</u>,
  325
- 148 Hieftje, G.M., Miller, R.M., Pak, Y. and Wittig, E.P., Anal. Chem., 1987, <u>59</u>, 2861
- .149 Belchamber, R.M. and Horlick, G., Spectrochim. Acta, 1982, <u>37B</u>, 17
- 150 Davies, J. and Snook, R.D., J. Anal. At. Spectrom., 1986, 1, 195.
- 151 Davies, J. and Snook, R.D., J. Anal. At. Spectrom., 1987, 2, 27.
- 152 Wendt, R.H. and Fassel, V.A., Anal. Chem., 1965, <u>37</u>, 920.
- 153 Davies, J. and Snook, R.D., Analyst, 1985, <u>110</u>, 887.
- 154 Davies, J. and Du, C.M., J. Anal. At. Spectrom., 1988, <u>3</u>, 433.
- 155 Kirkbright, G.F. and Sargent, M., 'Atomic Absorption and Fluorescence Spectroscopy', Academic Press, New York, 1974.
- 156 Bird, R.B., Stewart, W.E. and Lightfoot, E.M., 'Transport phenomena', Wiley, New York, 1960.

- 157 Gray, A.L., Proc. Soc. Anal. Chem., 1974, 11, 182.
- 158 Gray, A.L., Analyst, 1975, <u>100</u>, 289.
- Houk, R.S., Fassel, V.A., Flesch, G.D., Svec, H.J., Gray, A.L., and Taylor, C.E., Anal. Chem., 1980, <u>52</u>, 2283.
- 160 Gray, A.L., and Date, A.R., in Price, D., and Todd, J.F.J., Editors "Dynamic Mass Spectrometry", Volume 6, Heyden, London 1981.
- 161 Douglas, D.J., and French, J.B, Anal. Chem., 1981, 53, 37.
- 162 Date, A.R., and Gray, A.L., Analyst, 1981, <u>106</u>, 1255.
- 163 Gray, A.L., and Date, A.R., Analyst, 1983, <u>108</u>, 1033.
- 164 Date, A.R., and Gray, A.L., Analyst, 1983, <u>108</u>, 159.
- 165 Longerich, H.P., Fryer, B.J., Strong, D.F. and Kantipuly, C.J., Spectrochim. Acta, 1987, <u>42B</u>, 75.
- 166 Hutton, R.C and Eaton, A.N., J.Anal. At. Spectrom., 1988, 3, 547.
- 167 Munro, S., Ebdon, L., and McWeeny, D.J., J. Anal. At. Spectrom., 1986, <u>1</u>, 211.
- 168 Date, A.R., and Gray, A.L., Spectrochim. Acta, 1983, 38B, 29.
- 169 Lyon, T.B.D., Fell, G.S., Hutton, R.C., and Eaton, A.N., J.Anal. At. Spectrom., 1988, <u>3</u>, 601.
- 170 Crock, J.G., and Lichte, F.E., Anal. Chem., 1982, 54, 1329.
- 171 Christian, G.D. and Ruzicka, J., Spectrochim. Acta, 1987, <u>42B</u>, 157.
- 172 Greenfield, S., Spectrochim. Acta, 1983, 38B, 93
- 173 Ambrose, A., Ebdon, L., Foulkes, M.E., and Jones, P., J. Anal. At. Spectrom., 1989, <u>4</u>, 219
- 174 Zaray, G., Broekaert, J.A.C., Bohmer, R.G. and Leis, F., Talanta, 1987, <u>34</u>, 629

#### APPENDIX (i)

# COMPUTER PROGRAM TO CALCULATE % VOLUME-SIZE DISTRIBUTION FROM POPULATION-SIZE DISTRIBUTION.

```
1 REM mikel
  2 INFUT " sample number", S
  3 PRINT £2, TAB (12) "SAMPLE NUMBER", S
  4 PRINT £2, TAB (12) "-----"
  5 PRINT £2
  6 PRINT £2
  7 PRINT £2, TAB (1) "%. VOLUME", TAB (16) "DIA.microns"
  8 PRINT £2
  9 FRINT £2
 10 PRINT "HOW MANY RESULTS"
 20 INPUT X
 40 DIM A(X)
 SO DIM B(X)
 60 DIM C(X)
 70 DIM D(X)
 80 REM UM SIZE DATA MEANS
 90 A(1) := 1.44
100 FOR Y := 2 TO X - 1
    A(Y) := A(Y - 1) + 0.74
110
120 NEXT Y
130 REM ENTER VELOCITY NO- IN BIN
140 FOR Y := 1 TO X
      PRINT "VALUE OF VEL TOTAL FOR NO.", Y
.150
160
      INPUT B(Y)
161 NEXT Y
162 FRINT "DO YOU WISH TO CHANGE ANY VALUES"
163 PRINT "(Y/N)"
180 REM MEAN OF VELOCITY TOTALS
190 FOR Y := 2 TO X
200
      C(Y - 1) := (B(Y - 1) + B(Y)) / 2
210 NEXT Y
220 REM VOLUMES OF SPHERES OF DIAMETER A(Y)
240 FOR Y := 1 TO X - 1
    B(Y) := ( 3.141593 * (A(Y)) ^ 3) / 6
250
270 NEXT Y
280 REM SUM OF VOL OF SPHERES OF DIA. A(Y) IN BAND A(Y)
290 FOR Y := 1 TO (X - 1)
    D(Y) := B(Y) * C(Y)
300
310 NEXT Y
320 REM TOTAL NO. OF SPHERES BY SUMMATION
325 B(1) := D(1)
330 FOR Y := 2 TO X - 1
340
    B(Y) := B(Y - 1) + D(Y)
350 NEXT Y
360 \text{ S} := B(X - 1) : \text{ FRINT "SUM =", S}
370 FOR Y := 1 TO (X - 1)
280
      C(Y) := D(Y) * 100 / S
390 NEXT Y
400 \text{ FOR Y} := 1 \text{ TO } (X - 1)
      PRINT £2, C(Y), TAB (16) A(Y)
410
```

# COMPUTER PROGRAM TO CALCULATE & VOLUME-SIZE DISTRIBUTION FROM POPULATION-SIZE DISTRIBUTION.

```
415
      PRINT C(Y), A(Y)
420 NEXT Y ...
430 M := X - 1
440 REM find c(y) maximum
451 FOR Y := 1 TO M
    D(Y) :≕ C(Y)
452
453 NEXT Y
460 FOR Y := 1 TO M - 1
    IF D(Y) > D(Y + 1) THEN D(Y + 1) := D(Y)
470
480 NEXT Y
490 Z := (2 + INT(1 + D(H)))
500 SET MODE 80, 41, Z
510 SET ORIGIN 4, 1.5
515 L := - 1.5
517 IF M > 35 THEN L := - 1
520 LINE 0, 0; 41, 0
530 LINE 0, 0; 0, Z
531 PLOT "DIA. microns", 15, L
532 PLOT "VOL", - 3, Z / 2.3
533 PLOT "%", - 2, (Z / 2.3) - 0.5
540 FOR X := 0 TO 37 STEP 2
545
      SET POINTS STYLE 2
550
      Y := 0
      POINTS X, Y
560
570 NEXT X
571 FOR Y := 0 TO Z - 2 STEP 0.5
      SET POINTS STYLE 2
572
573
      X := 0
574
      POINTS X, Y
575 NEXT Y
580 FOR Y := 1 TO M
590
      SET POINTS STYLE 2
600
      FOINTS A(Y), C(Y)
610 NEXT Y
620 DIM A#(10)
630 FOR 1% := 0 TO 9
640
      READ AF(IX)
650 NEXT 1%
660 DATA "0","4","8","12","16","20","24","28","32","36"
670 FOR A := 0 TO 9
680
      Y := - 1
681
      IF N > 22 THEN Y := - 0.75
      IF M > 35 THEN Y := - 0.5
682
     PLOT A$(A), (4 % A) -
690-
                              0.25. Y
700 NEXT A
710 DIM B#(16)
720 FOR 1% := 0 TO (Z - 2)
730
      READ B#(IX)
740 NEXT 1%
745 DATA "0","1","2","3","4","5","6","7","8","9","10"
746 DATA "11","12","13","14","15","16"
750 FOR B := 0 TO (Z - 2)
750 FLOT B≢(B), - 1, B - 0.15
770 NEXT B
```

MEETINGS OF THE ROYAL SOCIETY OF CHEMISTRY

- (i) Joint Analytical Division and the Atomic Spectroscopy Group meeting, October, 1985, 'Sample Introduction and the ICP', University of Bristol.
- Joint Analytical Division and Special Techniques
   Group meeting, 4th December, 1985, 'Mineral
   Analysis', New Burlington Place, London.
- (iii) Joint Analytical Division and Particle Size Analysis Group meeting, 19th March, 1986, 'Electrical Sensing Zone Method for Particle Size Analysis', Chilton Hotel, Luton.
- (iv) Analytical Division Symposium, 15th April, 1986,
   'Atomic Spectroscopy Updates', Sheffield City
   Polytechnic.
- (v) Analytical Division meeting, 16th and 17th April, 1986, 'Research and Development Topics in Analytical Chemistry', UCL, London.
- (vi) Analytical Division joint meeting, 'SAC 86 International Conference and Exhibition on Analytical Chemistry' together with 'Third Biennial National Atomic Spectroscopy Symposium', 20th-26th July, 1986, University of Bristol.
- (vii) Joint Analytical Division and Atomic Spectroscopy Group meeting, 9th December, 1986, 'Atomic Spectroscopy – Problems with Real Samples', New Burlington Place, London.

lb

- (viii) Atomic Spectroscopy Group AGM, 16th December, 1986, 'Combination techniques in Analytical Atomic Spectroscopy', Imperial College, London.
- (ix) Analytical Division meeting, 8th and 9th July, 1987, 'Research and Development Topics in Analytical Chemistry', University of Strathclyde.
- (x) Joint Analytical Division and the Atomic Spectroscopy Group meeting, 3rd September, 1987, 'New Perspectives in Atomic Spectroscopy', Plymouth Polytechnic.
- (xi) Joint Analytical Division, Western Region and Chemometrics Group meeting, 29th October, 1987, 'What can Chemometrics do for you', University of Bristol.
- (xii) Joint Analytical Division and Atomic Spectroscopy Group/Molecular Spectroscopy Group meeting, 29th March, 1988. 'Recent advances in Atomic and Molecular Spectroscopy', University of Hull.
- (xiii) Analytical Division joint meeting with the Atomic Spectroscopy Group. 'Fourth Biennial National Atomic Spectroscopy Symposium', 29th June-1st July, 1988, University of York.
- (xiv) Analytical Division Meeting, 18th and 19th July, 1988, 'Research and Development Topics in Analytical Chemistry', Plymouth Polytechnic.

2 b

### LECTURES AND ASSOCIATED STUDIES

- (i) RSC lecture, 1st November, 1985, Plymouth Polytechnic, Dr D.T.E. Hunt, 'Trace Element Speciation in Aquatic Systems'.
- (ii) RSC lecture, 7th February, 1986, Plymouth Polytechnic, Professor A.F. Fell, 'Snapshot Chromatography - Biomedical applications of New Technology in HPLC'.
- (iii) RSC lecture, 7th March, 1986, Plymouth Polytechnic, Dr P. Campion, 'The Chemistry of PWR and AGR Nuclear Power Reactor Coolant'.
- (iv) Departmental Colloquium, 18 July, 1986, Plymouth Polytechnic, Dr C. Monnig, 'Tomographic Reconstruction for Diagnosis of Spectroscopic Sources'.
- (v) RSC 'Plasma Spectrometry School', 29th Septemberlst October, 1986, Loughborough University of Technology.
- (vi) RSC lecture, 30th October, 1986, Plymouth Polytechnic, Dr J.D.R. Thomas, 'Liquid and Enzyme Membrane Electrodes'.
- (vii) RSC lecture, 23rd January, 1987, Exeter University, Professor J. Miller, 'Illumination in Analytical Chemistry'.

lc

- (viii) RSC lecture, 29th January, 1987, UMIST, Cardiff, Dr K.W.C. Burton, 'Optimisation and Pattern Recognition'.
- (ix) RSC lecture, 20th February, 1987, Plymouth Polytechnic, Dr A. Ure, 'Atomic and Ion Spectra'.
- (x) SERC Vacation School, 13-18th September, 1987,UMIST, 'Instrumentation and Analytical Science'.
- (xi) RSC lecture, 13th November, 1987, Plymouth Polytechnic, Dr A. Howard, 'Speciation'.
- (xii) RSC lecture, 29th January, 1988, Plymouth Polytechnic, Professor A. Townsend, 'Flow Injection Analysis - the first decade'.
- (xiii) RSC lecture, 5th February, 1988, Plymouth Polytechnic, Professor D. Bryce-Smith, 'Environmental Influences on the Way we Think and Act'.

# PRESENTATIONS AND PUBLICATIONS

Resulting from the work reported in this thesis the following papers have been presented and published.

- (a) Presentations
- "Analysis of ores and minerals by Slurry Atomisation-Plasma Emission Spectrometry". Poster presentation at the Research and Development Topics in Analytical Chemistry meeting, University of Strathclyde, July 1987.
- 2. "Rapid Semi-Quantitative analysis of slurries by ICP-MS". Poster presentation at the Atomic Spectroscopy Group and Western Region conference on "New Perspectives in Atomic Spectroscopy", Plymouth Polytechnic, September, 1987.
- 3. "Some fundamental studies of Slurry Atomisation-Plasma Emission Spectrometry". Paper presented at the Fourth Biennial National Atomic Spectroscopy Symposium, University of York, June 1988.
- 4. "Slurry transportation and atomisation phenomena in the inductively coupled plasma". Poster presented at the Research and Development Topics in Analytical Chemistry meeting, Plymouth Polytechnic, July 1988.

- Foulkes, M.E., Ebdon, L. and Hill, S.J.
   "Ore and Mineral Analysis by Slurry Atomisation-Plasma Emission Spectrometry".
   Anal. Proc., 1988, 25, 92.
- Ebdon, L., Foulkes, M.E., Parry, H.G.M. and Tye, C.T.
   "Direct Atomic Spectrometric Analysis by Slurry Atomisation. Part 7. Analysis of Coal using Inductively Coupled Plasma Mass Spectrometry".
   J. Anal. At. Spectrom., 1988, 3, 753.
- 3. Ebdon, L., Foulkes, M.E., and Hill, S. "Direct Atomic Spectrometric Analysis by Slurry Atomisation. Part 10. Fundamental Studies of Refractory Samples".

J. Anal. At. Spectrom., 1989, In the Press.

- 4. Ebdon, L. and Foulkes, M.E. "Fundamental Studies of Slurry Atomisation in the Inductively Coupled Plasma". Chemia Analytyczna, 1989, In the Press.
- 5. Ebdon, L. and Foulkes, M.E. "Fundamental and Comparative Studies of Aerosol Sample Introduction for Solutions and Slurries in Atomic Spectrometry". Microchem. J., 1989, In the Press.

2 d