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SPARKES, SIMON TIMOTHY

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A thesis entitled

AGRICULTURAL ANALYSIS BY PLASMA EMISSION SPECTROSCOPY

WITH SLURRY ATOMISATION

presented by

SIMON TIMOTHY SPARKES, B.Sc.

in part fulfilment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

of the

COUNCIL FOR NATIONAL ACADEMIC AWARDS

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Agricultural Analysis by Plasma Emission Spectroscopy

with Slurry Atomisation

Simon Timothy Sparkes

Abstract

The three electrode direct current plasma (DCP), has been investigated for the analysis of samples introduced using aqueous solution nebulisation, hydride generation and slurry atomisation. For aqueous solutions, simplex optimisation with signal to background ratio as the criterion of merit, vertical viewing position was found to be most critical.

A continuous-flow hydride generator was interfaced to the DCP <u>via</u> a modified sample introduction chimney. Optimisation indicated that total sample introduction gas flow rates were essentially similar to those for conventional nebulisation and that vertical viewing position was again critical. Generation conditions for lead hydride were also simplex optimised. Acid, sodium hydroxide, and hydrogen peroxide concentration were all found to be critical. Detection limits for hydride generation were: As 4 ng cm⁻³, Se 4 ng cm⁻³, Pb 10 ng cm⁻³. Arsenic and selenium were accurately determined in various reference materials.

The determination of Mg in aqueous slurries of kaolin was optimised using the Mg(II) 279.079 nm line and conventional sample introduction. Vertical viewing position was again critical with the optimum on the boundary of the analytical zone and over the plasma core. A reduction of emission intensity at high slurry concentrations (> 12%), was observed.

Particle size was the most important parameter in slurry atomisation, < 5 µm being preferred. Soils, milk, plant materials and sewage sludges were successfully analysed by slurry atomisation. Where necessary, particle size was reduced using simple grinding procedures. For fibrous materials, prior matrix carbonisation was advantageous. Results obtained using these procedures and simple aqueous calibration showed excellent agreement with certified values of reference materials.

Electron number density (n), excitation temperature (T) and ionisation temperature (T), were measured for two series of kaolin slurries, (1-20% m/V), one containing 5 g l⁻¹ lithium as enhancement buffer. For the slurries containing added lithium, T and n were found to be reduced with increasing slurry concentration. Observed decreases in analyte emission with increased sample loadings (> 12%), are considered to be consistent with proposed excitation models.

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CHAPTER 1

INTRODUCTION

1.1 Overview of Agricultural Analysis for Metals

1.1.1 The Need for Metal Determinations

The determination of both major and trace levels of elements in materials such as soils, crops and animal feeds has long been of interest to the agriculturalist. The reasons for these analyses are varied, however they can be summarised into two main areas, firstly there are determinations regarding deficiencies of elements, and secondly determinations regarding excess levels of elements. Reviews relevant to this subject area have been produced by Bowen (1), by Ure and Berrow (2) with regard to the elemental constituents of soils and by Kabata-Pendias and Pendias (3) concerning trace elements in soils and plants.

As indicated above, many analyses are performed to monitor the nutrient status of either the soil for plant crops or of plant material as food. Of the macronutrients, Ca, Mg, Na, K, and P are routinely monitored, as are the micronutrients, Co, Cu, Fe, Mn, Mo, and Zn, although the elements determined will vary from sample to sample . In addition to the above, determinations of any potentially toxic elements are frequently made with Cd, Cu, Ni, Pb, Zn, As, and Se being typical examples.

The levels of interest for these elements ranges from the low % m/m for the macronutrients, to the $\mu g g^{-1}$ level for essential and toxic trace. elements in soils and to ng g^{-1} levels when the concern is about element deficiencies in soils or crops. The techniques used for these analyses are primarily applied to solution samples. For plant material the sample

-1-

is often dissolved using a mixture of acids, <u>e.g</u> nitric and perchloric acids, or by dry ashing at high temperature followed by dissolution of the ash, using for example hydrochloric acid. With soils, interest conventionally centres on various extraction procedures, in an attempt to assess the levels of elements present available for uptake via plant root systems, as opposed to total soil content where a considerable fraction of the element may be immobilised in the inorganic matrix of the soil. Sample preparation procedures for a range of sample materials as used in routine determinations can be found in HMSO publications (4,5), aspects of which are summarised in Table 1.

The solution samples so prepared can then be used for the spectrophotometric determination of the analyte element by the formation of a strongly absorbing coloured complex, or more recently by the use of atomic spectrometry. The main disadvantages of the colourimetric procedures are the time required for the analysis and interferences arising from concomitant elements or compounds, however, many of these procedures have been widely used, and some successfully developed for automated systems. Interest in the techniques of atomic spectrometry for these element determinations has developed in response to these problems, providing rapid analytical techniques that are element specific and relatively free from interferences.

1.1.2 Atomic Spectrometry in Agricultural Analysis

The techniques available for performing these metal determinations have recently been reviewed (6), with flame atomic absorption spectrometry (flame AAS) being described as the most ubiquitous technique available for the determination of many of these elements, providing an inexpensive,

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TABLE 1

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Summary of Routine Sample Preparation Procedures for Agricultural Materials (4,5)

Element	<u>Matrix</u>	Procedure
Mg, K, Na	Soil	Extract approx. lOg soil with lM ammonium nitrate (50 cm ³) for 30 minutes.
Cd, Co, Pb, Ni, Zn	Soil	Extract approx. 5g soil with 0.5M acetic acid (200 cm ³) for 16 hours.
Cd, Cu, Mn, Ni, Pb, Zn	Soil	Extract 15g soil with 0.05M ethyl- diaminetetraacetic acid (75 cm ²) for 1 hour.
Cd, Co, Cu, Pb, Ni, Zn	Soil	Heat 1g soil in 1+4 perchloric/nitric acid mixture (10 cm ³). Carefully take to dryness, cool, add 6M HC1 (4 cm ³). Make to volume then filter extract.
Cd, Co, Cu, Pb, Ni, Zn, Mg, Mo, P, Na, K	Plant Material	Heat gently 2g sample in 1+4 perchloric/nitric acid mixture (30 cm ³). Carefully take to dryness, cool, add ₃ 2M HCl (10 cm ³), boil, make to 50 cm ³ .
P	Soil	Extract 5g soil with 100 cm ³ sodium bicarbonate solution (pH 8.5) at 20°C for 30 minutes.
Se	Plant Material	Heat 2g sample in 1+4 perchloric/ nitric acid mixture (30 cm ³) gently to produce white fumes. Cool, add 6M HCl (5 cm ³), make to 50 cm ³ .

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sensitive and element specific analytical technique allowing determinations at the $\mu g g^{-1}$ level to be made rapidly and with good precision. By replacing the air-acetylene flame atom cell with an electrothermal atomizer the sensitivity of atomic absorption spectrometry can be considerably extended. Using this technique a small aliquot of sample is placed into the graphite tube of the atomizer which is then electrically heated to the required temperature, allowing analytical measurement to be made. This technique readily allows determinations in the ng g⁻¹ region to be made, however the technique is slow compared to flame AAS and susceptible to complex matrix effects which can result in corruption of the true analytical signal. Examples of applications of this technique for agricultural analysis can be found in the literature (7,8).

Hydride generation techniques, where the analyte is introduced into the atom cell in a gaseous form, have been found to be useful in particular for the determination of arsenic and selenium. These techniques are prone to two major problems, firstly the generation of the volatile species is critically dependant upon acid concentration in the sample solution (9) and secondly, severe interferences occur in the generation stage when high levels (10-100 μ g cm⁻³) of transition metals are present in solution (10).

At present, atomic absorption spectrometry, because of its element specific nature, simplicity and relatively low cost is the primary technique used for many of thses metal analyses in agricultural materials (6).

The more recently introduced techniques of atomic emission spectrometry using both the inductively coupled plasma (ICP) and direct current plasma (DCP) sources offer several potential benefits in agricultural analysis.

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These techniques offer superior powers of detection to flame AAS for most elements, long linear dynamic ranges, typically at least 5 orders of magnitude, which combined with a multielement determination capability can allow simultaneous determination of elements at major and trace levels, and as a consequence of the high temperature of these sources (ICP 8000 K, DCP 5500-6000 K) freedom from chemical interferences plus an ability to determine elements such as boron and phosphorus with adequate sensitivity.

The application of these techniques is becoming accepted when using the extraction and decomposition techniques outlined previously, with studies showing good agreement with alternative techniques for samples such as soil extracts (7, 11-15) in fertilizers (16-18) and in plant materials (12, 13, 19-22). As with atomic absorption spectrometry, the limitations on sensitivity for elements such as arsenic and selenium can be overcome using hydride generation techniques (23) although again restrictions imposed by acid concentrations can impair the simultaneous multielement capability of the emission techniques (24).

Although initially designed as techniques for application to solution samples, the versatility of these devices is such that it has been suggested that it may be possible to introduce solid samples and so allow the full benefits of these excitation sources to be achieved. The advantages of solid sample analysis include significant reductions in sample preparation time, reductions in potential sample dissolution hazards <u>e.g.</u> the use of perchloric and hydrofluoric acids, minimal analyte loss and reductions in contamination. In addition to these benefits this approach has the potential to reduce the cost of the analysis.

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As this work deals with the use of plasma emission sources for the analysis of agricultural materials, including solid sample introduction, summaries of atomic emission theory and of the analysis of solid samples follow.

1.2 Theory of Emission Spectrometry

Detailed reviews on the theoretical basis of emission spectrometry have been made by Boumans (25), with additional contributions from Mandelshtam (26) and in particular Sharp (27). Emission spectrometry can be summarised into four basic stages:

- the formation of ground state atoms in the gaseous form in the excitation source;
- the transition of a certain number of these atoms into a higher energy excited state;
- 3) the spontaneous transition of these excited state atoms to a lower energy state with the emission of specific spectral line radiation;
- 4) the isolation of the spectral line of interest from the total source radiation and the transformation of this information into a measurable signal.

Considering first the transition of ground state atoms to the first excited state (<u>i.e.</u> a resonance transition), for a system approaching thermodynamic equilibrium the population of atoms in the excited state,

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 $\mathbf{n}_{\mathbf{p}}$, is given by the Boltzman distribution:

$$\frac{n_k}{N_i} = \frac{g_k}{g_i} \exp(-E_k/kT)$$
 1.1

where

ⁿ k	=	number of atoms in state k (excited state) per unit volume
N i	=	number of atoms in state i (ground state) per unit volume
g _k	=	statistical weight for state k
9 _i	=	statistical weight for state i
E	=	energy difference between states i and k (J)
k	÷	Boltzman constant (1.38 x 10^{-23} J K ⁻¹)
т	=.	Thermodynamic temperature (K)

To make this formula useful for analytical spectrometry it is necessary to relate the number of atoms present in the excited state to the total number of atoms present, that is, the concentration of the analyte species. The total concentration of atoms, N, is given by the sum of the concentrations in each state, thus

 $N = \sum_{\substack{i = 0 \\ i = 0}}^{i = m} n_i$ 1.2

where m is the highest state that must be considered in the summation.

Expressing the population of these states as a function of temperature known as the 'partition function',

$$i = m$$

 $Z(t) = \sum_{i=0}^{n} g_{i} \exp(-E_{i}/kT)$ 1.3

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hence

$$\frac{n_{k}}{N_{i}} = \frac{q_{k} \exp(-E_{k}/kT)}{i=m}$$

$$\sum_{i=0}^{1.4} g_{i} \exp(-E_{i}/kT)$$

$$= \frac{q_{k} \exp(-E_{k}/kT)}{2 (t)}$$
1.5

Looking at the next stage in the process, where the spontaneous transition of an atom from the excited state, k, of energy E_k to a lower energy state E_i results in emission of radiation. The energy of the transition is given by;

$$h v_{ki} = E_k - E_i \qquad 1.6$$

where h is Planck's constant (6.6 x 10^{-34} J s⁻¹) and \mathcal{V}_{ki} is the frequency of the emitted radiation. For a resonance transition, the lower energy level is the ground state and $E_i = 0$. The probability per second of the transition of an atom in the excited state to the ground state is given by the Einstein transition probability A_{ki} . Therefore the power radiated, P, from a discrete volume ΔV of the source is given by;

$$P = h \mathcal{D}_{ki} A_{ki} \Delta V n_{k}$$
 1.7

It is more useful to express this in terms of brightness, B, the power emitted per unit area per unit solid angle. Therefore dividing 1.7 by 4π to give the power per steradian and by unit area to give depth of the source (L) along the viewing axis gives;

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$$B = \frac{1}{4\pi} h \rho_{ki} L n_k \qquad 1.8$$

The emitted photons are not monochromatic but distributed over a range of frequencies distributed about the central frequency, \mathcal{V} . The spectral profile of the line is usually expressed in the form of a normalized integral (27) such that $\beta(\mathcal{V})d\mathcal{V}$ is that fraction of photons of frequencies in the range \mathcal{V} to $(\mathcal{V} + d\mathcal{V})$ and

$$\int_{\nu}^{\infty} \beta(\nu) \, \mathrm{d}\nu = 1 \qquad 1.9$$

so that B in equation 1.8 is the integrated output, which is analytically more significant as the bandpass of the spectrometer is usually greater than the width of the analytical line.

By substituting for n_k (from equation 1.5) into equation 1.9, a relationship between the brightness of the source and number of free analyte atoms can be made to give an approximate model for atomic emission sources;

$$B = \frac{1}{4\pi} h \mathcal{V}_{ki} A_{ki} \frac{N_i g_k \exp(-E_k/kT)}{Z(t)}$$
 1.10

In the equation it must be noted that the assumptions made in deriving this equation are for that of an 'ideal source' and that these assumptions do not apply in practice. However for a system in thermodynamic equilibrium and where self absorption is negligible, at low analyte concentrations a plot of B against N is predicted by equation 1.10 to be a straight line. In addition equation 1.10 indicates that B will increase rapidly with increasing temperature, hence a high temperature

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source should provide the best analytical sensitivity.

1.3 Solid Sample Analysis

1.3.1 The Direct Analysis of Solid Samples

In a review of direct analysis of solid samples by atomic absorption spectrometry (AAS), Langmyhr (28), described the advantages of the approach as being the removal or reduction of sample preparation procedures resulting in considerable savings of time, reductions of sample decomposition hazards and reductions in contamination and analyte loss. Van Loon (29) reviewed this area to include atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS), in addition to AAS, concluding that the higher temperatures of the AES sources combined with the simultaneous multielement capabilities of these systems made them particularly attractive for solid sample analysis.

Several analytical techniques for the analysis of solid samples exist and indeed, some find extremely widespread and important use for many analyses, particularly minerals and metallurgical samples. X-ray fluorescence spectrometry (XRF) is one such technique for solid sample analysis. A full description of the theory and practice of XRF has been given by Jenkins <u>et al.</u> (30). The technique is non-destructive allowing the sample to be retained for further analyses, with the material requiring straightforward preparation such as the formation of homogeneous pellets or powders. XRF, however, does suffer from a number of disadvantages. Sensitivity can be a serious limiting factor for trace determinations with detection limits lying in the $\mu g q^{-1}$ range

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as opposed to the ng g⁻¹ region. The intensity of the emitted line is not only related to the concentration of the excited element, but also upon the influence of other elements in the specimen. These matrix effects can be compensated for by calculation, however, accuracy may still suffer for certain determinations. For light elements <u>e.g.</u> Na, Mg, Al and Si the internal re-absorption of fluorescence radiation, the 'Auger effect' can seriously reduce x-ray intensity and hence impair the detection limits for these elements. As a result of these matrix effects, calibration is normally achieved using carefully matched standards, therefore a wide range of well characterized standards are required for accurate analyses.

In a recent review of analytical techniques for soil analysis (6) XRF was described as being of use in major element determinations and for rapid determination of elements such as sulphur. The technique is not however widely used as a matter of routine for agricultural analyses.

Traditionally arc emission spectrometry has been a major technique in the direct analysis of solid samples. With this technique, a continuous electrical discharge is maintained between two electrodes in an inert gas. Molecules and atoms in the discharge are ionized, forming a plasma from which radiation is emitted. Analytically, the sample in a conducting form forms one of the electrodes (normally anode) and the arc is struck. The technique has been extensively developed for metallurgical analysis, where the samples can readily become the electrodes. For non-conducting materials, the sample in powdered form is mixed with a conducting powder e.g. carbon to produce a suitable electrode.

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Although a technique suitable for the direct analysis of solid samples, arc emission spectrometry does suffer some disadvantages, the major problem being instability in the discharge. The intensity of the emission can vary depending on the sample matrix and electrode material, although the use of a suitable spectroscopic buffer and calibration using materials of similar composition to the samples can overcome many of these problems. The use of arc emission spectrometry for soil analysis has been reviewed (6), with the conclusion that in recent years, plasma sources for atomic emission spectrometry are being found to be more popular, however the d.c arc can still be of considerable use with investigations requiring rapid multielement determinations. Recent applications of the technique to soils and to soils and sewage sludges can be found in (31,32).

The technique of Spark Source Mass Spectrometry (SSMS), where an intermittant discharge is used to produce ions for mass spectrometric detection is again a technique suited to the analysis of solid samples. The technique has been extensively reviewed by Bacon and Ure (33), describing its advantages of wide multielement nature and powers of detection for a range of sample matrices. The primary disadvantages of the technique are calibration, requiring matrix-matched standards, analysis time and cost, however the technique can be attractive for multielement survey work, as shown for soil analysis (34, 35).

The use of atomic absorption spectrometry for the direct analysis of solid samples has met with varied success. Early attempts at the direct analysis of solid materials included introducing the material, mixed with a solid dispersing agent <u>e.g.</u> NaCl using an archimeadian screw both directly into the flame (35) or <u>via</u> a gas stream (36) were found to be

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unsatisfactory as was the direct introduction of pellets of material into the flame (37). These methods all suffered from poor reproducibility and sensitivity.

Following the work by L'Vov on the direct analysis of samples using electrothermal atomization (ETA) for AAS (38, 39), the technique has been applied with success to a range of materials (40-42). An appraisal of the direct analysis of metal alloys by this technique was made by Headridge (43). Disadvantages associated with this technique include high background absorption signals, small sample size, relatively poor precision and calibration problems. These techniques are also limited by the temperatures available in the atomiser which may only allow the more volatile elements to be determined.

The advantage of the higher temperatures offered by plasma sources for the direct analysis of solid samples has attracted much interest. One approach for the direct introduction of solids is to use a graphite cup and rod to introduce the sample into the plasma, first reported by Salin and Horlick (44)and Ohls (45).Other work reported using similar devices can be found elsewhere (46-48). Most work using this technique has been performed by inserting the sample along the vertical axis of the plasma, and has been found to yield both low detection limits and large dynamic working ranges, however the response varies with position in the plasma. Disadvantages of the technique include poor reproducibility variations in response according to matrix and a limitation on the determination of the more refractory elements.

Another approach proposed for the analysis of solid samples is combined ETA-OES, where the sample is volatilized from an electrothermal atomizer

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and carried into the plasma. Although initially proposed for small volume samples for both ICP (49-51) and DCP (52). The technique has been used for the analysis of solid samples (53), in particular plant materials, inorganic powders and coal.

To avoid problems associated with volatility, spark discharges have been used for the vaporisation of solid samples with excitation in a plasma source (54, 55, 56). The technique appears to be more suited to conducting samples with the analysis of alloys (55) being particularly encouraging.

The use of laser ablation to volatilize samples for subsequent analysis by both ICP-OES (57-59), and ICP-MS (60), has been reported. The sample is either placed directly in the chamber or formed into a disc with a binder and then the laser used to ablate the sample, with the products being transported into the plasma by a flow of argon. Again these techniques suffer from poor reproducibility and calibration requires the use of matrix-matched materials.

1.3.2 Slurry Atomisation

The introduction of solid samples as suspensions or slurries of finely powdered material offers distinct benefits to the analyst in terms of requiring minimal sample pre-treatment, the potential to calibrate using simple standards and that conventional instrumentation can be used without major modification. Particular interest in this form of solid sample introduction, where the powdered material is suspended using either aqueous or organic media, is being expressed for analyses using flame, electrothermal and high temperature plasma atom cells.

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Gilbert (61), in early work using flame emission spectrometry, investigated the direct atomisation of soil introduced as a suspension in 1:1 isopropanol-glycerol. Mason (62) used slurry atomisation to determine potassium in plant materials using a similar procedure. Lebedev (63) investigated the application of the technique to minerals and found that the technique was suitable for the determination of alkali metals provided that the particle size was less than 5 µm. Other applications using flame atomizers include the determination of tin in ore concentrate (64), studies on the determination of wear metals in lubricating oils (65, 66), the determination of trace metals in titanium dioxide, soils and geological materials (67-70). In these papers, Willis (68) showed that atomisation efficiency was highly dependant upon particle size, with particles greater than 12 µm not contributing significantly to the observed signal, Stupar and Ajlec (69, 70) showed that particle size, flame temperature and position in the flame were all critical parameters for a successful determination.

Fry <u>et al</u> in a series of papers (71-75) have investigated slurry atomisation, avoiding problems of blockages in nebulizer and burner systems by using a Babington-type clog-free nebulizer and re-designed spray chamber and burner. Applications have included whole blood, milk (71), animal tissue (72), hotdogs (73) and coal (74) where atomisation efficiencies were approximately 20%.

Electrothermal atomisation techniques show greater freedom from the effects of particle size, in a comparison berween flame, electrothermal and ICP atomizers (75), these effects were only significant in ETA above 25 μ m. Applications of slurry analysis by ETA include the analysis of titanium dioxide (67, 75), copper, nickel and vanadium in coke (76),

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arsenic in coal, using aqueous calibration (77), trace metals in soils (78, 79), milk (80) and plant materials (81). Although successful for many applications, the attainable temperatures for atomisation may be insufficient to allow complete atomisation of more refractory matrices.

The use of plasma sources as atomisers for slurry analysis has been less widely described in the literature. Of the two most popular sources, the Inductively Coupled Plasma (ICP) and Direct Current Plasma (DCP), the application of the ICP to the analysis of clay minerals has been described in a preliminary investigation by Spiers et.al (82), and by Gray (83), who investigated the design of instrumentation, the effects of particle size and dispersants for kaolin and reference rocks. One conclusion from this study was that the internal diameter of the injector had a critical effect on particle transport into the plasma. The ICP has also been used for the determination of precious metals concentrated onto an ion exchange resin subsequently analysed by slurry atomisation (84). The DCP has been used to determine trace elements in animal tissue using a slurry procedure (85). In this study, a Babington-type nebulizer was used and the DCP was chosen because of the wide (7 mm) diameter of the sample introduction tip. More recently the DCP has been used for the slurry atomisation analysis of reference coal (86) using Triton x-100 as dispersant. Results obtained showed reasonable agreement with certified levels provided particle size was less than 10 $\mu\text{m}.$

The techniques of slurry atomisation have several advantages to offer in terms of simplicity, speed of analysis and availability of suitable instrumentation. The use of a high temperature plasma atom cell offers the ability to achieve complete matrix decomposition and thus avoid many of the problems associated with flame and electrothermal atomisation.

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Of the plasma sources available, the DCP offers additional benefits of low running costs compared to the ICP and advantages with regard to sample introduction configuration (outlined above and by Mohamed <u>et.al</u>., 85) that reduce the need for instrument modifications.

1.4 Objectives of this work

One of the main objectives of this work was to develop methods for the successful analysis of agricultural samples using the direct current plasma, introducing the samples as solids and using simple aqueous calibration. Reports in the literature (85, 86) indicate the suitability of the DCP for such an approach, however a more rigorous study of this plasma should allow the characteristics required for slurry atomisation to be elucidated. As yet little work has been directed to the analysis of refractory materials using this approach. Clearly the importance of particle size must be defined as should the effects of operating parameters (viewing position, nebulizer gas flow and plasma sleeve gas flow). For a technique suitable for the routine analysis of agricultural materials, calibration should be achieved using simple aqueous calibration, therefore the effect of changing sample matrix loading has required investigation with particular attention paid to temperature changes in - the plasma, to enable a deeper understanding of the technique to be developed.

A problem facing many determinations for elements such as arsenic and selenium is a lack of sensitivity from the analytical techniques used. As described earlier, the technique of hydride generation may be used to extend the sensitivity of atomic spectrometry. Hydride generation with DCP detection has been investigated for As, Se and Pb with particular

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attention paid to the optimisation of both instrument and solution conditions using a continuous flow system suitable for automation.

The techniques developed for sample introduction have been applied to a range of agricultural samples using appropriate sample preparation e.g. grinding and acid digestion where necessary.

REVIEW OF DIRECT CURRENT PLASMA EMISSION SPECTROMETRY

2.1 Description of Source

The development of the three electrode direct current plasma can be readily traced back to d.c plasma arcs and d.c plasma jets. A major problem with these devices is the poor line to background ratio resulting from analyte observation being in an area of high continuum intensity. Valente and Schrenk (87), improved the line to background ratio by inclining the electrodes at 30° to each other to form an inverted 'V' allowing analyte emission to be observed away from the plasma. With this device the sample aerosol was introduced with the gas forming the plasma jet. Using a similar design, but with aerosol introduced independantly from below the inverted 'V', Elliot (88) found that the aerosol was "trapped" beneath the plasma core with analyte emission maximum occurring at the apex of the zone, below and away from the plasma core, resulting in much improved line to background ratios. A problem with this device was found to be positional instability in the apex of the plasma (89), resolved by the development of the source used in this study consisting of two jets with a common cathode producing the characteristic inverted 'Y' discharge of the commercial DCP instrument (Fig. 1).

In this system argon flows through ceramic sleeves and over the electrodes, the arc is struck and the electrodes retract into their normal analytical

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λ.
configuration, allowing the introduction of sample aerosol from below the inverted 'Y'. The conventional sample introduction system consists of a robust ceramic crossflow nebulizer (Fig.2), a diamond-shaped spray chamber and sample introduction chimney that directs the aerosol towards the plasma (Fig.3). Sample is fed to the nebulizer using a two-channel peristaltic pump at approximately 1.5 mL min⁻¹; the second channel being used for spray chamber drainage. The analyte emission is optimum in the zone in the angle between the arms of the 'Y' and is isolated for the appropriate analytical line, in the commercial sytem, using an echelle grating spectrometer configured for manual wavelength selection.

Several authors have investigated the performance and capabilities of the source (90-94), of these Decker (93) investigated temperature distributions in the plasma showing the existence of distinct elementdependant emission profiles related to temperature. In addition some observations of enhancement effects on analyte emission were made. The importance of viewing position was demonstrated by Frank and Petersson (95) in optimising the DCP for simultaneous multi-element determinations, who used 0.25 M LiNO₃ as an enhancement buffer.

2.2 Analyte Excitation and Emission Enhancement

The subject of analyte excitation and analyte emission enhancement in the DCP has provided a fruitful area of study for several workers. In an investigation of the analytical characteristics of the DCP, Decker (93) concluded that the signal enhancements were caused by improved volatilisation of the sample in the plasma, and recommended sample dilution to avoid these effects analytically. Johnson <u>et al.</u> (96), investigated the enhancement effect more deeply, finding that easily

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Figure 3 DCP sample introduction system



ionized elements enhanced both atomic and ionic lines, made no significant change to the electron temperature or electron density in the analytical zone, but a slight cooling was found in the measured rotational temperature. In addition it was shown that the effect did not result from changes in sample transport efficiency. The authors concluded that the electron density of $N_e = 10^{15} \text{ cm}^{-3}$ was too low to maintain equilibrium conditions sufficient to "buffer" the plasma from enhancement effects, proposing a model where enhancement occurred as a result of increasing metastable argon populations.

In the first of a series of significant papers, Eastwood <u>et al.</u> (97), systematically investigated the enhancement of transition metal analyte emission in saline matrices. An objective of this work was to develop a predictive model for enhancement. This first model performed with moderate success establishing a relationship between the number of unpaired d-electrons and enhancement. Again no significant conclusions as to excitation mechanisms were drawn, apart from suggesting the DCP is not in local thermodynamic equilibrium (LTE). In a paper published shortly after the above, Nygaard and Gilbert (98), looked at various matrices and demonstrated that enhancement of analyte emission was inversely related to the ionisation potential of the matrix element. In addition they found that the temperature of the plasma core decreased and the temperature of the analytical zone increased in the presence of high levels of easily ionised elements (EIE).

In a continuation of earlier work, Eastwood, Hendrick and Miller (99), again studied enhancement of transition metal lines by saline matrices finding that for a particular spectrum (<u>e.g.</u> FeI) the enhancement and excitation potential of a line were found to be linearly related. In

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a later significant paper, these same authors critically reviewed analyte excitation and enhancement in the DCP. They proposed a model for excitation of which the main features are radiative transfer via argon resonance lines from the high current, analyte poor, plasma core to the low current, sample rich, areas of the plasma, followed by collisional redistribution to analytes from radiatively inverted first excitated state argon populations, with Penning ionisation dominant in these interactions. Additional aspects include the interception in the analytical zone, of resonance lines emitted by the core being dependant on the local stark broadening of lines which is proportional to the local electron density (n_e). n_e is itself dependant upon the local radiation density and the composition of the plasma.

EIE induce emission enhancement in this model by several pathways, firstly in providing additional channels for radiative transfer. Secondly the EIE act as electron donors in the analytical zone raising n_e , thus increasing the stark broadening of resonance lines involved in radiative transfer and the energy flow to the sample rich zone. Thirdly the excited EIE also have a large cross-section allowing resonant collisional interactions with analyte species. Observed reductions in background emission by the addition of EIE are explained by the accelerated cooling of the plasma core reducing emission from the core, which at low EIE concentrations is offset by the improved analytical zone absorption cross-sections, hence giving net enhancement of the analyte line. Although developed as a model for enhancements occuring from EIE, this model can be used to explain the effects caused by high levels (2.5 - 5 g 1^{-1}) of elements such as Cr, Cu, Fe, Mo, Ni reported by Fox (101,102).

Miller et al. (103) have investigated the validity of this proposed

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mechanistic model and developed an approximate prediction for enhancement by sodium for both atomic and ionic lines of a range of transition elements. In this work the mechanistic processes proposed earlier were substantiated indicating that EIE perturb Ar-Ar radiative transfer rather than the Ar-analyte transfer and that the main effects of EIE were to improve coreanalytical zone radiative coupling and radiatively cool the plasma, reducing the kinetic temperatures.

Several studies of electron density profiles in the DCP have been made (104-106), of which the work by Zander and Miller (106) is most significant. The authors spatially mapped the entire source and obtained detailed n_e^i profiles for a range of operating regimes. It was found that the flow of argon from the sample introduction system established a thermal pinch in the high current zone, thus steepening the temperature gradients in the plasma. In addition the electron density distributions were found to be more sensitive to changes in gas flow than changes in parameters such as arc current. Electron densities were not found to be affected by easily ionised elements or matrix constituents at analytical concentrations up to 1% m/v.

From the above work, it can be seen that the understanding of analyte excitation and emission enhancement in the DCP has developed considerably in recent years and that emission enhancement can be either controlled by buffering or, for certain elements, corrected mathematically.

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Sample introduction has been a major area of investigations for DCP users. Studies have been made using the conventional sample introduction system for aqueous solutions as well as more novel applications and modifications of this device.

The conventional DCP sample introduction system has been described earlier. Using this system, transport efficiency for aqueous solutions has been measured to be approximately 15% (93, 107, 108). Various estimates have been placed upon droplet size produced by the system, with values of between 3-10 μ m (94) and 1-20 μ m (85), being cited, thus providing some information on the characteristics of the device.

A modification suggested for aqueous solutions is the use of nitrogen as nebulizer gas as opposed to argon (109). Although this reduced running costs, it resulted in degraded analytical performance for determinations of refractory elements. More useful is a modification suggested by Mazzo <u>et al.</u> for coupled HPLC-DCP (107). Although the DCP is favourable towards high sample loadings compared to other emission techniques, not all the sample passes through the region where observation is made. Therefore the use of a novel interface with a reduced diameter sample introduction chimney was proposed which may lead to improvements in instrument performance.

The effects of introducing organic solvents into the DCP have been described by Gilbert and Penney (109). Using a 5.2 mm introduction chimney, they introduced hexane, dichloro-, trichloro-, and tetrachloromethane, and 4-Methyl-2-pentanone with higher transport efficiencies

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than observed for aqueous samples. Optimal nebuliser gas flow rates were between 4-6 1 min⁻¹. Above this level the plasma became unstable and at flows greater than 8 1 min⁻¹ the plasma was extinguished. Background emission, primarily from incandescent material, C_2 and CN bands, was reduced by adding 0.1 1 min⁻¹ of oxygen to the gas flow.

The use of the DCP in the determination of wear metals in oil has been well described (110-112). Subject to the particle size limitations resulting from nebulisation and aerosol conditioning processes in the sample introduction system, DCP spectrometry has been shown to perform favourably for this application. A comparison between direct nebulisation and acid digestion procedures is able to provide an insight as to the size of the wear metal particles, however, reported differences between the techniques may reflect incomplete atomisation of larger particles in addition to incomplete sample transport. These questions of particle transport and atomisation are of particular significance to slurry atomisation procedures. Published studies of DCP slurry atomisation have been discussed earlier (section 1.3.2).

Vapour generation techniques are widely used in atomic spectrometry for those elements that readily form a volatile moiety either as the element (Hg) or as a hydride (As, Se, Sb, Sn, Ge, Bi, Te and Pb). Reports on the application of the technique to the DCP have been few, and indicate that improvements in sensitivity of approximately a factor of twenty over aqueous nebulisation can be achieved. Panaro and Krull (113) used a continuous flow hydride generation system to determine arsenic in spiked water and fish samples, and Hayrynen <u>et al.</u> (114) introduced selenium and tellurium into a DCP using a hydride trapping stage, achieving detection limits of 1.5 ng cm⁻³ and 5 ng cm⁻³ respectively. Other reports

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on DCP vapour generation techniques include the determination of mercury in blood and fish samples (115), mercury in iodine monochloride (116) and the determination of arsenic in sediments by chloride formation (117).

The coupling of the separatory power of chromatography with the selectivity and sensitivity of atomic spectrometry provides a powerful technique, with the ability to quantify different elemental forms, allowing rapid trace element speciation. The role of the DCP in such coupled techniques has been identified with DCP detection being used in gas chromatography, (118-122), HPLC (123-128) and gel filtration chromatography (129, 130).

Applications regarding gas chromatography, for which a heated interface was advantageous include the determination of organometallic compounds of Cu, Cr and Zn (118), organomanganese compounds in gasoline (119), alkyl derivatives of Si, Ge, Sn and Pb (120), Si in silicone polymer using pyrolysis gas chromatography (121) and a DCP with vacuum u.v. spectrometer as a sulphur specific detector for gas chromatography (122). Coupled HPLC-DCP techniques have been used to determine various transition metal complexes with detection limits in the sub ng range (123, 124). Reversed phase HPLC with DCP detection has been shown to provide a viable method for the determination of Cr (III) and Cr (VI) speciation (125), with detection limits of 5-10 ng $\rm cm^{-3}$ for 100 mm 3 injections. Krull and Panaro (126), have described procedures for the determination of tin and organotin species by HPLC-DCP including a hydride generation stage. Using this procedure detection limits of 25 ng cm^{-3} were obtained for the mono- and dimethyl- species and 40 ng cm⁻³ for the trimethyl species using a 200 mm³ injection. A separation of phosphorus species has been outlined by Biggs et al. (127), with a detection limit of 0.2 μ g P and RSD between 1-5%. Analyses were found to show good agreement with the conventional procedure.

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A growth area in trace element speciation is the determination of elementprotein associations. Gel filtration chromatography with simultaneous detection has been used to study protein-bound copper, iron and zinc speciation in serum and intravenous infusion fluids (128, 129). The direct coupling of the two techniques was found to reduce contamination and increase sample throughput compared to fraction collection procedures. Detection limits were 3.2 ng cm⁻³ Cu, 3.9 ng cm⁻³ Fe and 9.3 ng cm⁻³ Zn, · adequate for the species of interest.

While reports of sample introduction studies for the DCP may not be as numerous as for other techniques, the versatility of this plasma can be seen from the above work. The DCP, however, does provide a robust excitation source able to tolerate samples in liquid (aqueous and organic), gaseous or solid forms.

2.4 Applications of DCP-OES

The DCP has been used for a wide range of element determinations in various matrices. Applications using coupled techniques, vapour generation and solid sampling have been described earlier, however, the majority of reports refer to analyses performed using conventional sample dissolution procedures.

The commercially available system of the DCP source in combination with the high resolution echelle grating monochromator has attracted much interest for metallurgical samples, where line-rich spectra can compromise trace level determinations. A range of elements have been determined in steels using this technique with interest directed at tungsten (130), niobium (131), as well as more comprehensive analyses (132, 133). Neodymium and boron were determined in Nd-Fe-B alloys (134), the boron 249.678 nm line used being found to be adequately resolved from the iron 249.653 nm emission line. Samarium, europium, gadolinium and dysproprium were determined in uranium containing materials (135). Using a solvent extraction - ion exchange procedure these elements could be determined at the ng cm⁻³ level.

The use of DCP-OES for the determination of wear metals in lubricating oils has been investigated and reviewed by Eisentraut <u>et al.</u> (110-112, 136). A similar sample type is found in vegetable oil. Dijkstra and Meert (137), used a DCP to determine phosphorus, nickel and copper in edible oils, showing good agreement with conventional procedures. Calibration was achieved by diluting oil soluble standards with sunflower oil. One of the main advantages of developing analytical procedures using plasma spectrometers is saving time compared to analysis using classical procedures.

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This has been particularly the case for boron determinations, for example in engine coolants (138) and glass (139). Techniques for the determination of impurities in a range of ceramic materials have been described (140, 141), using matrix-matched standards for calibration. Papers describing the determination of platinum group metals in alumina ceramic based materials have been discussed earlier (101,102). In this work enhancement effects were mediated by the addition of 3.5 g 1^{-1} lithium and 2.5 g 1^{-1} lanthanum to sample and standard solutions.

The levels of beryllium (142) and vanadium (143), in industrial aerosols have been determined, with results comparing favourably with independant techniques.

Several authors have determined elements in waters using DCP spectrometry (144-148). These studies include determinations of pollutant elements arsenic, copper, cadmium, chromium, nickel and lead (144). In this paper however, the authors failed to correct adequately for enhancement effects by using a suitable buffer. For the determination of boron in a range of water samples (145), Ball et al. concluded that the DCP procedure was more sensitive, accurate and rapid than conventional procedures with good agreement obtained for reference samples. Arsenic, boron, carbon, phosphorus, selenium and silicon in water samples were studied by Urasa (146), claiming a detection limit of 1 μ g cm⁻³ for carbon using the 247.86 nm line. More recently the above author has studied iron and phosphorus speciation in water samples (147). DCP spectrometry has been found to be applicable to a wide range of environmental materials, including waters and biological materials (148), sediments (149-151) and rocks (152, 153). For these latter sample matrices, where fusion techniques are employed, care is required in matching easily ionised element content in solutions.

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The use of coupled gel filtration chromatography DCP-OES for the determination of metal protein speciation has been described earlier (128, 129). This instrumentation has also been used for the determination of Al, Ba, Si and Sr in amniotic fluid (154), Ca, P and Cr in a metabolic study concetning food and faeces (155), a study of Ca, Zn and Mg in serum and urine (156), and a study of V in urine and blood (157).

Of particular relevance to the topic of this work are papers concerning the application of the DCP to agricultural materials. The advantages of plasma sources for the determination of boron in fertilisers have been described in Chapter 1. For these analyses (16,17), the boron was extracted with HCl and samples made up to contain 2 g 1^{-1} lithium enhancement buffer. Feedstocks for fertiliser manufacture have been monitored for a range of elements (158,159), again showing agreement with conventional procedures, but with improvements in sample throughput rates obtainable. These advantages hold for the analysis of plant materials, especially with determinations concerning boron (19). Examples of applications for plant material analysis by DCP can be found in various papers (20, 160-162). In the last of these papers (162), molybdenum was determined at 0.2 μ g g⁻¹ in pine needles and birch leaves using a digestion/ solvent extraction procedure. Other papers of relevance to this area include the determination of mercury in blood and fish (115), the determination of 14 elements in animal tissues by a simultaneous multielement procedure (95), and the determination of alkali and alkaline earth metals in orange juice (163).

In addition to these conventional application papers, studies have been made using a vacuum u.v. spectrometer to determine sulphur (164), and to study the u.v. spectrum from 100 to 200 nm (165).

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Two recent papers have used the DCP as a light source for atomic spectrometric techniques. Messman <u>et al.</u> (166) have evaluated the DCP as a primary pseudocontinuum radiation source for wavelength modulated AAS. The use of the DCP reduced stray radiation compared to a xenon arc lamp, but signal to noise ratios were degraded because of plasma source noise. Goliber <u>et al.</u> (167) used a DCP as an excitation source for flame atomic fluorescence by introducing high concentrations of a metal into the plasma.

Literature reports of application of the DCP are less common than for other plasma sources, however, it can be seen that the DCP is able to determine a wide range of elements in many different sample matrices. In many of these reports the DCP has been shown to provide accuracy and reproducibility at least as good as comparative techniques, and have advantages in the time required for analysis.

2.5 Instrumentation Used

The direct current plasma source and spectrometer used was a Spectraspan IIIA (Beckman RIIC Ltd., Progress Road, High Wycombe, Bucks), with three electrode DCP source and 0.75 m echelle grating spectrometer. Instrument specification and typical operating conditions are given in Table 2, with Figs. 1 to 3 showing details of the plasma nebuliser and sample introduction system respectively.

Spectral scans were obtained by using an electrical motor drive for wavelength scan, obtained from a Pye Unicam SP9 graphite furnace autosampler system and type L30 stabilised voltage power supply (Farnell Instruments Ltd., Wetherby, Yorks.), run at between 10 V to 25 V.

Data collection was <u>via</u> the 0-10 V output from the DCP computer to a chart recorder (Lloyd Instruments, Brook Lane, Warsash, Southampton).

In routine operation the instrument uses less than 7 l min⁻¹ argon and less than 1000 W electricity. The DCP represents an economical plasma source for atomic emission spectrometry.

TABLE 2

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Direct Current Plasma Instrument Specification Summary

Excitation source	Three electrode direct current argon plasma. Inverted Y configuration between tungsten cathode and two carbon anodes.			
Nebuliser Gas Flow	3.0 l min ⁻¹			
Sleeve Gas Flow	3.5 l min ⁻¹			
Sample Delivery Rate	1.6 cm ³ min ⁻¹ (0.45 mm i.d. tube)			
Spectrometer	Spectraspan IIIA (Beckman RIIC Ltd.,High Wycombe, Bucks), echelle grating spectrometer of modified Czerny-Turner design with 30° prism for order separation. Spectral range 190-800 nm			
Entrance Slits (µm)	width 25, 50, 100, 200, 500, height 100, 200, 300, 500. (Typically 50 x 200)			
Exit Slits (µm)	width 25, 50, 100, 200, height 100, 200, 300, 500. (Typically 100 x 300)			
Detector	Hammamatsu type R 292 with voltage adjustable in 50V stages from 550 to 1000V			

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CHAPTER 3

SIMPLEX OPTIMISATION OF A DIRECT CURRENT PLASMA

3.1 Introduction

Several workers have discussed the presence of distinct vertical emission maxima for various emission lines in the DCP (93, 95, 98, 100), with Decker (93), indicating that the observed distribution is related to temperature distributions in the analytical zone. In addition to these observations interaction between the DCP operating parameters has been shown to affect the analytical response of the instrument (93, 98, 100). The parameters, under operator control on the commercial instrument, directly associated with these effects and with the operation of the plasma are: the vertical and horizontal viewing positions, nebuliser gas flow, and sleeve gas flows. Decker (93), has shown that the position of the analytical zone is dependant on the gas flows but independant of electrode length. Parameters such as the electrode angle and the sample introduction chimney orifice diameter again may also affect the analytical response of the device, however, these factors are fixed during operation and thus are not normally variable during instrument operation.

Simplex optimisation is an established technique for the optimisation of a number of interrelated continuously variable parameters (168-171). The most popular optimisation procedure is the modification proposed by Nelder and Mead (169), of the original sequential simplex procedure of Spendly <u>et al.</u> (168). The use of the variable step-size simplex speeds the optimisation and allows the closer definition of the optimum, and is free from the risk of attaining false optima. Yarbro and Deming (170),

-37-

have demonstrated the desirability of commencing the optimisation with a large step size to allow the majority of factor space to be explored before the simplex contracts onto the optimum. In this work, the authors described a matrix and equations to design the initial simplex conditions. Deming and Parker (171), have reviewed the use of simplex optimisation in analytical chemistry.

Cave (172), provides an excellent description of the mechanism of simplex optimisation. The simplex is defined as a geometric figure in factor space equal to one plus the number of parameters considered in the optimisation (n+1). Thus for a two parameter optimisation, the simplex is a triangle. Using this simple model, the optimisation proceeds by rejecting the point in the simplex with the worst response and forming a new simplex with a point at a mirror image reflected away from the previous worst point. The modified simplex procedure of Nelder and Mead allows the simplex to expand or contract at this point allowing the progress to the optimum to be accelerated. If the point in the new simplex should give a worse response an oscillation between the old and new simplexes could occur, thus halting the optimisation. In this situation the new point is taken as a reflection away from the second worst point in the simplex and the optimisation is able to proceed. The effect of errors in measurement of the response factor is to falsely hold the simplex away from the optimum. This problem can be ameliorated by re-evaluating any point held for n+1 successive vertices, thus allowing any errors to be compensated for.

Relevant applications of the technique include its use for optimisation of the ICP, where Ebdon <u>et al.</u> (173), have used the technique to compare the performance of argon and nitrogen cooled plasmas and by Moore <u>et al.</u>,

-38-

(174), where the technique was used to optimise response in nitrogen cooled plasmas. Carpenter and Ebdon (175) have recently described the use of simplex optimisation for the evaluation of different sample introduction systems for ICP emission spectrometry.

3.2 Experimental

The DCP plasma spectrometer used has been described in section 2.4. The rules of the modified simplex procedure of Nelder and Mead (169), and the rules for the definition of the initial simplex proposed by Yarbro and Deming (170), are available on BASIC software written for an Apple IIe microcomputer (176).

The angle of the 'Y' of the plasma was set as zero in the manner suggested by Blades and Lee (105), (Fig.4). Thus more positive viewing positions are away from the plasma core. In contrast to Blades and Lee (105), the zero position was not referenced to the position of the ceramic sleeves because the position of the plasma core varies with gas flow independently of any external reference point. In this work the zero was set by imaging the continuum on the entrance slit and using the sharp increase in background at the edge of the core to locate the angle of the plasma. An alternative procedure used by Frank and Petersson (95), to reference the plasma to the maximum emission for a particular line (<u>e.g.</u> vanadium 437.92 (I)), is attractive but since this work sought to optimise the vertical position (amongst other parameters), this was considered inconsistent with the objectives of the study.

The initial simplex was calculated with boundary conditions within the experimental constraints of whether or not a stable plasma could be

-39-

Figure 4 Spatial reference positions for direct current plasma

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HORIZONTAL 0 mm

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maintained and within the physical constraints of the instrument (vertical position -4.5 to +4.0 mm, horizontal position +2 mm to -2 mm, sleeve gas 2.0 to 4.0 l min⁻¹, nebuliser gas 0 to 4.5 l min⁻¹). Signal to background ratio (SBR), was used as the response factor, the intrinsic merit of this measure being described by Greenfield and Burns (177). SBR has been used by several authors in the optimisation of plasma sources (172-175). The response for each vertex was entered into the simplex until successive vertices yielded no significant improvement in response. The optimisation was then terminated and a univariate search procedure employed where one parameter was varied whilst the other parameters are held constant at the optimum value defined by the simplex method. This provided information on the influence of the individual parameters on the operation and performance of the plasma.

As the main objective of this work was to assess the application of the DCP to agricultural samples, the optimisation was performed using the B 249.47 nm, Mg 280.27 nm, Co 345.35 nm and Mo 386.41 nm lines. This provided a selection of elements of agricultural significance with lines with a range of excitation energies. The response of the system was evaluated by aspirating a 1-2 μ g cm⁻³ solution of the element for the line under investigation with 1 g 1⁻¹ lithium as enhancement buffer.

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3.3 Results and Discussion

The results of the simplex optimisation are given in Table 3, and the univariate searches are shown in Figs. 5 to 8 inclusive. The solid vertical lines on the figures indicate the range of the parameter at the stopping condition. The optimum value for the parameters reported in Table 3 is the centroid of the range.

Table 3 Optimum operating conditions for aqueous samples

Element	Wavelength /nm	Horizontal Position /mm	Vertical Position /mm	Nebuliser gas flow / l min	Sleeve gas flow / l min	Excitation Energy /(eV)
B (I)	249.77	0	+0.6	3.3	3.2	4.68
Mg (II)	280.27	0	+0.2	3.3	2.8	11.81*
Co (I)	345.35	0	+0.9	3.5	2.5	3.38
Mo (I)	386.41	0	+0.7	3.8	3.0	3.02

* sum of 1st ionisation energy and excitation energy

The value of 0 mm for the emission maxima for horizontal position corresponds to the centre of the observation zone for a symmetrical plasma jet. This value was observed for all the elements studied. It has been noted that asymmetry in the plasma jet can result in horizontal displacement of the emission maxima (93), but this was not observed in this work.

The range of values resulting from the optimisation of the vertical viewing position show the presence of a distinct vertical distribution of emission maxima for the lines investigated, this distribution being generally

-42-

related to the different excitation energies of the lines. This is in agreement with other workers (93, 95, 98, 100, 105). By considering the univariate search for this parameter, it can be seen that these positional differences are significant in instrument optimisation because of the sharp nature of the optimum. Small changes in this parameter can result in pronounced effects on the response. The emission maxima can be seen to lie below the plasma core in the angle of the 'Y'. This is indicated on the univariate search for this parameter by the change in background signal indicating the position of the plasma core.

Nebuliser gas flow, in addition to its significance concerning nebulisation efficiency, may also displace the vertical optimum relative to an external point. This displacement effect can be seen in the univariate searches from changes in background signal from the plasma core. The relatively sharp optimum for this parameter is again a function of the small size of the emission maximum in the observation zone.

The range of sleeve gas flows suggests that this parameter is the least critical. This is confirmed by the univariate searches which show that changes in this parameter only cause small changes in response. There are indications that lower sleeve gas flows may provide marginal improvements in signal to background ratio, however, this also results in increased wear on the ceramic sleeves arising from the reduced cooling effect on the argon flow.

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The optimisation produced no significant change in sensitivity but it did indicate the importance of each parameter in the operation of the instrument. The critical nature of the vertical viewing position can be seen and the results found using this technique agree with findings of other workers in showing a distinct vertical profile (93, 95, 98, 100, 105). The univariate searches show the small size of the zone of maximum SBR. The size and distinct distribution of these maxima indicate the potential limitations and compromise required for simultaneous multielement determinations at trace levels. The smooth response surfaces obtained and the close coincidence of the peaks obtained in the univariate searches with the stopping conditions of the simplex optimisation, suggests that the variable step-size simplex procedure provides a rapid and effective means for optimising the DCP for atomic emission spectrometry.

Given the above results, for routine operation of the instrument, the sleeve gas flow, nebuliser gas flow and horizontal viewing position should be set at the appropriate optimum conditions and the response maximised by careful profiling of the vertical viewing position.

-44-



Figure 5b Univariate search of horizontal position for magnesium 280.27nm





Figure 5d Univariate search of horizontal position for boron 249.77nm



-46-

Figure 6a Univariate search of vertical viewing position for cobalt



Figure 6b Univariate search of vertical viewing position for magnesium



-47-



Figure 6d Univariate search of vertical viewing position for boron



Figure 7a Univariate search of nebuliser gas flow for cobalt



Figure 7b Univariate search of nebuliser gas flow for magnesium







Figure 7d Univariate search of nebuliser gas flow for boron





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Figure 8b Univariate search of sleeve gas flow for magnesium

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Figure 8c Univariate search of sleeve gas flow for molybdenum.

Figure 8d Univariate search of sleeve gas flow for boron



HYDRIDE GENERATION

4.1 Introduction

The analytical potential of the generation of gaseous covalent hydrides for atomic spectrometry was first demonstrated by Holak (178), who investigated the determination of arsenic using the zinc metal reduction of arsenic to arsine. The technique has been further developed for the determination of the elements Se, Sn, Sb, Ge, Bi, Te and Pb in addition to As (9). The popularity of the technique arises from the need to determine many of these elements at trace levels, where the low wavelength of their primary resonance lines, coupled with the low efficiency of conventional sample nebulisation results in insufficient sensitivity from the analytical instrumentation. The use of hydride generation, where 100% analyte transport efficiency is achievable can significantly increase the sensitivity of both atomic absorption spectrometry, where silica atom traps (9), are frequently used to further increase sensitivity, and atomic emission spectrometry, where the removal of the low efficiency nebulisation stage can result in significant improvements in sensitivity 179, 180). As yet, only a little interest has been displayed in DCP hydride generation (113, 114). These papers have been discussed earlier (chapter 2).

Various reducing agents have been described for hydride generation (181), the most popular being sodium tetrahydroborate (III), which gives rapid production of the volatile hydride, thus potentially decreasing analysis time. As solutions of sodium tetrahydroborate (III) are unstable, the

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-53-

usual practice is to stabilise the reagent by the addition of 0.1 mol dm^{-3} sodium hydroxide (182).

The relationship between acid concentration and sensitivity has been studied by several workers (24, 179, 180), and it has been shown that the generation of covalent gaseous hydrides is often critically dependant upon acid concentration. With single element determinations using this technique, few limitations are imposed upon the analysis, however, for multi-element determinations using atomic emission spectrometry, the need for compromise acid conditions can result in reduced sensitivities, or the inability to generate gaseous hydrides of some elements (24).

Acid concentration is also significant in the control of interferences in the hydride generation reaction. In an extensive study of interelement interferences in hydride generation, Hershey and Keliher (10), investigated the effects of 50 elements and concluded that the analyte signal suppression observed could be significantly reduced, although not always eliminated by appropriate manipulation of the acid concentration. In a series of papers by Welz and co-workers (183-186), the interferences observed for arsenic and selenium hydride generation procedures have been investigated, with the conclusion that the effects are again best controlled by appropriate acid and sodium borohydride concentration. In addition, these workers proposed a mechanism for these effects where the interfering metal ion is preferentially reduced to a lower oxidation state or to the metal. This material then captures and decomposes the hydride. With this mechanism, the increase in acid concentration reduces the severity of the interference as a result of the better solubility of the metal in the higher concentration acid. When using hydrochloric acid, the formation of chloro-complexes with the interfering metal reduces

-54-

the concentration of free metal ions and the higher concentration of acid reacts with the excess tetrahydroborate (III) leaving less available to react with any interfering species. In a slight modification to this mechanism for the interference, Bye (187), suggested that metal borides are the reacting species rather than the metal precipitate proposed by Welz (183-186).

Present trends in hydride generation are away from the batch operation of earlier workers (9), and towards continuous flow systems (10, 179-182). With batch systems, the hydrogen and analyte hydrides produced in the reaction cell are passed simultaneously into the atomisation cell in a discrete peak so disturbing the equilibrium conditions of the flame or plasma. This can result in degradation of the analytical signal. Using a continuous flow approach to hydride generation, a steady flow of hydrogen passes into the atomiser giving permanent equilibrium conditions, with the analytical measurement made on the signal produced from the atomisation of the hydride over the constant background resulting from the continuous production of hydrogen. Other benefits arising from this approach include improved precision from the ability to integrate a continuous as opposed to a transient signal and the simplicity of instrument automation. One potential disadvantage of this approach is the rate at which reagents and sample are used compared to batch operation.

The objectives of this study were to investigate the application of hydride generation to DCP-AES. Initial interest was focussed on the determination of arsenic and selenium, with particular attention to the optimisation of instrument parameters. In addition, hydride generation was investigated for the determination of lead with a view to extending the analytical capability of the DCP.

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4.2 Instrumentation

A continuous flow hydride generator (P.S Analytical Ltd., Orpington, Kent), was interfaced via an argon sheathed sample introduction chimney (Fig.9), to the DCP instrument. The hydride generator has been described in detail by Ward and Stockwell (188), the flow pattern is represented schematically in Fig.10. The constant speed peristaltic pump was used to deliver sodium tetrahydroborate (III) at 4.7 cm³ min⁻¹, with acid blank and sample solutions at 9.4 cm³ min⁻¹. This was achieved using 0.5 mm and 0.8 mm i.d. silicone rubber tubing respectively.

4.3 Optimisation for selenium and arsenic

4.3.1 Reagents.

Several authors have suggested that the optimal reagent conditions for the determination of arsenic and selenium by hydride generation are 1% m/v sodium tetrahydroborate (III) in 0.1 M sodium hydroxide and 5 M hydrochloric acid (182-186, 188). This was confirmed by univariate searches on the tetrahydroborate (III) concentration and hydrochloric acid concentration (Figs.11 and 12). These parameters are considered to be independant of instrument operating parameters and thus may be optimised separately. For the optimisation, unless otherwise stated, all reagents were of analytical reagent grade.

> Sodium tetrahydroborate (III) solution -Sodium tetrahydroborate (III) (10g, 98%, Aldrich Chemical Co.) dissolved in sodium hydroxide solution (0.1 M, 1000 cm³).

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Figure 10 Schematic diagram of continuous flow hydride generator

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sodium tetrahydroborate (III) concentration
(% m/V)

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Hydrochloric acid concentration (M 1^{-1})

Hydrochloric acid -

Diluted to 5 M solution (BDH Chemicals Ltd., Poole, Dorset).

Selenium standard -Pepared by serial dilution from 1000 μ g cm⁻³ stock solution to give 250 ng cm⁻³ in 5 M HCl.

The stability of selenium solutions can be improved by the addition of 1% m/V potassium bromide (182). This was done to both sample and acid blank solutions.

4.3.2 Procedure

Instrument operating conditions for DCP hydride generation were optimised using the modified simplex procedure as described in chapter 3. Signal to background ratio was chosen as the criterion of merit. The operating parameters of carrier argon $(0-1.7 \ 1 \ min^{-1})$, sheathing argon $(0-1.7 \ 1 \ min^{-1})$, plasma sleeve argon $(2.7-4.0 \ 1 \ min^{-1})$, and vertical viewing position $(+3 \ to \ -4 \ mm)$, were investigated. Horizontal position was set at the optimum in the centre of the analytical zone as defined earlier. The optimisation was terminated when successive vertices brought no significant improvement in response and the optimum investigated by a univariate search procedure (Figs.13-16).

















4.3.3 Results and Discussion

The univariate searches show the critical nature of the vertical viewing position upon response. The range of the optimum values for this parameter at the stopping conditions, are shown by the vertical lines on the Figure. The region of optimum signal to background ratio occurs in the analytical zone close to the plasma core. The sleeve argon flow to the plasma was found to be essentially similar to the values obtained in chapter 3. The total sample introduction gas flow into the plasma (carrier gas + sheathing gas), was found to be essentially similar to the total gas flow required for solution analysis. This reflects the work by Zander and Miller (106), who have shown that a nebuliser gas flow is essential in the formation of the characteristic thermal pinch of the analytical zone. Of these two parameters, carrier gas flow is the more critical with the vertical displacement of the analytical zone being a major effect. The role of the sheathing gas is to constrain the carrier gas flow to the centre of the analytical zone, but additional effects include assisting the formation of the thermal pinch (described above), and in producing vertical displacement of the analytical zone.

For normal operation, optimisation can be readily achieved by setting the gas flows to the conditions given in Table 4, and then vertically profiling to obtain maximum SBR.

The improvements in detection limit obtainable by using hydride generation are shown in Table 5.

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Table 4Operational parameters for determination of arsenic and seleniumby hydride generation Direct Current Plasma emission spectrometry

Carrier gas/l min ⁻¹		1.1
Sheathing gas/l min ⁻¹		1.5
Plasma sleeve gas∕l min ⁻¹		3.1
Vertical viewing position/mm	As	+0.1
	Se	+0.2

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Element	Wavelength	Solution detection limit	Hydride detection limi	
	nm	ng cm	ng cm ⁻³	
As	193.696	80	4	
Se	196.026	100	4	

Table 5 Comparison of solution and hydride generation detection limits

Improvements in sensitivity of 10² can be obtained by ICP users for hydride generation (179, 180), however, the improvements available to the DCP are a factor of 20-25. These values reflect the higher transport efficiency of the DCP for solution analysis compared to the ICP, (15% opposed to 1-2%), and may also be a result of less efficient analyte excitation in the DCP.

The detection limits obtained are higher than those quoted for AAS using a silica atom trap of 0.04 and 0.07 ng cm⁻³ respectively for As and Se (188). For ICP hydride generation, detection limits of 1 ng cm⁻³ and 0.6 ng cm⁻³ for As and Se have been quoted (190), again superior to those obtained in this work. For DCP hydride generation, the values obtained in this study are superior to published values of 20-25 ng cm⁻³ As (113). Although DCP hydride generation does not appear to surpass the performance of hydride generation techniques using AAS and ICP, the technique does provide significant improvements in sensitivity compared to the nebulisation of aqueous solutions.

4.4 Determination of Arsenic and Selenium in Reference Samples

Arsenic and selenium in two reference materials, NBS 1571 (orchard leaves), and NIES 6 (mussel), were determined by DCP hydride generation.

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These two elements were also determined in soil samples provided by the Agricultural Development Advisory Service (ADAS), in which these elemental levels were known. Unless otherwise stated, all reagents used were of analytical reagent grade.

4.4.1 Dissolution of Reference Materials

The reference materials NBS 1571 and NIES 6 were dried at 85°C for four hours according to the certificate procedure. Sample (1 g) was heated overnight with concentrated nitric acid (15 cm³, BDH Chemicals, Poole), in a programmable digestion unit (Tecator AB, Hoganas, Sweden), using a heating programme of 4 hours at 40°C, 4 hours at 80°C and 4 hours at 110°C. After digestion, the samples were cooled and made to volume (50 cm³) with 5M HCl. Arsenic and selenium in the samples were determined using the instrumentation and conditions described above.

4.4.2 Extraction of Soil Samples

Soil samples from ADAS were extracted using the procedure followed at the ADAS Starcross laboratory (191), as described below.

Soil samples, ground to pass a 2 mm sieve were provided by ADAS Starcross. Soil (0.2-0.5 g) was placed in a borosilicate glass beaker (100 cm³), to which saturated magnesium nitrate solution (25 cm³) was added. Samples were heated to dryness, boiling to evolve brown fumes, then placed in a muffle furnace and ashed at 450°C for 30 minutes. Samples were allowed to cool and distilled water (10 cm³) added. Hydrochloric acid (20 cm³) was added gradually, then the samples were transferred to 50 cm³ volumetric flasks and diluted to the mark with

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5 M hydrochloric acid. Samples were filtered using a Whatman GF/A filter (ll cm), and the filtrate retained for analysis by DCP hydride generation. As and Se in the sample solutions were determined using the instrumentation and conditions outlined above, and calibration with aqueous standards in 5 M hydrochloric acid.

4.4.3 Results

Results for arsenic and selenium determinations in reference materials and ADAS soil samples are given in Table 6. Good agreement can be seen between the certified and known values and the values obtained by DCP hydride generation, with RSD of less than 5% at the 1 μ g g⁻¹ level.

4.5 Determination of Lead by DCP Hydride Generation

4.5.1 Introduction

Using conventional nebulisation of solution samples, detection limits for lead by DCP-AES are reported as 10-20 ng cm⁻³ (189). Although this level is suitable for many applications, the potential for hydride generation to improve analyte transport efficiency may provide improved sensitivity for trace level determinations.

The use of hydride generation for the determination of lead was first reported by Thompson and Thomerson (9), however, the conversion efficiency was found to be below five per cent. Fleming and Ide (192), used plumbane generation to determine lead in steel. In this work, tartaric acidpotassium dichromate matrix was found to improve the efficiency of the generation stage. Vijan and Wood (193), reported that the acid concentration

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Sample	Element	DCP hydride generation µg g	hd d Kuomu
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NBS 1571 Orchard leaves	As	13.4 ± 1.2	10 ± 2
NIES 6 Mussel	Se	1.4 ± 0.1	(1.5)
ADAS Soil samples			
SAC 397	As	12.5 ± 1.0	13.8
SAC 391	As	45.2 ± 2.0	40.5
SAC 1482	Se	1.1 ± 0.4	1.4

Table 6 Determination of arsenic and selenium in reference materials and soil samples by Direct Current Plasma hydride generation

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and sodium tetrahydroborate (III) concentration were both very critical. In addition, they reported the need to oxidise the lead to the Pb (IV) state prior to reduction to the hydride. Additionally, interferences from iron and copper were observed and controlled by using citric acid potassium cyanide solution, the inherent hazard of the technique was noted. Other workers (194-199), have investigated aspects of the determination of lead by hydride formation, using various reagents and atomic absorption or atomic emission detection. The main conclusions from these workers are the need to control acid concentration in the sample and the need to oxidise the lead to the Pb (IV) state prior to reduction. The most extensive studies on the generation of plumbane for analytical purposes, are by Jin and Taga (197), and by Castillo et al. (198,199). These authors investigated various reaction matrices with the conclusion that hydrogen peroxide was a suitable oxidising agent. Other oxidising agents investigated by these workers are ammonium persulphate, potassium dichromate, potassium permanganate and cerium sulphate. An additional theme common to these papers (195, 198, 199), is the interdependant nature of the reagents in producing response. Therefore to attain optimal reagent concentrations, it would be beneficial to apply a rigourous optimisation technique, such as the simplex procedure, to attain true optimum reagent conditions.

4.5.2 Simplex Optimisation of Solution Conditions for Lead Hydride Generation

The simplex optimisation procedure described in chapter 3 was used to optimise the solution concentrations of sodium borohydride, sodium hydroxide, acid concentration and hydrogen peroxide. Gas flows to the plasma were set at the conditions derived in 4.3, vertical viewing position

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being selected by profiling through the analytical zone and maximising response. These instrument conditions were considered to be independent of solution conditions. Signal to background ratio was used as the criterion of merit. Reagent concentrations of sodium tetrahydroborate (III) and sodium hydroxide were prepared according to the conditions generated by the simplex as were solutions containing sulphuric acid and hydrogen peroxide. The sulphuric acid - hydrogen peroxide solution was made up to contain 0.5 μ g cm⁻³ lead. The optimum conditions derived, when no further improvement in response was achieved, were investigated using the univariate search procedure (Figs. 17-20).

4.5.3 Results and Discussion

The optimum solution conditions for the determination of lead by hydride generation are shown in Table 7.

Table 7 Optimum Conditions for Lead Hydride Generation

Sulphuric acid	0.4M
Sodium Tetrahydroborate (III)	4.1% m/V
Sodium hydroxide	0.15M
Hydrogen peroxide	2.5% m/V

 $\lambda = 405.783$ nm

From the univariate searches (Figs. 17-20), it can be seen that acid concentration is critical in the lead hydride generation process. The range of conditions derived as optimum by the simplex is shown by the parallel vertical lines on the univariate search. At acid concentrations

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Hydrogen peroxide (% m/V)





Sodium tetrahydroborate (III) solution (% m/V)

-77-

less than 0.2 M and greater than 0.6 M the generation of the hydride becomes sharply reduced, as shown by the reduction of SBR to a value of one. The optimum of 0.4 M H_2SO_4 is similar to values suggested by other workers (197, 199, 200). These workers did not, however, investigate the effect of the sodium hydroxide present as the stabilising agent in the tetrahydroborate (III) solution. This work has shown that this parameter is also critical to the generation of lead hydride. The univariate search shows that low sodium hydroxide concentrations are optimal. The addition of hydrogen peroxide to the sample solution is also critical with the proposed mechanism being one of oxidising the lead to the Pb (IV) state prior to the hydride generation (199). As for the above reagents, the concentration of the hydrogen peroxide must be within a relatively narrow range with concentrations of less than 1% m/V and greater than 3% m/V, resulting in reduced response. The concentration of sodium tetrahydroborate (III) solution was found to be the least critical of the parameters investigated. High concentrations of this reagent (i.e. >5%) caused pulsing in the gas liquid separator and instability in the plasma. Tetrahydroborate concentrations below 2% m/V were found to depress the analytical response of the system. The narrow range of conditions derived by the simplex indicate that the optimum for this parameter was rapidly obtained on the large plateau region of the response surface.

Using this system the detection limit was calculated as 10 ng cm⁻³ for the Pb 405.783 nm line. This can be compared to the aqueous detection limit of 20 ng cm⁻³ (189). Although this technique produced improvements in analytical response, the improvement obtained was not as large as expected, possibly indicating incomplete conversion of the lead to its volatile form or decomposition of the plumbane during transport.

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4.6 Conclusions to DCP Hydride Generation

Hydride generation readily provides a technique for improving the sensitivity of DCP-AES for the elements arsenic and selenium. The use of continuous flow hydride generation combined with an argon sheathed sample introduction chimney, produced a 20-25 fold improvement in analytical sensitivity over the nebulisation of aqueous solution samples. The detection limit of 4 ng cm⁻³ obtained for As is an improvement over the 25 ng cm⁻³ previously reported by Panaro and Krull (113), for DCP hydride generation. Arsenic and selenium in reference materials and independently analysed soils were determined by DCP hydride generation with good agreement obtained with the certified and independent values, and relative standard deviations of less than 5% at the 1 μ g g⁻¹ level.

Simplex optimisation has been found to be a useful tool for the investigation of conditions for the determination of lead by hydride generation. Acid concentration and hydrogen peroxide concentration in the sample solution were found to be critical as was the concentration of the sodium hydroxide solution. Each of these parameters was found to have a narrow range of reagent concentration where plumbane generation occurred.

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CHAPTER 5

DIRECT CURRENT PLASMA SLURRY ATOMISATION

5.1 Introduction

As outlined in Chapter 1, slurry atomisation, where the sample is introduced into the the instrument as a suspension or slurry of finely powdered solid material, offers several potential advantages to the analyst. These benefits include the potential to reduce sample preparation time by introducing solid material, the instrumentation requires no major modification and that calibration can be achieved using simple aqueous solution calibration. In this Chapter, the parameters controlling successful slurry atomisation procedures (<u>i.e.</u> where atomisation efficiency of the slurry = 100%), are investigated and procedures for the analysis of various materials by slurry atomisation described.

5.2 Particle Size Characteristics of Sample Transport System

In a study of geochemical analysis by slurry atomisation ICP-AES, Gray (83), found that the main constraints upon the development of a successful slurry atomisation procedure were the particle size of the solid material in suspension and the particle size transport characteristics of the sample introduction system. This was further developed to show that the main losses of particulate material occurred at the constriction of the injector tube, and that using a larger diameter, (3.0 mm as opposed to 2.2 mm) injector, satisfactory analyses could be performed using slurries where the particle size of the solid material

-80-

was less than 7 μ m. Mohamed <u>et al.</u> (85), and McCurdy <u>et al.</u> (86), using a DCP with a Babington-type nebuliser, confirmed that particle size is a critical parameter in slurry atomisation.

5.2.1 Instrumentation

The standard plasma jet from a Spectraspan IIIA DCP Spectrometer, (Beckman RIIC Ltd., High Wycombe) was used with the standard cross flow nebuliser. Slurries of powdered material were kept in homogenous suspension by using a magnetic stirrer, and introduced to the sample introduction system using the peristaltic pump of the instrument. The particle size characteristics of the original and collected materials were determined using a Coulter counter TAII particle size analyser (Coulter Electronics Ltd., Luton, Bedfordshire), fitted with a 140 µm sampling tube. A full description of the theory and practice of particle size measurement using the Coulter counter (electrical sensing zone technique), is given by Allen (200). The advantages of this technique are its speed, ability to determine distributions by particle volume and in particular for slurry atomisation, the particle size measured is that present in a suspension sample. Potential problems with the technique are that the electrolyte solution used in the measuring cell may cause particle flocculation, the measurement is made on a very dilute suspension of material, therefore requiring great care in sub-sampling the analytical slurry and that for biological matrices e.g. plant material, the osmotic strength of the electrolyte solution may result in changes in cell size and hence misleading results. An additional characteristic that may produce misleading results is that the technique is based on the assumption that the particles in suspension are spherical. The measurement of non-spherical particles (rods, fibres) by this technique may therefore produce anomalous results.

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The certified reference material soils SO-1, SO-2 (Canada Centre for Mineral Energy Technology, Ottawa, Ontario, Canada), have polydisperse particle size (Figures 21, 22). Slurries of each of these materials were prepared by suspending soil (lg), without sample pre-treatment, in distilled water (100 cm³), and stirring as described above. The slurry so produced was pumped into the sample introduction system of the DCP, at the optimum conditions for solution analysis, and the material passing through the system collected. The material collected after passing through the entire sample introduction system was re-suspended in water and the particle size distribution of the solid material passing through determined. The results of these particle size determinations are shown in Figs. 23, 24, for soil SO-1 and SO-2 respectively. Comparison between Figures 21 and 23 for soil SO-1 and Figures 22 and 24 for soil SO-2 clearly show that particles of size > 8µm will not pass through the sample introduction system. Therefore for successful slurry atomisation procedures to be developed, the particle size of the solid material should ideally fall below 8µm when using this instrumentation.

5.3 Optimisation for Slurry Atomisation

The success of the Modified Simplex Procedure in deriving optimum conditions for both solution and hydride generation procedures suggested its application to the determination of optimum conditions for DCP slurry atomisation.

Gray (83), has shown that kaolin is a suitable material for the development of slurry atomisation procedures. Kaolin can be obtained in finely

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Particle size (µm)



Particle size (µm)

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-86-

powdered (< 10 µm) form, it is readily dispersed into suspension and although a refractory silicate matrix, it can be successfully atomised in the ICP. Because of these characteristics, the preliminary studies on optimisation were performed using kaolin (Kaolin light, B.D.H. Chemicals Ltd.,), with the particle size distribution determined in Fig. 25. The particle size distribution of this material shows the majority of the kaolin is < 8 µm. The dispersion of the kaolin can be significantly improved by the use of aqueous ammonia, as discussed by Gray (83). A full description of the theory of the dispersion of powders in liquid media is given by Allen (200), with three processes being identified. Firstly there is wetting of the surface of the solid material. Secondly, disaggregation of clusters of solid material and thirdly, stabilisation of the dispersion formed. Aqueous ammonia acts as a wetting agent for the dispersion of kaolin in aqueous systems (200), additionally it is considered to form an ionic double layer around the solid material so stabilising the dispersion (83).

Seven parameters were selected for optimisation, the horizontal and vertical viewing positions, nebuliser gas flow, plasma sleeve gas flow, ammonia dispersant concentration, added lithium enhancement buffer concentration and the concentration of the slurry. The four plasma parameters were included to allow comparisons with solution conditions to be made. The use of a dispersant, in this case aqueous ammonia, can have potential effects on both the nebuliser efficiency and on the behaviour of the plasma. Slurry concentration may dictate the amount of dispersant required and at high concentrations (<u>i.e.</u> > 10%), may affect the performance of the plasma and the accuracy of the technique. In preliminary studies on slurry atomisation, it was observed that analyte emission was enhanced by the addition of easily ionised elements in a

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similar fashion to solutions.

All reagents used were of analytical reagent grade unless otherwise stated.

Ammonia Solution, 35%, sp. gr 0.880, (B.D.H. Chemicals). Lithium Solution, (40 g litre Li). Dissolve 213 g of Lithium Carbonate (B.D.H. Chemicals), in a minimum amount of nitric acid (B.D.H. Chemicals), and dilute to 1 litre. Approximately 250 cm³ of concentrated nitric acid is required to completely dissolve the lithium carbonate.

These reagents were diluted as necessary for the sample slurries.

As can be seen in Fig. 26, the addition of increasing levels of EIE to both a solution and a slurry of approximately equal analyte concentration produces emission enhancement of equivalent magnitude for both matrices. This parameter was therefore included to determine the optimum concentration of EIE as added lithium for slurry atomisation.

The optimisation was performed for the determination of magnesium in kaolin using the software described in Chapter 3, and the Mg (II) 279.079 nm emission line. The criterion of merit was taken as the signal to background ratio corrected for slurry concentration. This emission line was chosen as it is rectilinear over the concentration range of the slurries prepared, therefore self-absorption of analyte emission was not considered to be significant.

The optimisation was terminated when successive vertices brought no significant improvement in response. The optimum conditions derived are

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Figure 26 Relative emission enhancement curves for Mg 279.55 nm line

-90-

given in Table 8, with univariate searches about each parameter shown in Figs. 27-33. The optimum range of each parameter about the centroid value of the simplex at the stopping condition is shown by the vertical lines on each univariate search. The success of the simplex procedure in deriving the optimum for each parameter is clearly shown. Of the seven parameters investigated, gas flows to the plasma (Figs. 27, 28), were essentially the same as those determined as optimum for the analysis of aqueous solutions. Variations in the added lithium concentration (Fig 29), only produced small changes in the SBR. This indicates that there is little difference between the analyte enhancement for solutions and slurries. The optimum for this parameter as derived by the simplex of 4.35 g 1^{-1} Li compares with the plateau region of the typical enhancement curve as shown in Fig. 26.

The use of aqueous ammonia as dispersant for the kaolin was not found to provide any significant improvement in response (Fig. 30). This curve shows two distinct parts, the first part at ammonia concentrations up to 3% m/V showing a plateau with a gradual decline in SBR at ammonia concentrations greater than 3% m/V. A possible explanation is that on the early part of the curve, the ammonia is assisting in wetting the surface of the solid material and dispersing the material, increasing the number of small particles in suspension and hence the response. The enhancement buffer of 4.35 g l⁻¹ lithium, an electrolyte, reduces the energy barriers between the particles and allows flocculation to occur. At ammonia concentrations greater than 3% m/V flocculation may become dominant, hence reducing SBR.

Horizontal and vertical viewing positions were again found to be critical. Horizontal position (Fig. 31), was found to have a sharp optimum,

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Horizontal position	0 mm
Vertical position	-1.05 mm
Nebuliser argon	$3.2 l min^{-1}$
Sleeve argon	3.7 l min ⁻¹
Added ammonia	3.1% m/V
Added lithium	4.35 g 1 ⁻¹
Slurry concentration	8.1% m/V


Figure 27 Slurry atomisation, univariate search nebuliser

Nebuliser argon (1 min⁻¹)



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Figure 29 Slurry atomisation, univariate search added lithium

Added lithium (g 1^{-1})

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Added aqueous ammonia (% m/V)

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Horizontal position (mm)

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Vertical position (mm)





% m/V kaolin slurry

-99-

with maximum response in the centre of the analytical zone as occurs for solution analysis. Vertical viewing position is again a critical parameter, with the optimum response for this line falling over the boundary of the plasma core and analytical zone (Fig. 32). The maximum in response for slurry atomisation was found to concur with that for solution analysis with the line used in this optimisation. This agreement between emission maxima for solution and slurry samples was found for other major elements (Table 9).

The univariate search for % m/V slurry concentration (Fig. 33), is of interest because of the curvature introduced at slurry concentrations > 12% m/V kaolin. This curvature is not considered to be caused by selfabsorption as this analytical line is linear in response up to 600 μ g cm⁻³ (189), and the analyte concentration in the slurries used did not exceed 130 μ g cm⁻³. This indicates that at high slurry concentrations, the analytical response can become severely impaired, either through reductions in transport efficiency or as a result of effects on the plasma. These effects are discussed in greater depth in Chapter 6.

The success of the modified simplex procedure in deriving optimum conditions for DCP slurry atomisation has been shown. Vertical viewing position in the observation zone was found to be the critial parameter, the other parameters showing less severe gradients on their response surfaces. Slurry concentration was found to impair analytical response at above 12% m/V. For routine use, optimisation can be readily performed by setting to the appropriate instrument operating conditions and profiling the vertical viewing parameter.

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Table 9 Relative vertical viewing position emission maxima for

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slurry and solution analysis

Element	(nm)	Relative vertical (mm from	viewing position core)
		Slurry	Solution
Ма	279,079	-0.5 to -1.5	0.00 to -1.5
Mg	279.553	0.15 to 0.25	0.15 to 0.25
Si	251.610	0.15 to 0.25	0.15 to 0.25
Al	308.210	0.70 to 0.80	0.70 to 0.80
Fe	259.940	0.50 to 0.60	0.50 to 0.60

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5.4.1 Initial Studies

Using the optimum conditions described above, the major element composition of certified reference soils SO-1 and SO-2 (CANMET, Ontario, Canada), was investigated. Soil SO-1 is an 80% clay subsoil of mixed mineralogy and soil SO-2 is a sandy soil with approximately 10% organic material (201). Both soils are supplied ball-milled to $< 74 \ \mu m$. The particle size distributions of soils SO-1 and SO-2 as supplied are shown in Figs. 21 and 22 respectively. Slurries of 0.1, 0.2 and 0.5% m/V of these materials were prepared to contain 5 g 1^{-1} lithium and 3% m/V added ammonia with no pre-treatment of the solid material. Using aqueous standards prepared to contain equivalent concentrations of lithium and ammonia as the slurry samples, major and minor elements in SO-1 (Table 10) and SO-2 (Table 11) were determined. These results show atomisation efficiencies of approximately 50% for soil SO-1 and 20% for soil SO-2 where atomisation efficiency has been defined for flame AAS by Willis (67), as "the ratio of the concentration of free atoms of the analyte in the flame (plasma) when a suspension of particles is sprayed to the concentration in the same part of the flame (plasma) when the same amount of analyte is sprayed as a solution".

These results show that higher atomisation efficiency is achieved with the sample having the finer particle size distribution. As described earlier, material > 8 μ m does not pass through the sample introduction system and enter the plasma. For the determination of major elements in kaolin atomisation efficiencies of 80-90% are achievable (Table 12). The particle size distribution of this material is shown in Fig. 25,

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	without sample pre-tre	<u>eacment</u>	
Element	Slurry Atomisation % m/m	Certificate Value % m/m	Atomisation Efficiency &(Slurry/Ref)
Si	14.4 ± 0.2	25.72 ± 0.22	56
Al	4.16 ± 0.12	9.38 ± 0.17	44
Fe	3.26 ± 0.07	6.00 ± 0.13	54
к	1.74 ± 0.03	2.68 ± 0.08	67
Mg	1.20 ± 0.05	2.30 ± 0.10	52 .
Ca	0.95 ± 0.01	1.80 ± 0.07	53
Ti	0.27 ± 0.01	0.53 ± 0.02	. 51
Mn	0.042 ± 0.001	0.084 ± 0.003	50

Table 10 Major elements in reference soil SO-1 by slurry atomisation

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without sample pre-treatment

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Element	Slurry Atomisation % m/m	Certificate Value % m/m	Atomisation Efficiency %(Slurry/Ref)
Si	4.43 ± 0.13	24.99 ± 0.23	17
Al	1.87 ± 0.20	8.07 ± 0.18	23
Fe	1.79 ± 0.02	5.56 ± 0.16	32
к	0.58 ± 0.01	2.45 ± 0.04	24
Ca	0.18 ± 0.01	1.96 ± 0.10	13
Ti	0.121 ± 0.002	0.86 ± 0.02	10
Mg	0.069 ± 0.003	0.54 ± 0.03	14
Mn	0.015 ± 0.001	0.072 ± 0.002	21

Table 11 Major elements in reference soil SO-2 by slurry atomisation

without sample pre-treatment

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with the majority of the material being < 8 μ m. The comparison of the atomisation efficiencies obtained for these samples with the respective particle size distributions for each sample indicate that particle size is a critical parameter in achieving high atomisation efficiencies.

Table 12 The determination of major elements in BDH kaolin

	Reference Value % m/m	Slurry Atomisation % m/m	Atomisation Efficiency %(Slurry/Ref)
SiO ₂	46.6	40.8	87.5
A12 ⁰ 3	38.5	29.6	76.9
Fe2 ⁰ 3	0.49	0.40	82.1
MgO	0.19	0.16	84.3

5.4.2 Analysis of Finely Ground Soil

As indicated above, higher atomisation efficiencies may be achieved using material < 8 μ m. As shown in Figs. 23 and 24 material > 8 μ m does not appear to pass through the DCP sample introduction system. Therefore, grinding of the soil to reduce the particle size of the solid material may provide significant improvements in atomisation efficiency.

5.4.2.1 Preparation of Finely Ground Soil Slurries

The particle size of reference soils SO-1, SO-2 and BCR 142, a light sandy soil (Bureau of Community Reference, Brussels, Belgium), was reduced by wet grinding 1 g of soil material using 3 mm zirconia beads (Glen Creston Ltd., Dalston Gardens, London), with 3 cm³ lithium nitrate (5 g Li litre⁻¹ prepared by dilution from solution prepared in 5.3), in a 30 $\rm cm^3$ polythene bottle on a laboratory flask shaker. The particle size of the solid material was reduced to < 5 μ m in three hours. The slurries were separated from the grinding elements by washing the material through a Buchner funnel, using a lithium solution (5 g 1^{-1}), into a volumetric flask (50 cm^3). The particle size distributions for slurries of reference soils SO-1, SO-2 and BCR 142 so prepared are shown in Figs. 34-36. For the samples SO-1 and SO-2, these distributions show that the majority of the material in these slurries is less than 5 µm and for BCR 142 less than 6.4 µm. The initial size distribution of the material is shown by the solid line on the diagram, with the size distribution of the of the solid material in the slurry twenty four hours later shown by the dotted line. This shows that the fine particle size distributions in the slurries prepared from these materials are stable over a long period.



Figure 34 Particle size distribution of finely ground reference soil SO-1

Particle size (µm)

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Particle size (µm)





The major and trace element constituents of the three reference soils SO-1, SO-2 and BCR 142 were determined by slurry atomisation. In addition several elements were determined in BCR 143 (Bureau of Community Reference, Brussels), a sewage sludge amended soil reference material. Calibration was achieved using aqueous standards prepared in 5 g 1^{-1} Li enhancement buffer. The results obtained (Tables 13-16) show atomisation efficiencies approaching 100% for major components Si, Fe, K, Mg and Ca, and good agreement between slurry analysis and certificate values for the minor and trace elements. The low recoveries experienced for aluminium may be explained by incomplete decomposition of thermally stable Aluminium-Oxygen species in the plasma. Decomposition of the soil matrix can be inferred from the high recoveries observed for silicon, however the temperature of the DCP may be insufficient to completely dissociate the aluminium oxide matrix. Studies by Porter et al. (202), have indicated that stable AlO can exist in the vapour phase for some experimental systems, however this requires verification for the DCP.

5.5 Milk Analysis by DCP Slurry Atomisation

Much interest is expressed in the major and trace element composition of milk. Milk provides a sample naturally suited to slurry analysis, with the particle size of the solid material (Fig. 37), showing that the majority of the material naturally falls below 5 μ m, below the critical particle size range for high atomisation efficiency. Andersen (80), suggested that reconstituted milk powder suspensions can be stabilised by the addition of Triton X-100. Triton X-100 (0.01% m/V) was found to help maintain stable suspensions for up to twenty four hours.

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Element	Slurry Atomisation % m/m	Certificate Value % m/m
Si	25.0 ± 0.4	25.72 ± 0.22
Al	7.48 ± 0.05	9.38 ± 0.17
Fe	. 6.00 ± 0.08	6.00 ± 0.13
Ca	1.78 ± 0.06	1.80 ± 0.07
Na	1.91 ± 0.03	(1.90)
к	2.39 ± 0.09	2.68 ± 0.08
Mn	0.078 ± 0.002	0.089 ± 0.003
Ρ	0.071 ± 0.003	0.062 ± 0.010
Mg	2.31 ± 0.04	2.31 ± 0.10
	Slurry Atomisation µg g	Certificate Value µg g

Table 13 Major, minor and trace elements in finely ground soil SO-1

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Cr	160 ± 10	160 ± 15
Co	20 ± 1	(32)
Cu	57 ± 2	61 ± 3
Ni	86 ± 4	94 ± 7
Pb	17 ± 3	21 ± 4
Zn	132 ± 4	146 ± 5

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Element	Slurry Atomisation % m/m	Certificate Value % m/m
Si	23.5 ± 0.3	24.99 ± 0.23
Al	5.27 ± 0.09	8.07 ± 0.18
Fe	5.16 ± 0.09	5.56 ± 0.16
Ca	1.65 ± 0.04	1.96 ± 0.10
Na	1.77 ± 0.06	1.90 ± 0.05
ĸ	2.21 ± 0.07	2.45 ± 0.04
Mg	0.46 ± 0.03	0.54 ± 0.03
P	0.34 ± 0.02	0.30 ± 0.02
Mn	0.069 ± 0.002	0.072 ± 0.002
	Slurry Atomisation µg g	Certificate Value µg g
Cr	13.2 ± 0.5	16 ± 2
Co	6.5 ± 0.8	9 ± 2
Cu	7.2 ± 0.4	7 ± 1
Ni	14 ± 2	8 ± 2
Pb	24 ± 3	21 ± 4
Zn	120 ± 4	124 ± 5

Table 14 Major, minor and trace elements in finely ground soil SO-2

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Element	Slurry Atomisation % m/m	Indicated Value % m/m
Si	27.1 ± 0.6	31
Al	3.18 ± 0.04	5.0
Fe	2.01 ± 0.06	2.0
Ca	3.58 ± 0.09	3.5
к	1.76 ± 0.05	2.0
Na	0.71 ± 0.02	0.7
Mn	0.053 ± 0.004	0.057
	Slurry Atomisation µg g	Certificate Value µg g
Cr	80 ± 4	75 ± 9
Co	6.1 ± 0.8	7.9 ± 1.1

27.5 ± 0.6

 29.2 ± 2.5

37.8 ± 1.9

92.4 ± 4.4

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30 ± 1

37 ± 3

37 ± 3

86 ± 3

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Cu

Ni

Рb

Zn

Table 15 Major, minor and trace elements in finely ground soil BCR 142

Element	Slurry Atomisation Pg g	Certificate_Value µg g
Cd	30.2 ± 1.6	31.1 ± 1.2
Cu	233 ± 8	236.5 ± 8.2
Pb	1370 ± 35	1333 ± 39
Zn	1230 ± 30	1272 ± 30

Table 16 Analysis of finely ground soil BCR 143

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Using 1, 5 and 10% m/V suspensions of reconstituted milk powder containing 5 g 1^{-1} Li enhancement buffer and 0.01% Triton X-100, major and trace elements in a commercially available infant milk and in certified reference milk BCR 63 (Bureau of Community Reference, Belgium), were determined. Calibration was achieved using aqueous standards containing 5 g 1^{-1} lithium and 0.01% Triton X-100. The results obtained show excellent agreement with values obtained from an independant laboratory (Table 17), and with the certified values of the reference material (Table 18), at both major and trace element levels.

5.6 DCP Slurry Atomisation of Plant Material

A major constraint upon the development of successful slurry atimisation procedures for plant material is the difficulty in reducing the sample particle size to the desired range. The success of the zirconia bead grinding technique for soil samples prompted an investigation of this technique for plant material.

5.6.1 Direct Grinding of Plant Material

The critical parameters in the grinding process were identified by a series of grinding experiments using a grass sample supplied by ADAS, milled to pass a 2 mm mesh. A series of 30 cm³ bottles were loaded with 0.5 g sample and varying charges of beads and water. After one hour, the particle size distribution of each sample was determined. Using % volume of solid material below 10 μ m as the criterion of merit, the results obtained (Figs. 38, 39), show that a mixture of 0.5 g sample to 10 g zirconia beads to 12 cm³ liquid produces the slurry with finest particle size distribution. The use of dispersants <u>e.g.</u> Triton X-100, was found

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Element	Slurry Atomisation µg g	Independant_Analysis µg g
P	2170 ± 40	2300
Ca	2860 ± 60	2900
Na	1530 ± 30	1500
к	5100 ± 70	4500
Mg	310 ± 20	340
Cu	3.90 ± 0.06	3
Fe	58 ± 3	52
Zn	31 ± 2	·35
Mn	0.27 ± 0.05	0.3

Table 17 Major and trace elements in dried milk (infant formula)

Table 18 Major and trace elements in reference milk powder BCR 63

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Element	Slurry Atomisation µg g	Certificate_Value µg_g_
P	9900 ± 200	10400 ± 300
Ca	12600 ± 300	12600 ± 500
Na	4700 ± 100	4570 ± 160
к	18400 ± 700	17800 ± 700
Mg	1160 ± 30	1120 ± 30
Cu	0.63 ± 0.05	0.545 ± 0.030
Fe	1.4 ± 0.2	2.06 ± 0.25
Zn	37 ± 2	(42)
Mn	0.22 ± 0.09	(0.226)





to reduce the grinding efficiency by causing foaming in the grinding pot.

5.6.2 Analysis of Plant Materials BCR 60, 61, 62

Slurries of the certified reference materials BCR 60, Aquatic Plant, BCR 61, Aquatic Plant, and BCR 62, Olive Leaves (Bureau of Community Reference, Belgium), were prepared in 30 cm³ polythene bottles using 0.5 g sample to 10 g beads to 10 cm³ lithium nitrate solution (5 g 1^{-1} Li enhancement buffer). Samples were ground using a laboratory flask shaker for three hours. The particle size distributions obtained for each of these materials are given in Figs. 40-42. The slurries were made to volume as described in 5.4.2. The levels of Cu, Mn, Pb and Zn were determined is these samples by DCP slurry atomisation using aqueous calibration, with the standards containing 5 g 1^{-1} lithium as enhancement buffer. The results obtained show good agreement with the certified levels with typical precision for copper, manganese and zinc, of less than 5%. The values obtained for lead show poorer accuracy and precision as a result of performing determinations at low concentrations in the sample with incomplete correction of spectral interferences arising from magnesium and calcium in the sample matrix, (Table 19).

Despite the agreement between certificate and slurry atomisation results for BCR 60, BCR 61, and BCR 62, the particle size distributions for these slurries (Figs. 40-42), do not fit the ideal characteristics of being below 8-10 µm as described earlier. Some of these size effects can be readily explained by the varied response of the Coulter counter to the shape, and the type of material undergoing particle size analysis. The presence of fibres in the slurry can lead to errors in the size

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Particle size (µm)









Element	BCR	BCR 60		BCR 61		BCR 62	
	Slurry µg g	Certificate µg g	Slurry µg g	Certificate µg g	Slurry µg g	Certificate µg g	
Cu	54 ± 3	51.2 ± 1.9	690 ± 20	720 ± 31	45 ± 2	46.6 ± 1.8	
Mn	.1740 ± 90	1759 ±51	3710 ± 130	3771 ± 78	62 ± 7	57.0 ± 2.4	
Pb	66 ± 10	63.8 ± 3.2	51 ± 9	64.4 ± 3.5	34 ± 5 [.]	25.0 ± 1.5	
Zn	305 ± 10	313 ± 8	560 ± 10	566 ± 13	20 ± 1	16.0 ± 0.7	

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Table 19 Determination of Copper, Manganese, Lead and Zinc in reference plant materials

BUR 60, BUR 61 and BUR 62 by Slurry atomi

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distribution observed (200). More seriously, the presence of fibres in the slurry indicates the resistance of plant material to being finely ground. In addition to this, some plant materials contain components, <u>e.g.</u> polysaccharides, that can appreciably increase the viscosity of sample slurries at low (1-2% m/V) slurry concentration.

This effect was observed to be particularly severe for samples of lichen. Lichens are used as indicators of environmental pollution and this material was provided dried and ground to less than 180 μ m (201). Slurries of these materials were prepared by grinding using the bead technique with a sample to bead to liquid ratio of 1:10:10. The results obtained for a range of elements are given in Table 20.

Sample	Element µg g ⁻¹						
	Fe	Мо	Na	Cu	Se	Cđ	
1	740	4.6	830	180	<5	<0.2	
2	1020	1.4	720	9.9	<5	<0.2	
2	1.40	(0 F	252				
د	140	<0.5	250	4.2	<10	<0.5	
- 4	200	<0.5	60	4.5	<10	<0.5	

Table 20 Analysis of lichen by DCP slurry atomisation

This problem of increased viscosity can be overcome using a suitable added internal standard <u>e.g.</u> scandium, however, the advantage of the high sample loadings compared to digestion techniques is subsequently lost. A potential solution to both of these problems is to use a simple carbonisation or charring procedure and grind the material to the desired size range. A procedure such as this has been suggested for analysis of plant materials by XRF by Satake and Uehiro (203). In addition to improving the grinding of the slurry, this technique has the potential to significantly increase sample loading in the slurry.

5.6.3 Sample Charring for Slurry Atomisation

5.6.3.1 Preliminary Studies

Preliminary studies on sample charring were performed using a sample of straw provided by ADAS. The fibrous nature of straw is highly resistant to grinding. A sample of straw (10 g), was placed in a porcelain crucible, placed in a muffle furnace (Carbolite, Sheffield), and the temperature raised to 200 ± 25 °C. The sample was left overnight for twelve hours. The charred sample was transferred to a polythene bottle (100 cm³, Nalgene), and zirconia beads and lithium nitrate solution (20 cm³, 5 g l⁻¹ Li) added. The sample was ground as described earlier using the laboratory flask shaker for 30 minutes. The particle size distribution of this slurry after this time is shown in Fig. 43. This approach where the low temperature char destroys the resistant fibrous nature of the plant material allows the successful grinding fo the plant material to the desired particle size range. Using such a procedure, the charring temperature must be closely regulated to avoid losses of volatile elements such as cadmium from the sample matrix.

5.6.3.2 Carbonisation - Slurry Atomisation of Reference Materials NBS 1573 Tomato Leaves and BCR 62 Olive Leaves

The two reference materials NBS 1573 Tomato leaves (National Bureau of Standards, Washington D.C., U.S.A), and BCR 62 (Bureau of Community

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Reference, Brussels), were selected as two plant materials with a fibrous nature.

Sample (5 g), was charred in an acid-washed porcelain crucible in a muffle furnace at 200 \pm 25 °C for 12 hours, transferred to a polythene bottle (Nalgene, 100 cm³) and zirconia beads (30 g) and lithium nitrate solution (20 cm³, 5 g l⁻¹ Li) added. Samples were ground for three hours using the flask shaker. The slurry produced was separated from the grinding elements by washing with lithium nitrate solution (5 g l⁻¹ Li), through a Buchner funnel. The slurries were made to volume (50 cm³), using the same lithium solution. Boron, lead, cadmium, copper, and zinc were determined in the slurries using DCP emission spectrometry, with calibration achieved using aqueous standards matched for lithium content. The results obtained are shown in Table 21.

Table 21 Analysis of plant material by carbonisation - slurry atomisation

Element Slurry $\mu g g^{-1}$ Certificate $\mu g g^{-1}$ Slurry $\mu g g^{-1}$ Ce	ertificate µg g ⁻¹
B 31 ± 1.5 (30) 19 ± 2	(20)
Cd 2.8 ± 0.5 (3) <0.3	0.10 ± 0.02
Cu · 11 ± 0.3 11 ± 1 46 ± 1.5	46.6 ± 1.8
Pb 6 ± 1 6.3 ± 0.3 29 ± 2	25 ± 1.5
$Zn = 56 \pm 3$ 62 ± 6 14 ± 1	16 ± 0.7

These results show good agreement between the slurry and certificate values. Compared to the slurries prepared by direct grinding of the material, precision appears to be improved, in particular for lead.

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The charring procedure was found to provide a suitable method for avoiding the viscosity effects described in 5.6.2. No loss of cadmium or lead was observed for this procedure.

5.7 The Analysis of Sewage Sludge by Slurry Atomisation

Two sewage sludges BCR 144 and BCR 145 (Bureau of Community Reference, Belgium), were analysed using slurry atomisation procedures. BCR 144 is described as a sewage sludge of domestic origin and BCR 145 described as a sewage sludge of mixed domestic/industrial origin. The materials are homogeneous powders of a particle size less than 90 μ m. The material consists of both organic and mineral matrices.

5.7.1 Direct Grinding of Sewage Sludge

Slurries of the two reference sewage sludges BCR 144 and BCR 145 were prepared using the procedure described in 5.6.2 for plant materials using approximately 1g of material. The results obtained (Table 22), show reasonable agreement with certified levels.

Table 22 The analysis of sewage sludge by slurry atomisation

	SEWAGE SLUI Found µg g	DGE BCR 144 Certificate µg g		SEWAGE SLU Found µg g	DGE BCR 145 Certificate µg g
Cd	4.0 ± 0.5	3.41 ± 0.25	Cd	17.8 ± 1.6	18.0 ± 1.2
Cu	696 ± 15	713 ± 26	Cu	422 ± 20	429 ± 10
РЪ	490 ± 15	495 ± 19	Pb	334 ± 15	349 ± 15
Zn	3080 ± 50	3143 ± 103	Zn	2750 ± 60	2843 ± 64

The precision observed for cadmium for BCR 144 is poorer than observed for the other elements determined, reflecting that the determination was performed at the ng cm⁻³ level.

In the analysis of these slurries, some material was observed to float at the air/slurry interface. Therefore to produce more homogeneous slurries the carbonisation procedure used for plant material was applied to the sewage sludges.

5.7.2 Carbonisation - Slurry Atomisation of Sewage Sludge

Slurries of the reference materials BCR 144 and BCR 145 were prepared using the procedure described in 5.6.3.2 with approximately 5 g of material used per sample. The results obtained using aqueous calibration are given in Table 23.

Table 23 Analysis of sewage sludge by carbonisation - slurry atomisation

	BCR	144	BCR 145			
Element	Slurry	Certificate	Slurry	Certificate		
Cđ	4.6 ± 0.5	3.41 ± 0.25	17.6 ± 1.0	18.0 ± 1.2		
Cu	720 ± 10	713 ± 26	445 ± 15	429 ± 10		
Pb	480 ± 15	495 ± 19	358 ± 15	349 ± 15		
Zn	2990 ± 75	3143 ± 103	2790 ± 45	2843 ± 64		

Again reasonable agreement between slurry and certificate values can be seen. The value obtained for cadmium for BCR 144 is again high, possibly indicating under-correction of a spectral interference on this line. Overall there appears to be little difference between the results

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obtained using both the direct and carbonisation slurry procedures.

5.8 Summary

The parameters that govern the development of successful slurry atomisation procedures have been identified. Particle size of the solid material has been shown to be critical with particles with a diameter of less than 5-8 µm being able to pass directly through the sample introduction system. The variable step-size simplex procedure has been used to derive optimum conditions for the determination of magnesium in kaolin. The critical parameters were found to be the horizontal viewing position, with the maximum lying in the centre of the analytical zone, and vertical viewing position, with the emission maxima for the line studied in the optimisation lying over the boundary between the plasma core and the analytical zone. The other parameters investigated were not found to be critical, although evidence for a reduction in sample atomisation at high sample loadings was obtained.

For slurry samples where the particle size is reduced to less than 5 µm, atomisation efficiencies of approximately 100% can be obtained. Using a simple grinding technique where necessary, materials such as soils, milk, plant materials and sewage sludges, have been analysed using slurry atomisation procedures. Calibration was achieved using simple aqueous calibration and the results obtained show good agreement with certificate values and independant analyses. A technique of sample charring prior to grinding the material has been proposed for plant materials that are resistant to grinding. The results obtained show good agreement with certificate levels for the elements determined.

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Slurry atomisation has been shown to be viable for materials such as soils, milk, plant material and sewage sludge, with calibration achieved using aqueous standards and commercially available instrumentation.

CHAPTER 6

THE EFFECT OF SLURRY ATOMISATION ON EXCITATION TEMPERATURE, IONISATION TEMPERATURE AND ELECTRON DENSITY IN THE DCP

6.1 Introduction

The measurement of excitation temperature (T_{exc}) , ionisation temperature (T_{ion}) , and electron density (n_e) , provides a useful diagnostic tool for the investigation of plasma processes. The absolute and relative magnitude of each of the above parameters has been studied in the development and investigation of models for excitation mechanisms in plasmas. Significant contributions in this area regarding the DCP include Miller, Eastwood <u>et al.</u> (97, 99, 100, 103, 106), Decker (93), and Blades and Lee (105). The conclusions from these investigations and the excitation mechanisms proposed has been discussed in Chapter 2. The potential of slurry atomisation in further developing these studies has yet to be investigated.

In a recent paper, Ramsey and Thompson (204), studied matrix effects in the ICP. From this work they concluded that the loss of analyte emission observed could be attributed to cooling of the plasma by the matrix. In addition, the degree of cooling caused was related to the energy required to dissociate and ionise the matrix. The implication of this work to slurry atomisation is clear. In slurry analysis, the energy required to dissociate the solid matrix may exacerbate the magnitude of any matrix effects, particularly at high (<u>e.g.</u> > 10% m/V), slurry concentration with refractory materials.

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In the DCP, the classical emission intensity against EIE concentration curve gives a rapid rise to a plateau region, followed by a gentle decline in intensity at higher EIE concentrations (Fig. 43). This shape has been explained by Miller <u>et al.</u> (100), who suggest that the curve occurs as the result of two processes. Firstly the saturation of EIE derived energy transport mechanisms (<u>e.g.</u> radiative transfer by EIE resonance lines) results in the observed enhancement. Secondly, these improvements in coupling energy from the core to the analytical zone cause a gradual cooling of the plasma and thus reducing the emission intensity. With slurry atomisation, the effects of increasing the sample matrix concentration upon the plasma requires investigation to allow for an improved understanding of these effects to be developed.

The parameters most frequently used as diagnostic tools in emission spectrometry are the excitation temperature, which characterises the populations of the various atomic energy levels, the ionisation temperature, which describes equilibrium between atomic and ionic states in the plasma and the electron density. Electron density is of interest again from the viewpoint of ionisation equilibrium, but also from the proposed role of electrons in analyte excitation (100, 105, 205).

The techniques for the measurement of T_{exc} , T_{ion} and n_e are described in detail by Boumans (25), Kornblum and De Galen (206), Alder <u>et al</u>. (205), and Griem (207). The latter of these being of particular significance in the determination of n_e . The techniques used to determine these T_{exc} and T_{ion} conventionally assume that local thermodynamic equilibrium (LTE) exists within the system under investigation. For a system in thermodynamic equilibrium, the values obtained for T_{exc} and T_{ion} are numerically equal to each other, and equal to the electron temperature and gas temperature

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which describe the energies of the electrons and neutral atoms respectively. In a non-homogeneous system such as an analytical plasma, the temperature gradients present do not allow the overall attainment of thermal equilibrium, however, it is customary to consider the plasma in discrete volumes and refer to the attainment of local thermodynamic equilibrium. The theoretical background concerning the measurement of these parameters is given below.

6.1.1 Excitation Temperature

The equation for the measurement of T using the intensity ratio of exc two lines is readily derived for a system in LTE, from equation (1.10);

$$B = \frac{1}{4\pi} h \dot{V}_{ki} A_{ki} \frac{N_{i} g_{k} \exp(-E_{k}/kT)}{Z(t)}$$
1.10

Labelling the lines a and b, and omitting the subscripts i and k for clarity, for the two lines belonging to the spectrum emitted by the atom or ion of an element (e.g. Fe(I));

$$\frac{Ba}{Bb} = \frac{(g A)_a \dot{V}_a}{(g A)_b \dot{V}_b} \exp \left[-\left(E_a - E_b\right) / kT\right] \qquad 6.1$$

This equation can be re-arranged (25), to give the practical equation:

$$T = \frac{5040 (V_a - V_b)}{\log (g A)_a / (g A)_b - \log \lambda_a / \lambda_b - \log B_a / B_b}$$
 6.2

where V is the excitation potential of the line (eV), A the relative transition probability, g the statistical weight, λ the wavelength (m), and B the relative intensity. Subscripts a and b refer to the two lines

respectively. In performing temperature measurements using this procedure the precision and accuracy of the measurement can be improved by using spectral lines where the difference in V_a and V_b is large and the ratio (g A)_a / (g A)_b is large. This avoids the use of extreme values of B_a and B_b. Bridges and Kornblith (208) have published values for transition probabilities of the Fe(I) spectrum with accuracies to ± 10 %.

6.1.2 Ionisation Temperature

The ionisation temperature for a system in LTE can be determined using the combined Boltzman - Saha equation (206), given below;

$$\frac{[x^+]}{[x]} = \left(\frac{2\pi M_e kT}{h^3}\right)^{3/2} \frac{2Z_x^+}{Zx} \frac{1}{[n_e]} \exp(-E_{ion} / kT_{ion}) \quad 6.3$$

where $[X^+]$ and [X] are the respective concentrations of the ionic and atomic states.

	M _e	=	mass of the electron	(9.11	х	10 ⁻³¹	kç	3)
	k	=	Boltzman_ constant	(1.38	x	10 ⁻²³	J	к ⁻¹)
	h =	=	Planck's constant	(6.62	x	-34 10	J	s ⁻¹)
	Tion	=	ionisation temperature	(K)				
zx+	and ZX	=	ionisation potentials of the ion					
			and atom states respectively					
	n e	Ξ	electron density	(m ⁻³)				
	E ion	=	the energy of the upper state	(eV)				

From this equation, it can be seen that the concentration of the two species in consecutive ionisation stages is inversely proportional to n_e . Determination of T_{ion} can be performed by measuring the relative intensities of atom and ion lines of a particular thermometric species, determining the electron density and inserting these values into the Boltzman-Saha equation (206).

6.1.3 Electron Density

The electron density can be determined by measuring the Stark half-width $(\Delta\lambda s_1)$ of the broadened H $\dot{\beta}$ Balmer line at 486.133 nm. This method, described by Griem (207), relates n to $\Delta\lambda s_1$ by the relationship;

$$n_{e} = C(n_{e}, T) \Delta \lambda s_{\frac{1}{2}}^{3/2} \qquad 6.4$$

where C is a weak function of n and T. Values of C have been tabulated (207), so that values for n can be estimated with an accuracy of \pm 10%. The advantage of the H β Stark broadening measurement in determining n e is that no assumptions are made concerning the existence of LTE.

In this study, the effect of increasing slurry concentration on T_{exc} , T_{ion} and n_e was investigated. No spatially resolved information was sought and the information was obtained using the instrument operating conditions found optimal for solution and slurry analysis.

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6.2 Experimental

6.2.1 Excitation Temperature

Two sets of kaolin slurries covering the range from 1% m/V kaolin, to 20% m/V kaolin were prepared using the kaolin, 5 g 1^{-1} lithium solution and aqueous ammonia dispersant, as described earlier. One set of slurries was prepared at the optimal conditions for slurry analysis described in Chapter 5, the other was prepared containing no added lithium solution. For reference purposes, two solutions of 500 μ g cm⁻³ Fe, one containing lithium solution (5 g 1^{-1} Li) were prepared. To allow comparison between the slurries, all results were obtained using the emission intensity maximum in each matrix of the Fe(II) 259.940 nm line as a spatial reference point. The choice of thermometric species was governed by the concentration of the element in the kaolin. For the determination of T_{exc} Fe was found to be present in sufficient concentration to allow the use of weak transitions (Table 12). In addition, tabulations of line g A values are readily available (208). Facilities for the calibration of the monochromator and detector for spectral intensity were not readily available. Therefore, to compensate for the variation in spectral characteristics both between and within orders of the echelle spectrometer -(209), emission line pairs within close proximity of each other were used.

The lines used and relative transition probabilities as reported by Bridges and Kornblith are given in Table 24. Each line in the pair was scanned using the instrumentation described in Chapter 2. The relative intensities obtained were used to determine T_{exc} using equation 6.2.

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Fe(I) wavelength /nm	Transition Probability/ Statistical weight (g A)	Excitation Potential /eV
371.993	0.3715	3.33
372.256	0.0525	3.42
372.438	0.1995	5.61
372.762	0.5945	4.29

The results obtained are shown in Figs. 44 and 45. Although variation exists in the absolute value for T_{exc} , a consistent trend in cooling of the plasma for high slurry concentrations can be seen , with lithium present.

6.2.2 Ionisation Temperature

The ionisation temperature was determined by measuring the relative intensities of the Zn(I) 213.856 nm and Zn(II) 206.200 nm lines using the slurries and procedure described above. T_{ion} was calculated from equation 6.3 using the value obtained for n_e from the H β measurement (see section 6.2.3) and using a computer program to evaluate the two terms of T_{ion} therein (Appendix I). As for the measurement of T_{exc} , constraints were imposed on the choice of thermometric species for the measurement of T_{ion} . The results obtained (Figs. 46, 47), show average values of T_{ion} of 8090 K and 7660 K respectively, for the lithium added and no lithium added slurries. The variation in T_{ion} observed for both sets of slurries falls within the error for these measurements.



Figure 44 Variation of Texc with slurry concentration, 5 g 1⁻¹ added lithium

% m/V slurry concentration



Figure 45 Variation of Texc with slurry concentration, no added lithium







The electron density, n_e was determined by measuring the Stark half-width $(\Delta\lambda s_j)$, of the broadened H line at 486.133 nm. This was achieved by slowly scanning the H β line (approximately 0.5 nm min⁻¹), using entrance slits on the monochromator of 25 µm. Doppler broadening and instrumental broadening were determined by scanning the Ti(I) 487.014 nm line. The Doppler component can be calculated using equation 6.5 (206), assuming a temperature of 5000 K;

$$\Delta \lambda_{\rm D} = 7.16 \times 10^{-7} ({\rm T/M})^{\frac{1}{2}} \lambda_{\rm O}$$
 6.5

where $\Delta \lambda_D$ is the Doppler half-width, T the temperature, M the mass number of the species used (Ti = 47.9), and λ_O the spectral wavelength of the species used. The Doppler half-width was calculated to be 0.0036 nm. The instrumental broadening $\Delta \lambda_{ins.}$ was obtained by the relationship (205);

$$\Delta \lambda_{\text{ins.}} = \left[\left(\Delta \lambda_{\frac{1}{2}} \text{ at } 487.014 \right)^2 - \left(\Delta \lambda_{D} \right)^2 \right]^{\frac{1}{2}} \qquad 6.6$$

The instrumental broadening was calculated to be 0.0145 nm. The Stark half-width, $\Delta \Lambda s_{\frac{1}{2}}$ was then obtained by removing the instrumental and Doppler components from the measured half-width of the H β line. Values of C(N_e, T) at 5000 K for electron densities of 10²⁰ m⁻³, 10²¹ m⁻³ and 10²² m⁻³ were obtained from Griem (207) and interpolated for electron densities over the range 10²⁰ - 10²² m⁻³ (Table 25). The electron density was obtained by converting the Stark half-width $\Delta \Lambda s_{\frac{1}{2}}$ into Angstrom units, selecting the closest value of C(N_e, 5000 K) to the value of $\Delta \Lambda s_{\frac{1}{2}}$ from Table 25, and then inserting the values of C (N_e, T) and $\Delta \lambda s_{\frac{1}{2}}$ into equation 6.4.

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n_e , m ⁻³	С(n _e , 5000 K)	$\Delta \lambda s_{\frac{1}{2}}, (\mathring{A})$
1.0×10^{20}	3.84×10^{20}	0.407
2.0×10^{20}	3.82×10^{20}	0.649
3.0×10^{20}	3.81×10^{20}	0.853
4.0×10^{20}	3.79×10^{20}	1.037
5.0 x 10^{20}	3.77×10^{20}	1,207
6.0×10^{20}	3.75×10^{20}	1.368
7.0 x 10^{20}	3.73×10^{20}	1.521
8.0×10^{20}	3.72×10^{20}	1.666
9.0 x 10^{20}	3.70×10^{20}	1.809
1.0×10^{21}	3.68×10^{20}	1.947
2.0×10^{21}	3.65×10^{20}	3.108
3.0×10^{21}	3.63×10^{20}	4.088
4.0×10^{21}	3.60×10^{20}	4.979
5.0×10^{21}	3.57×10^{20}	5.810
6.0×10^{21}	3.55×10^{20}	6.586
7.0×10^{21}	3.52×10^{20}	7.340
8.0×10^{21}	3.49×10^{20}	8.069
9.0 x 10^{21}	3.47×10^{20}	8.729
	•	
1.0×10^{22}	3.44×10^{20}	9.454

Table 25 Interpolated values for n_e , $C(n_e, T)$ and $\Delta\lambda S_{\frac{1}{2}}$ (207)

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The results obtained (Table 26), show excellent agreement with previously determined values of 2 x 10^{21} - 3 x 10^{21} m⁻³ for the DCP analytical zone (100, 105). Both series of slurries showed a reduction in n_e with increasing slurry concentration (Figs. 48, 49), the reduction for the slurry containing added lithium being more severe.

Fable 26	Values	for	ⁿ e	in	slurries	with	and	without	added	lithium
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Slurry Concentration % m/V	n , slurry with added lithium	n , slurry without eadded lithium
Reagent blank	3.44×10^{21}	2.78×10^{21}
1	3.28×10^{21}	2.65×10^{21}
5	3.51×10^{21}	2.54×10^{21}
10	3.09×10^{21}	2.46 x 10^{21}
15	2.29×10^{21}	2.83×10^{21}
20	2.33×10^{21}	2.45×10^{21}

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slurry concentration (% m/V)





The values obtained for T_{exc} (5500 K), T_{ion} (7700 K), and n_e (3 x 10²¹ m⁻³), show reasonable agreement with those obtained for the analytical zone by other workers. T_{exc} has been shown to be approximately 5000 to 6000 K depending on viewing position and thermometric species used (93, 99, 100). T_{ion} has been estimated as being 6600 to 7000 K (99, 100), and n_e as being in the range 1 x 10²¹ to 3 x 10²¹ m⁻³ depending on viewing position, (99, 100, 105, 106).

Eastwood <u>et al.</u> (99), have shown that the addition of EIE to a solution does not produce a significant change in T_{ion} . This is confirmed in this study when considering the values obtained for solutions and for slurry concentrations < 5% m/V. In the same work, Eastwood <u>et al.</u> (99), indicated no change in n_e in the analytical zone when sodium was added as EIE. These authors did however, report that the temperature observed from the atomic spectrum of the element increased approximately 500 K when 0.5 M sodium was added. The results from this study do not show this trend. Such lack of agreement may be attributed to the thermometric species or the method of temperature measurement used (25), thus further study in this area may provide significant data.

The most striking result for both the measurement of T_{exc} and n_e is the reduction of these parameters with increased slurry concentration in the presence of 5 g l⁻¹ added lithium. This indicates a cooling in the plasma at higher slurry concentrations. If the temperature curves in Fig. 4**4** are compared to Fig. 32, the univariate search performed on slurry concentration in the optimisation for slurry atomisation, it can be seen that this apparent reduction in temperature occurs at similar slurry

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concentration in both. This indicates that the effects observed in Chapter 5 may be attributed to this observed cooling of the plasma. To confirm that this effect does not arise from changes in transport efficiency, the net transport efficiency was assessed by passing a known amount of slurry through the plasma and collecting the material not being transported from waste. These measurements were made using the optimum gas flows described earlier, allowing two minutes for equilibrium conditions to be attained in the sample introduction system. Transport efficiency was calculated from;

Transport Weight of slurry introduced - weight of slurry collected = Efficiency weight of slurry introduced

The results obtained gave an average transport efficiency for both slurries of 15% and are shown in Fig. 50.

The reduction in n_e observed for the slurries containing added lithium (Fig. 48), again indicates a cooling of the plasma. That this measure is independant of the content of a thermometric species in the slurry is further evidence for a suggested cooling of the plasma, again occurring at slurry concentrations > 10% m/V. The gentle reduction in the value of n_e for the slurry without added lithium (Fig. 49), indicates the vertical displacement of the plasma with increasing slurry concentration. This is consistent with the steep temperature gradients known to exist in the DCP analytical zone (93, 99, 100, 103-106).

In reviewing analyte excitation in the DCP, Miller <u>et al.</u> (100, 103), describe the effects of adding an EIE to the plasma as being improved radiative coupling between the plasma core and the analytical zone and

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slurry concentration (% m/V)

an antagonistic acceleration of the radiative cooling of the plasma via the EIE resonance lines.

The effects observed for T_{exc} and n_e are consistent with this proposed model that the addition of EIE accelerates the rate of energy transfer in the plasma. The reduction in n_e , T_{exc} observed for the slurries with added lithium may arise because of the accelerated cooling mechanisms proposed (100). The presence of EIE at levels in excess of 1 M has been shown to produce a quenching effect on analyte emission as a result of the dominance of the radiative cooling of the plasma (100). Therefore, the high sample matrix loading may be contributing to the radiative cooling effect, leading to the results observed from this study.

Evidence for a cooling of the plasma by the energy requirement for matrix dissociation, as proposed by Ramsey and Thompson (204), may be proposed as the mechanism for the observed gentle decline in the parameters at low slurry concentrations. The cooling effects observed at high slurry concentrations can be readily explained by existing models of DCP analyte excitation and enhancement, indicating that no major differences exist between analyte excitation for solution or slurry matrices.

From a practical viewpoint, these results indicate a limitation on the use of DCP slurry atomisation. If the analyte elements are susceptible to emission enhancement, this can be controlled by the addition of 5 g 1^{-1} Li (Fig. 25). This however, can limit the useful working range of slurry concentration to below 10% m/V for a refractory matrix such as kaolin , and compromise the advantage of the technique of relatively high sample loadings.

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 T_{exc} , T_{ion} and n_e have been measured within a range of kaolin slurry concentrations < 20% m/V both with and without the presence of 5 g l⁻¹ Li. T_{exc} and n_e were found to decrease with increasing slurry concentration for the slurries containing lithium. This decrease is attributed to an increase in the rate of radiative cooling caused by the presence of EIE (100), to which the high sample matrix loading is considered to contribute. For sample matrices where enhancement buffering is required, the use of 5 g l⁻¹ Li may limit the useful working range for slurry concentration to below 10% m/V. Where no enhancement buffering was used, sample loadings of 20% m/V did not significantly cool the plasma. Analyte excitation and enhancement for slurry atomisation is believed to be essentially similar to that proposed for solutions.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1 Conclusions

This work has shown the DCP as being a versatile device for atomic emission spectrometry. The DCP is able to atomise and excite elements introduced in liquid, vapour and particulate solid forms.

Simplex optimisation has been found to be a valuable tool for the investigation of DCP operating parameters. With regard to the analysis of aqueous solutions, the use of simplex optimisation in the study of the operating parameters under direct operator control clearly showed that vertical viewing position was the most critical parameter in instrument optimisation. Individual emission lines were shown to have distinct emission maxima within the analytical zone of the plasma related to the excitation energy of that line. This study suggested that for routine operation of the instrument, gas flows to the plasma should be set at the appropriate values, horizontal viewing position set to the centre of the plasma and response maximised by vertically profiling the analytical zone.

In studies of DCP hydride generation, the simplex procedure was found to be able to identify optimum instrument operating conditions for the determination of arsenic and selenium using a continuous flow system. Vertical viewing position was again found to be critical in the optimisation. In this work two gas flows (carrier and sheathing), replaced the single nebuliser gas flow. Of the two, carrier gas was critical with significant

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displacement of the plasma core occurring with variation in this parameter. The combined gas flow was found to be essentially similar to the sample introduction gas flow derived as optimum for solution analysis. Zander and Miller (106), have suggested that this level of nebuliser gas flow plays a major role in the development of the thermal pinch observed for this plasma.

The use of hydride generation was found to provide a 20-25 fold improvement in detection limit over the nebulisation of aqueous samples for As and Se and an improvement of 5 over previously reported values for the determination of arsenic by DCP hydride generation (113). Arsenic and selenium in reference materials and independantly characterised soils were determined using this technique. Good agreement was found between the certified (or independant) results and the results obtained by DCP hydride generation, with RSD's of less than 5% at the 1 μ g g⁻¹ level using the hydride generation procedure.

The simplex optimisation procedure was used to investigate the conditions required for the determination of lead by hydride generation. Acid concentration in the sample solution was found to be highly critical, as was the concentration of sodium hydroxide in the sodium tetrahydroborate (III) solution. Additionally, hydrogen peroxide concentration in the sample solution was found to be critical. The hydrogen peroxide is believed to oxidise the lead to the Pb(IV) state, prior to reduction to the hydride. Detection limits achieved using this procedure were marginally improved over conventional nebulisation detection limits.

The parameters controlling the development of successful slurry atomisation procedures have been investigated. Solid material with

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particle size $< 5 \ \mu m$ has been shown to be able to pass through the sample transport system. Therefore high atomisation efficiencies can only be achieved using slurries where the particle size is $< 5 \ \mu m$.

Simplex optimisation was used to determine the optimum conditions for the direct determination of Mg in kaolin. The parameters included in this investigation were vertical and horizontal viewing positions, nebuliser gas flow, sleeve gas flow, added lithium concentration, added ammonia concentration and slurry concentration. Viewing position was again found to be a critical parameter, with optimum vertical position for the Mg(II) 279.079 nm line used, found to lie on the boundary of the plasma core. Optimum horizontal viewing position was again found to lie in the centre of the analytical zone and plasma gas flows were found to be essentially similar to those obtained for solution analysis. Of the slurry reagent parameters, slurry concentration was of interest with high slurry concentrations > 12% m/V showing a decrease in analyte emission. This study indicated that optimisation of response for slurry atomisation for routine operation could again be achieved by setting the instrument operating parameters to conventional values and then vertically profiling the analytical zone.

Successful slurry atomisation procedures have been developed for soils, milk, plant materials and sewage sludges. For materials where particle size is greater than the 5 µm cut off of the DCP sample introduction system, particle size can be reduced using a simple grinding technique. Major and trace elements were determined in four reference soils by slurry atomisation. Soil material was reduced to < 5 µm in three hours by this unattended grinding technique, and the slurries so produced were found to be stable for over 24 hours. Using aqueous calibration,

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good agreement was achieved between the slurry and certificate results with RSD's of approximately 5% at the $\mu g g^{-1}$ level. Good agreement was also achieved for the direct analysis of reconstituted dried milks. In milk, the particle size of the suspended material naturally falls below 5 μ m, thus allowing direct slurry atomisation of the sample. With these samples, elements were determined at both major and trace levels with RSD's of < 5% for many elements at the $\mu g g^{-1}$ level.

Slurry atomisation procedures were also developed for plant materials and sewage sludges. The analysis of slurries produced by the direct grinding of these materials gave results showing reasonable agreement with certified values. In plant materials, RSD for Cu, Mn and Zn was generally less than 3%, however, for Pb RSD was found to be approximately 8% , possibly as a result of performing determinations at levels approaching the detection limit for the analyte in the slurry matrix. In sewage sludges, good agreement was achieved with RSD for Cu, Pb and Zn of 2-3%. Plant materials were found to be resistant to grinding because of their fibrous nature. In addition, increase in the viscosity of the slurry was observed with high sample loadings. Therefore, a simple carbonisation pre-treatment stage was investigated. Using a carbonisation-slurry atomisation procedure, B, Cd, Cu, Pb and Zn were determined in plant materials. Good agreement was achieved between the slurry and certificate values with RSD of 2-10% at the low $\mu g g^{-1}$ level. The carbonisationslurry atomisation procedure was applied to the sewage sludge samples and again good agreement was obtained.

The results obtained using various reference materials show the viability of slurry atomisation procedures using aqueous calibration and commercially available instrumentation.

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In these studies of slurry atomisation, the addition of lithium to the slurry sample was found to cause enhancements in a similar fashion as for solutions. To elucidate information on this effect T, T, and exc, ion $\boldsymbol{n}_{\underline{A}}$ in the plasma were determined whilst introducing a range of sample matrices. Values derived for these parameters showed good agreement with those obtained by other workers using solutions. Two series of slurries of increasing kaolin content were used, one containing 5 g l⁻¹ added lithium, the other containing no enhancement buffer. For the slurries containing added lithium, T and n were found to be reduced with increasing slurry concentration, the reduction occurring at a point similar to that observed earlier during the optimisation of the slurry procedure, where linear increases in slurry concentration above 10% m/V produced a reduction in analyte response (Fig. 33). This effect is attributed to a cooling of the plasma. Such a cooling effect could be caused by two mechanisms, firstly cooling from the energy requirement for the dissociation of the solid sample matrix or secondly, an increase in the rate of radiative cooling of the plasma caused by the presence of the EIE to which the high sample matrix loading may attribute. The first mechanism is not considered to be dominant as no severe cooling was observed in the slurry atomisation experiments without added lithium. The cooling observed with added lithium suggests that the EIE is significant and an increase in radiative cooling would concur with the present model for analyte excitation and enhancement in the DCP (100).

This work has shown that the DCP is able to atomise and excite analyte elements introduced in vapour, liquid or solid forms. Procedures for the analysis of agricultural materials by slurry atomisation have been developed and the parameters that regulate sample transport and analyte excitation investigated.

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In Chapter 3, the influence of plasma parameters upon response was investigated. This study was limited to those parameters directly under operator control, thus allowing the infromation derived to be applicable to the commercially available system. The use of simplex optimisation in the evaluation of instrument characteristics has been described by Ebdon <u>et al.</u> (173, 175). It may be possible to use information obtained from such studies to improve instrument design. For the DCP this could be achieved by including electrode angle, current applied to the plasma and sample introduction chimney characteristics into a simplex experiment. Such experiments could also be designed to <u>extend</u> the sensitivity available by hydride generation techniques.

The success of simplex optimisation in finding optimum reagent conditions for the determination of lead by hydride generation for the reagent system used has been described in Chapter 4. Work by Castillo <u>et al.</u> (200, 201), suggests that reagent systems containing ammonium persulphate may provide improved analytical response. As yet no rigorous optimisation procedure such as provided by the simplex technique has been applied to the determination of these interdependant conditions. Such a study, including the concentration of the acid, oxidising and reducing reagents, time and conversion efficiency could yield useful information on the application and mechanisms of lead hydride generation. Other applications of simplex optimisation to DCP hydride generation could include instrument optimisation for the determination of other analyte elements, and the determination of compromise conditions for multielement determinations using hydride generation.

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With regard to slurry atomisation, the characterisation of those parameters affecting the development of successful slurry atomisation and the development of successful procedures for some samples indicates the need for work in several areas. The success of the DCP in atomising materials such as kaolin and soil suggests that other plasmas such as the ICP should have the ability to perform in a similar fashion. Indeed the higher temperature of the ICP should assist in the decomposition of such matrices. Any such investigation applied to ICP atomic emission spectrometry could also be applied to ICP-Mass Spectrometry with advantages in sensitivity and the potential to obtain information on the complete dissociation of particles in the plasma being possible benefits.

The samples used in this study have been well characterised reference materials. To develop the techniques described here for routine use will require the acquisition of more extensive data from a larger number of samples of varying type. The analysis of such data combined with comparative studies between techniques would allow a rigorous evaluation of slurry atomisation procedures.

One of the potential advantages of slurry atomisation is the ability to reduce sample preparation time. The grinding technique described in this work can require long periods to achieve suitable particle size reduction. Therefore, to attain the goal of reducing sample preparation time, effort could be directed towards the development of rapid particle size reduction methods. Using rapid particle size reduction, slurry atomisation could be of value to on-line process control systems. To achieve maximum benefit for such applications, investigations into the automation of sample preparation and sample introduction would also be required.

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With regard to more theoretical studies, the use of slurry atomisation in the characterisation of plasmas has been briefly indicated in this work. In the DCP the effects observed with increasing slurry concentration and added lithium could be investigated in more detail. These studies could be performed with a view to collecting spatial rather than point information, thus allowing models of temperature emission distribution in the analytical zone to be developed. A parameter not evaluated in this work, but one that may be of considerable interest to slurry atomisation is the rotational temperature. This parameter is generally considered to be comparable to the kinetic temperature and is therefore significant when concerning the dissociation of solid matrices. Miller et al. (100), indicate values of 5000 K for the rotational temperature and that the addition of EIE may cause its reduction. Boumans (25), and Abdallah and Mermet (210), provide summaries of the procedure for the determination of the rotational temperature using various molecular band emissions. The measurement of the rotational temperature may help to investigate the postulated incomplete dissociation of some species in the plasma.

The work of Ramsey and Thompson (204), suggests a wide range of studies to which slurry atomisation could be applied. The use of various matrix energy demand (MED) slurries in the predictive model they propose could provide significant data in the understanding of plasma matrix effects in the ICP. In the DCP, radiative cooling of the plasma by the presence of EIE appears to be mechanistically dominant. The use of various MED slurries could provide further information on these processes.

At present, the processes of slurry atomisation are sufficiently characterised to allow the development of successful procedures for a range of sample matrices. To achieve a deeper understanding of the

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technique, it will be necessary to investigate the mechanisms of matrix dissociation and analyte excitation within the plasma.

REFERENCES

- Bowen, H.J.M., "Environmental Chemistry of the Elements", Academic Press, London, 1979.
- Ure, A.M., and Berrow, M.L., "The Elemental Constituents of soils", in Bowen, H.J.M., ed. "Environmental Chemistry - Vol 2", Royal Society of Chemistry, London, 1982.
- Kabata-Pendias, A., and Pendias, K., "Trace elements in Soils and Plants", CRC Press, Boca Raton, Florida, 1984.
- The Analysis of Agricultural Materials (2nd edition)", Ministry of Agriculture Fisheries and Food, RB427, HMSO, London, 1981.
- "Extractable Metals in Soils, Sewage Sludge treated soils and Related Materials 1982", HMSO, London, 1983.
- Bain, D.C., Berrow, M.L., McHardy, W.J., Paterson, E., Russel, J.D.,
 Sharp, B.L., Ure, A.M., and West, T.S., Anal. Chim. Acta, 1986, <u>180</u>, 163.
- 7. Baucells, M., Lacourt, G., and Roura, M., Analyst, 1985, 110, 1423.
- 8. Borggard, O.K., Christensen, H.E.M., and Lund, S.P., Analyst, 1984 109, 1174.
- 9. Thompson, K.C., and Tomerson, D.R., Analyst, 1974, 99, 595.
- 10. Hershey, W.J., and Keliher, P.N., Spectrochim. Acta, 1986, <u>41B</u>, 713.
- 11. Isaac, R.A., and Johnson, W.C., Spectrochim. Acta, 1983, 38B, 277-282.
- Spiers, G.A., Dudas, M.J., and Hodgins, L.W., Comm. in Soil Sci.
 Plant Anal., 1983, <u>14</u>, 629.
- 13. Jones, J.B., Comm. in Soil Sci. Plant Anal., 1977, 8, 349.
- 14. Munter, R.C., and Grande, R.A., in Barnes, R.M., (ed.), "Developments in Atomic Plasma Spectrochemical Analysis", Heyden, London, 1981, 649.
- 15. Thompson, M., and Zao, L., Analyst, 1985, <u>110</u>, 229.

-163-

- Melton, J.R., Hoover, W.L., and Morris, P.A., J. Assoc. Off. Anal. Chem., 1977, <u>60</u>, 873.
- 17. Woodis, T.C., Hunter, G.B., Holmes, J.H., and Johnson F.J., J. Assoc. Off. Anal. Chem., 1980, 63, 5.
- 18. Jones, J.B., Spectrochim. Acta, 1983, <u>38B</u>, 271.
- Melton, J.R., Hoover, W.L., Morris, P.A., and Gerald, J.A.,
 J. Assoc. Off. Anal. Chem., 1978, <u>61</u>, 504.
- 20. DeBolt, D.C., J. Assoc. Off. Anal. Chem., 1980, <u>63</u>, 802.
- 21. Lyons, D.J., and Roofayel, R.L., Analyst, 1982, 107, 331.
- 22. Lyons, D.J., Spann, K.P., and Roofayel, R.L., Analyst, 1985, 110, 955.
- 23. Pahlavanpour, B., Thompson, M., and Thorne, L., Analyst, 1980, 105, 756.
- 24. Rose, D.A., Anal. Proc., 1983, 20, 436.
- 25. Boumans, P.W.J.M., 'Theory of Spectrochemical Excitation', Adam Hilger, Ltd., London and Plenum Press, New York, 1966.
- 26. Mandelshtam, S.L., Spectrochim. Acta, 1978, 33B, 577.
- Sharp, B.L., Selected Annual Reviews of the Analytical Sciences, 1976, <u>4</u>, 37.
- 28. Langmyhr, F.J., Analyst, 1979, 104, 993.
- 29. Van Loon, J.C., Anal. Chem., 1980, <u>52</u>, 955A.
- 30. Jenkins, R., Gould, R.W., Gedcke, D., 'Quantitative X-Ray Spectrometry', Marcel Dekker Inc., New York, 1981.
- 31. Spackova, A., Al-Bassam, K., Mirza, N., Ibrahim, R., and Salman, G., Spectrochim. Acta, 1982, 37B, 745-746.
- 32. Berrow, M.L., and Stein, W.M., Analyst, 1983, 108, 277.
- 33. Bacon, J.R., and Ure, A.M., Analyst, 1984, 109, 1229.
- 34. Ure, A.M., and Bacon, J.R., Analyst, 1978, 103, 807.
- 35. Coudert, M.A., and Vergnaud, J.M., Anal. Chem., 1970, <u>42</u>, 1303.
- 36. Govindaraju, K., Melvelle, G., and Chouard, C., Anal. Chem., 1974, <u>46</u>, 1872.
- 37. Venghattis, A.A., Atom. Absorption Newslett., 1967, 6, 19.
- 38. L'Vov, B.V., Talanta, 1976, 23, 109.
- 39. L'Vov, B.V., Spectrochim. Acta, 1978, <u>33B</u>, 153.
- 40. Langmyhr, F.J., Stubergh, J.R., Thomassen, Y., Hanssen, J.E., and Doležal, J., Anal. Chim. Acta, 1974, <u>71</u>, 35.
- 41. Ottaway, J.M., and Hutton, R.C., Analyst, 1976, 101, 683.
- 42. Headridge, J.B., and Nicholson, R.A., Analyst, 1982, 107, 1200.
- 43. Headridge, J.B., Spectrochim. Acta, 1980, <u>35B</u>, 785.
- 44. Salin, E.D., and Horlick, G., Anal. Chem., 1979, 51, 2282.
- 45. Sommer, D., and Ohls, K., Fresenius, Z., Anal. Chem., 1980, <u>304</u>, 97.
- 46. Li-Zing, Z., Kirkbright, G.F., Cope, M.J., and Watson, J.M., Appl. Spectrosc., 1983, 37, 250.
- 47. Abdullah, M., Fuwa, K., and Haraguchi, H., Spectrochim. Acta, 1984, <u>39B</u>, 1129.
- 48. McLeod, C.W., Clarke, P.A., and Mowthorpe, D.J., Spectrochim. Acta, 1986, 41B, 63.
- 49. Gunn, M.A., Millard, D.L., and Kirkbright, G.F., Analyst, 1978, <u>103</u>, 1066.
- 50. Kirkbright, G.F., and Snook, R.D., Anal. Chem., 1979, <u>51</u>, 1938.
- 51. Millard, D.L., Shan, H.C., and Kirkbright, G.F., Analyst, 1980, <u>105</u> 502.
- 52. Elliot, W.G., Matusiewicz, H., Barnes, R.M., Anal. Chem., 1986, <u>58</u>, 1264.
- 53. Hull, P.R., and Horlick, G., Spectrochim. Acta, 1984, <u>39B</u>, 843.
- 54. Scott, R.H., Spectrochim. Acta, 1978, <u>33B</u>, 123.
- 55. Marks, J.Y., Fornwalt, D.E., and Yung, K.E., Spectrochim. Acta, 1983, <u>38B</u>, 107.
- 56. Aziz, A., Broekaert, J.A.C., Laqua, K., and Leis, F., Spectrochim. Acta, 1984, <u>39B</u>, 1091.

- 57. Thompson, M., Goulter, J.E., and Sieper, F., Analyst, 1981, 106, 32.
- 58. Carr, J.W., and Horlick, G., Spectrochim. Acta, 1982, 37B, 1.
- 59. Iskizuka, T., and Uwamino, Y., Spectrochim. Acta, 1983, <u>38B</u>, 519.
- 60. Gray, A.L., Analyst, 1985, <u>110</u>, 551.
- 61. Gilbert, P.T., Anal. Chem., 1962, <u>34</u>, 1025.
- 62. Mason, J.L., Anal. Chem., 1963, <u>35</u>, 874.
- 63. Lebedev, V.I., Zh. Anal. Khim., 1969, 24, 337.
- 64. Harrison, W.W., and Juliano, P.O., Anal. Chem., 1971, <u>43</u>, 248.
- Burrows, J.A., Heart, J.C., and Willis, J.B., Anal. Chem., 1965, <u>37</u>,
 579.
- Taylor, J.H., Bartels, T.T., and Crump, W.L., Anal. Chem., 1971, <u>43</u>, 1780.
- 67. Fuller, C.W., Analyst, 1976, 101, 961.
- 68. Willis, J.B., Anal. Chem., 1975, 47, 1752.
- 69. Stupar, J., and Ajlec, R., Analyst, 1982, <u>107</u>, 144.
- 70. Ajlec, R., and Stupar, J., Vestn. Slov. Kem. Drus., 1982, 29, 4.
- 71. Fry, R.C., and Denton, M.B., Anal. Chem., 1977, 49, 1413.
- 72. Mohamed, N., and Fry, R.C., Anal. Chem., 1981, 83, 450.
- Fietkau, R., Wichman, M.D., and Fry, R.C., Appl. Spectrosc., 1984, 38, 118.
- 74. Mohamed, N., McCurdy, D.L., Wichman, M.D., Fry, R.C., and O'Reilly, J.E., Appl. Spectrosc., 1985, <u>39</u>, 979.
- 75. Fuller, C.W., Hutton, R.C., and Preston, B., Analyst, 1981, 106, 913.
- 76. Langmyhr, F.J., and Aadalen, V., Anal. Chim. Acta, 1980, 115, 365.
- 77. Ebdon, L., and Pearce, W.C., Analyst, 1982, <u>107</u>, 942.
- 78. Jackson, K.W., and Newman, A.P., Analyst, 1983, 108, 261.
- 79. Hinds, M.W., Jackson, K.W., Newman, A.P., Analyst, 1985, 110, 947.
- 80. Andersen, J.R., Analyst, 1985, 110, 315.

- 81. Stephen, S.C., Littlejohn, D., and Ottaway, J.M., Analyst, 1985, <u>110</u>, 1147.
- 82. Spiers, G.A., Dudas, M.J., and Hodgins, L.W., Clay and Clay Minerals, 1983, <u>5</u>, 31.
- 83. Gray, A.R., PhD Thesis, (Plymouth Polytechnic, CNAA, 1985).
- 84. Watson, A.E., and Moore, G.L., South African J. of Chem., 1984, 37, 81.
- Mohamed, N., Brown, R.M., and Fry, R.C., Appl. Spectrosc., 1981, <u>35</u>, 153.
- McCurdy, D.L., Wichman, M.D., and Fry, R.C., Appl. Spectrosc., 1985,
 <u>39</u>, 984.
- 87. Valente, S., and Schrenk, W.G., Appl. Spectrosc. 1970, 24, 197.
- Elliot, W.G., Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1974.
- 89. Bankston, D.C., and Fisher, N.S., Anal. Chem., 1977, 49, 1017.
- 90. Kiers, C.D., and Vickers, T.J., Appl. Spectrosc. 1977, <u>31</u>, 273.
- 91. Skogerboe, R.K., and Urasa, I.T., Appl. Spectrosc. 1978, 32, 527.
- 92. Reednick, J., Am. Lab., 1979, 28, 383.
- 93. Decker, R.J., Spectrochim. Acta, 1980, 35B, 19.
- 94. Zander, A.T., Ind. Res. Dev., 1982, 24, 146.
- 95. Frank, A., and Petersson, L.R., Spectrochim. Acta, 1983, <u>38B</u>, 207.
- 96. Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., Appl. Spectrosc., 1980, 34, 19.
- 97. Eastwood, D., Hendrick, M.S., and Sogliero, G., Spectrochim. Acta, 1980, <u>35B</u>, 421.
- 98. Nygaard, D.D., and Gilbert, T.R., Appl. Spectrosc., 1981, 35, 52.
- 99. Eastwood, D., Hendrick, M.S., and Miller, M.H., Spectrochim. Acta, 1982, <u>37B</u>, 293.
- 100. Miller, M.H., Eastwood, D., and Hendrick, M.S., Spectrochim. Acta, 1984, 39B, 13.

- 101. Fox, R.L., Appl. Spectrosc., 1984, 38, 644.
- 102. Fox, R.L., Spectrochim. Acta, 1985, 40B, 287.
- 103. Miller, M.H., Keating, E., Eastwood, D., and Hendrick, M.S., Spectrochim. Acta, 1985, <u>40B</u>, 593.
- 104. Williams, R.R., and Coleman, G.N., Spectrochim. Acta, 1983, 38B, 1171.
- 105. Blades, M.W., and Lee, N., Spectrochim. Acta, 1984, 39B, 879.
- 106. Zander, A.T., and Miller, M.H., Spectrochim. Acta, 1985, 40B, 1023.
- 107. Mazzo, D.J., Elliot, W.G., Uden, P.C., and Barnes, R.M., Appl. Spectrosc., 1984, 38, 585.
- 108. Boyko, W.J., and Keliher, P.N., Can. J. Spectrosc., 1982, 27, 51.
- 109. Gilbert, T.R., and Penney, B.A., Spectrochim. Acta, 1983, <u>38B</u>, 297.
- 110. Brown, J.R., Saba, C.S., Rhine W.E., and Eisentraut, K.J., Anal. Chem., 1980, <u>52</u>, 2365.
- 111. Kauffman, R.E., Saba, C.S., Rhine, W.E., and Eisentraut, K.J., Anal. Chem., 1982, <u>54</u>, 975.
- 112. Saba, C.S., Rhine, W.E., and Eisentraut K.J., Anal. Chem., 1981, <u>53</u>, 1099.
- 113. Panaro, K.W., and Krull, I.S., Anal. Lett., 1984, <u>17(A2)</u>, 157.
- 114. Häyrynen, H., Lajunen, L.H.J., and Perämäki, P., At. Spectrosc., 1985, <u>6</u>, 88.
- 115. Lajunen, L.H.J., Kinnunen, A., and Yrjänheikki, E., At. Spectrosc., 1985, <u>6</u>, 49.
- 116. Smith, M.R., Anal. Chem., 1980, 52, 583.
- 117. Miyazake, A., Kimura, A., and Umezaki, Y., Anal. Chim. Acta, 1979, <u>107</u>, 395.
- 118. Lloyd, R.J., Barnes, R.M., Uden, P.C., and Elliot, W.G., Anal. Chem., 1978, <u>50</u>, 2025.
- 119. Uden, P.C., Barnes, R.M., and Disanzo, F.P., Anal. Chem., 1978, 50, 852.

- 120. Estes, S.A., Poirier, C.A., Uden, P.C., and Barnes, R.M., J. Chromatogr., 1980, <u>196</u>, 265.
- 121. Riska, G.D., Estes, S.A., Beyer, J.O., and Uden, P.C., Spectrochim. Acta, 1983, <u>38B</u>, 407-417.
- 122. Treybig, D.S., and Ellebracht, S.R., Anal. Chem., 1980, 52, 1633.
- 123. Uden, P.C., Quimby, B.D., Barnes, R.M., and Elliot, W.G., Anal. Chim. Acta, 1978, <u>101</u>, 99.
- 124. Uden, P.C., and Bigley, I.E., Anal. Chim. Acta, 1977, 94, 29.
- 125. Krull, I.S., and Panaro, K.W., J. Chromatogr. Sci., 1983, 21, 460.
- 126. Krull, I.S., and Panaro, K.W., Appl. Spectrosc., 1985, 39, 960.
- 127. Biggs, W.R., Gano, J.T., and Brown, R.J., Anal. Chem., 1984, 56, 2653.
- 128. Brätter, P., Gardiner, P.E., Negretti, V.E., Schulze, G., and Van Stockhausen, H.B., Trace Element Anal. Chem. Med. Biol. Int. Workshop. (2nd), 1982, Publ., 1983 Berlin, p45-59.
- 129. Gardiner, P.E., Brätter, P., Negretti, V.E., and Schulze, G., Spectrochim. Acta, 1983, <u>38B</u>, 427.
- 130. Czech, N., and Wunsch, G., Spectrochim. Acta, 1981, 36B, 553.
- 131. Griffin, H., and Savolainen, A., Spectrochim. Acta, 1983, 38B, 183.
- 132. Fernando, L.A., Anal. Chem., 1984, <u>56</u>, 1970.
- 133. Fernando, L.A., Heavner, W.D., and Gabrielli, C.C., Anal. Chem., 1986, <u>58</u>, 511.
- 134. Potter, N.M., and Vergosen, H.E., Talanta, 1985, 32, 545.
- 135. Flavelle, F., and Westland, A.D., Talanta, 1986, 33, 445.
- 136. Eisentraut, K.J., Newman, R.W., Saba, C.S., Kauffman, R.E., and Rhine, W.E., Anal. Chem., 1984, 56, 1087 A.
- 137. Dijkstra, A.J., and Meert, D., J. of the Am. Oil Chem. Soc., 1982, <u>59</u>, 199.
- 138. Potter, N.M., and Lovelace, R.R., Anal. Chim. Acta, 1984, 162, 419.
- 139. Burdo, R.A., and Snyder, M.L., Anal. Chem., 1979, <u>51</u>, 1502.

- 140. Czupryna, G., and Natansohn, S., Mater. Sci. Res., 1983, 15, 491.
- 141. Natansohn, S., and Czupryna, G., Spectrochim. Acta, 1983, 38B, 317.
- 142. Chang, A.E., Morse, B., Harley, N.H., Lippmann, M., and Cohen, B.S., Am. Ind. Hyg. Assoc. J., 1982, <u>43</u>, 117.
- 143. Pyy, L., Lajunen, L.H.J., and Hakala, E., Am. Ind. Hyg. Assoc. J., 1983, 44, 609.
- 144. Dellafield, R.J., and Martin, T.D., At. Spectrosc., 1982, 3, 165.
- 145. Ball, J.W., Thompson, J.M., and Jenne, E.A., Anal. Chim. Acta, 1978, <u>98</u>, 67.
- 146. Urasa, I.T., Anal. Chem., 1984, 56, 904.
- 147. Urasa, I.T., and O'Reilly, A.M., Talanta, 1986, 33, 593.
- 148. Grogan, W.C., Spectrochim. Acta, 1983, <u>38B</u>, 357.
- 149. Sinex, S.A., Cantillo, A.Y., and Helz, G.R., Anal. Chem., 1980, 52, 2342.
- 150. Cantillo, A.Y., Sinex, S.A., and Helz, G.R., Anal. Chem., 1984, 56, 33.
- 151. Bowker, P.C., and Mannheim, F.T., Appl. Spectrosc., 1982, 36, 378.
- 152. Johnson, G.W., and Sisneros, T.E., Rare Earths Mod. Sci. Technol., 1982, <u>3</u>, 525.
- 153. Bankston, D.C., Humphris, S.E., and Thompson, G., Anal. Chem., 1979, <u>51</u>, 1218.
- 154. Hall, G.S., Carr, M.J., Cummings, E., and Lee, M., Clin. Chem., 1983, <u>29</u>, 1318.
- 155. Roberts, N.B., Fairclough, D., and Taylor, W.H., Ann. Clin. Biochem., 1984, <u>21</u>, 213.
- 156. Roberts, N.B., Fairclough, D., McLoughlin, S., and Taylor, W.H., Ann. Clin. Biochem., 1985, <u>22</u>, 533.
- 157. Pyy, L., Hakala, E., and Lajunen, L.H.J., Anal. Chim. Acta, 1984, <u>158</u>, 297.

Ļ

- 158. Hunter, G.B., Woodis, T.C., and Johnson, F.J., J. Assoc. Off. Anal. Chem., 1981, <u>64</u>, 25.
- 159. Norman, J.D., Stumpe, L.A., Trimm, J.R., and Johnson, F.J., J. Assoc. Off. Anal. Chem., 1983, <u>66</u>, 949.
- 160. Tempini, G., Pugliese, F., Franco, G., Riganti, V., Specchiarello, M., and Perotti, A., G. Ital. Med. Lav., 1982, 4, 83.
- 161. Sneddon, J., and Fuavo, V.A., At. Spectrosc., 1984, 5, 108.
- 162. Lajunen, L.H.J., and Kubin, A., Talanta, 1986, 33, 265.
- 163. Mchard, J.A., Twigg, K.M., Bach, D.T., and Winefordner, J.D., Spectrosc. Lett., 1984, <u>17</u>, 285.
- 164. Ellebracht, S.R., Fairless, C.M., and Manahan, S.E., Anal. Chem., 1978, <u>50</u>, 1649.
- 165. Carr, J.W., and Blades, M.W., Spectrochim. Acta, 1984, <u>39B</u>, 667.
- 166. Messman, J.D., O'Haver, T.C., and Epstein, M.S., Anal. Chem., 1985, <u>57</u>, 416.
- 167. Goliber, P.A., Hendrick, M.S., and Michel, R.G., Anal. Chem., 1985, 57, 2520.
- 168. Spendly, W., Hext, G.R., and Himsworth, F.R., Technometrics, 1962, <u>4</u>, 441.
- 169. Nelder, J.A., and Mead, R., Compt. J., 1965, 7, 308.
- 170. Yarbro, L., and Deming, S.N., Anal. Chim. Acta, 1974, 73, 391.
- 171. Deming, S.N., and Parker, L.R., CRC Critical Reviews in Analytical Chemistry, 1978, 187.
- 172. Cave, M.R., PhD Thesis, Sheffield Polytechnic, 1980.
- 173. Ebdon, L., Cave, M.R., and Mowthorpe, D.J., Anal. Chim. Acta, 1980, 115, 179.
- 174. Moore, G.L., Humphries-Cuff, P.J., and Watson, A.E., Spectrochim. Acta, 1984, <u>39B</u>, 915.
- 175. Carpenter, R., and Ebdon, L., J. Anal. Atomic Spectrom., 1986, <u>1</u>, 265.

-171-

- 176. Norman, P., Plymouth Polytechnic, Unpublished work.
- 177. Greenfield, S., and Burns, D.T., Spectrochim. Acta, 1979, 34B, 423.
- 178. Holak, W., Anal. Chem., 1969, 4!, 1712.
- 179. Thompson, M., Pahlavanpour, B., Walton, S.J., and Kirkbright, G.F., Analyst, 1978, 103, 568.
- 180. Thompson, M., Pahlavanpour, B., Walton, S.J., and Kirkbright, G.F., Analyst, 1978, <u>103</u>, 705.
- 181. Godden, R.G., and Thomerson, D.R., Analyst, 1980, <u>105</u>, 1137.
- 182. Ebdon, L., Wilkinson, J.R., and Jackson, K.W., Anal. Chim. Acta, 1982, <u>136</u>, 191.
- 183. Welz, B., and Melcher, M., Analyst, 1984, 109, 569.
- 184. Welz, B., and Melcher, M., Analyst, 1984, 109, 573.
- 185. Welz, B., and Melcher, M., Analyst, 1984, 109, 577.
- 186. Welz, B., and Schubert-Jacobs, M., J. Anal. At. Spectrom., 1986, 1, 23.
- 187. Bye, R., Talanta, 1986, 33, 705.
- 188. Ward, R.W., and Stockwell, P.B., J. Automatic Chem., 1983, 5, 193.
- 189. Handbook of Spectral line characteristics for the D.C. Plasma echelle systems, Beckman RIIC Ltd., 1982.
- 190. Parker, L.R., Tioh, N.H., and Barnes, R.M., Appl. Spectrosc., 1985, <u>39</u>, 45.
- 191. Chapman, D.J., Personal communication.
- 192. Fleming, H.D., and Ide, R.G., Anal. Chim. Acta, 1976, 83, 67.
- 193. Vijan, P.N., and Wood, G.R., Analyst, 1976, 101, 966.
- 194. Vijan, P.N., and Sadana, R.S., Talanta, 1980, 27, 321.
- 195. Ikeda, Y., Nishibe, J., Hamada, S., and Tujino, R., Anal. Chim. Acta, 1981, 125, 109.
- 196. Smith, R., At. Spectrosc., 1981, 2, 155.
- 197. Jin, K., and Taga, M., Anal. Chim. Acta, 1982, <u>143</u>, 229.

- 198. Castillo, J.R., Mir, J.M., Martinez, C., Val, J., and Colon, M.P., Mikrochim. Acta, 1985, <u>1</u>, 253.
- 199. Castillo, J.R., Mir, J.M., Val, J., Colon, M.P., and Martinez, C., Analyst, 1985, <u>110</u>, 1219.
- 200. Allen, T., "Particle size measurement", 3rd edition, Chapman and Hall Ltd., London 1981.
- 201. Richardson, D., Personal communication.
- 202. Porter, R.F., Schissel, P., and Inghram, M.G., J. Chem. Phys, 1955, 23, 339.
- 203. Satake, K., and Uehiro, T., Analyst, 1985, 110, 1045.
- 204. Ramsey, M.H., and Thompson, M., J. Anal. Atomic Spectrom., 1986, <u>1</u>, 185.
- 205. Alder, J.F., Bombelka, R.M., and Kirkbright, G.F., Spectrochim. Acta, 1980, <u>35B</u>, 163.
- 206. Kornblum, G.R., and De Galen, L., Spectrochim. Acta, 1977, 32B, 71.
- 207. Griem, H.R., 'Plasma Spectroscopy', McGraw-Hill, New York, 1964.
- 208. Bridges, J.M., and Kornblith, R.L., Astrophys. J., 1974, 192, 793.
- 209. Zander, A.T., Miller, M.H., Hendrick, M.S., and Eastwood, D., Appl. Spectrosc., 1985, <u>39</u>, 1.
- 210. Abdallah, M.H., and Mermet, J.M., Spectrochim. Acta, 1982, 37B, 391.

Appendix I - Computer program to calculate ionisation temperature

DIM T(21) 2 DIM D(21) 3 (4 DIM A(21) PRINT "ENTER IONIZATION POTENTIAL" 10 INPUT V 20 30 PRINT PRINT "ENTER APPROXIMATION FOR TEMPERATURE" 40 INPUT T 50 60 PRINT PRINT "ENTER ELECTRON DENSITY" 70 INPUT E 80 90 PRINT PRINT "ENTER ION LINE INTENSITY" 100 INPUT N 110 . 120 PRINT PRINT "ENTER ATOM LINE INTENSITY" 130 140 INPUT M PRINT 150 155 L = LOG (E * N / M) - 49.9289 160 T(1) = TFOR I = 1 TO 20 170 180 A(I) = L - 1.5 * LOG (T(I)) + 11605 * V / T(I) 190 D(I) = 1.5 / T(I) - 11605 * V / (T(I) * T(I))200 T(I + 1) = T(I) - A(I) / D(I)IF T(I - 1) = T(I) AND T(I) = T(I + 1) THEN GOTO 230 205 PRINT "IONIZATION TEMPERATURE = "; INT (T(I + 1) + 0.5) 210 NEXT I 220 230 PRINT PRINT "SAME ELEMENT AND ELECTRON DENSITY (Y/N)" 240 250 GET R\$ IF R\$ = "Y" THEN 90 260 PRINT "NEW ELECTRON DENSITY (Y/N)" 270 280 GET R≉ IF R\$ = "Y" THEN GOTO 60 220 300 PRINT "QUIT (Y/N)". 340 GET R\$ IF R\$ = "Y" THEN STOP 320 330 GOTO 10

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Lectures and associated studies

- Series of lectures on 'Advanced Analytical Atomic Spectroscopy',
 Plymouth Polytechnic, June August 1984.
- ii. Weekly meetings of the Chemistry of Natural and Polluted Environments Research Group, Plymouth Polytechnic, October 1983 to September 1986.
- iii. RSC lecture, Prof. J.N. Miller, 'Hunting the snark Recent developments in ultra-sensitive molecular spectroscopy', 17th February 1984, Plymouth Polytechnic.
- iv. RSC lecture, Dr. D. Woodcock, 'Fungicides and the Environment', 16th November 1984, Plymouth Polytechnic.
- v. RSC lecture, Dr. P.S. Liss, 'The role of the oceans in the Chemistry of the atmosphere', 15th March 1985, Plymouth Polytechnic.
- vi. Departmental colloquium, Dr. J. Harnley, 'Recent developments in analytical atomic spectroscopy', 10th September 1985, Plymouth Polytechnic.
- vii. RSC lecture, Dr. T.E. Hunt, 'Trace element speciation in aquatic systems', 1st November 1985, Plymouth Polytechnic.
- viii. RSC lecture, Prof. A.F. Fell, 'Snapshot chromatography biomedical applications of new technology in HPLC', 7th February 1986, Plymouth Polytechnic.
- ix. RSC lecture, Dr. P. Campion, 'The Chemistry of PWR and AGR nuclear power reactor coolants', 7th March 1986, Plymouth Polytechnic.

Meetings of the Royal Society of Chemistry

- i. Research and Development Topics in Analytical Chemistry, Analytical Division, UMIST, Manchester, June 1984.
- Second Biennial National Atomic Spectroscopy Symposium,
 Analytical Division, University of Leeds, July 1984.
- iii. Annual Reports on Analytical Atomic Spectroscopy, AnalyticalDivision Symposium, Sheffield City Polytechnic, April 1985.
- iv. Sample Introduction and the ICP, Analytical Division Symposium, University of Bristol, October 1985.
- Atomic Spectroscopy Updates Symposium, Analytical Division,
 Sheffield City Polytechnic, April 1986.
- vi. Research and Development Topics in Analytical Chemistry, Analytical Division, Birkbeck College, London, April 1986.
- vii. SAC '86 / Third Biennial National Atomic Spectroscopy Symposium, Analytical Division, University of Bristol, July 1986.

Resulting from the work reported in this thesis, the following papers have been presented and published:-

(a) Presentations

- 'Studies of slurry atomisation using a D.C. Plasma',
 L. Ebdon and S.T. Sparkes, 1985 Winter Conference on Plasma Spectrochemistry, Leysin, Switzerland, January 1985.
- 'Slurry atomisation ICP and DCP spectroscopy',
 L. Ebdon, P. Norman, and S.T. Sparkes, 1986 Conference on
 Plasma Spectrochemistry, Hawaii, January 1986.
- 'Aspects of slurry atomisation for agricultural samples',
 S.T. Sparkes and L. Ebdon, Research and Development Topics in Analytical Chemistry, London, April 1986.
- 'Agricultural sample analysis by slurry atomisation plasma emission spectroscopy',

S.T. Sparkes and L. Ebdon, Third Biennial National Atomic Spectroscopy Symposium, Bristol, July 1986.

'Slurry atomisation by DCP - Some theoretical considerations',
 S.T. Sparkes and L. Ebdon, Third Biennial National Atomic
 Spectroscopy Symposium, Bristol, July 1986.

(b) Publications

1. Ebdon, L., and Sparkes, S.,

'A selected bibliography of direct current plasma - optical emission spectroscopy',

ICP Information Newsletter, 1985, 10(10), 797.

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2. Sparkes, S.T., and Ebdon, L.,

'A selected review of sample introduction techniques for the direct current plasma', ICP Information Newsletter, 1986, <u>12(1)</u>, 1.

- 3. Ebdon, L., Norman, P., and Sparkes, S.T., 'Simplex optimisation of a direct current plasma', Spectrochim. Acta, in the press.
- 4. Sparkes, S.T., and Ebdon, L.,

'Agricultural sample analysis by plasma emission spectrometry', Analytical Proceedings, in the press.

DCP CORNER

A Selected Review of Sample Introduction Techniques for the Direct Current Plasma

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Introduction

Sample introduction has been a major area of investigation for direct current plasma (DCP) users. Studies have been made of the conventional, commercial, sample introduction for aqueous solutions as well as more novel applications of this device and different modifications. This review also discusses the introduction of solid samples, gases (e.g. hydrides), and chromatographic eluents into the DCP.

Aqueous Solutions

The conventional DCP sample introduction system consists of a ceramic crossflow nebulizer (Fig. 1), diamond shaped spray chamber, and a sample introduction chimney that directs the aerosol towards the plasma (Fig. 2). Sample is fed to the nebulizer using a two-channel peristaltic pump at approximately 1.5 mL/min; the second channel is used for spray chamber drainage. Using this system, transport efficiency has been measured to be approximately 15% with aqueous solutions [1-3]. Various estimates have been placed upon droplet size produced by the system; values of between 3-10 μ m [4] and 1-20 μ m [5] have been cited and provide some information on the characteristics of the device. Although overall the DCP may seem favorable to relatively high sample loadings compared to other emission techniques (for example the inductively coupled plasma) not all the sample passes through the region where maximum emission is observed. The design of a novel interface for coupled HPLC-DCP [2] (see below) indicates there may be improvements in mechanical efficiency by using a narrower diameter introduction chimney.





Fig. 1 DCP nebulizer

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Fig. 2 DCP sample introduction system

Organic Solvents

The effects of organic solvents on the DCP have been described by Gilbert and Penney [6]. Using a narrow (15.2 mm) introduction chimney, they introduced

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hexane, dichloro-, trichloro- and tetrachloromethane, and 4-methyl-2-pentanone with higher transport efficiencies than observed for aqueous samples. Optimal nebulizer gas flow rates were found to be between 4-6 L/min. Above this level the plasma became unstable and at flows greater than 8 L/min the plasma was extinguished. Background emission, primarily from C, and CN bands and incandescent material was reduced by adding 0.1 L/min of oxygen to the gas flow.

The use of DCP-AES in the determination of wear metals in oil has been well documented [7-9]. Subject to the particle size limitations resulting from nebulization and aerosol conditioning in the spray chamber and introduction system, DCP-AES has been shown to perform favorably for this application. A comparison between direct nebulization and acid digestion procedures is able to provide an insight as to the size of the wear metal particles; however, reported differences between the techniques may reflect incomplete atomization of larger solid particles in addition to incomplete sample transport.

Solid Samples

These questions are of paramount importance in slurry atomization type procedures. Mohamed et al. [5] suggested the need to produce slurries with finer size distribution than the aerosol production and transport particle characteristics of the sample introduction system. This is supported by further studies by McCurdy et al. [10], where studies of slurry atomization of finely ground coal showed reasonable agreement with certified materials. Recent work by Ebdon and Sparkes [11] using slurry atomization procedures for kaolin and soil samples confirm this particle size dependant effect when using conventional instrumentation (Figs. 3, 4). More recent studies using finely ground soil have indicated approximately 100% atomization. The growing interest in solid sample introduction on the grounds of reduced sample preparation time, reduced contamination or analyte losses, and in minimizing hazards is being reflected in the efforts applied to slurry atomization. Examples of materials for which slurry atomization procedures are being developed include soil, kaolin, plant material, milk, cereal, coal and minerals. The main constraint on any protocol is that the material can be readily reduced in particle size to (ideally) less than 10 µm and dispersed to form a homogeneous suspension.



Additional work concerning solid sample introduction includes the analysis of refractory carbides [12].

Hydride Generation

Hydride generation is a widely used technique in atomic spectroscopy for the determination of those elements which form gaseous convalent hydrides, e.g. As, Se, Sb, Sn, Ge, Bi, Te and Pb. Sodium borohydride is most commonly used asthe reducing agent [13]. Reports on the application of the technique to DCP-AES have been few [11, 14, 15], and indicate that improvements in sensitivity are

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approximately a factor of 20 over aqueous nebulization. This is less than the gain in sensitivity reported for hydride generation ICP-AES and probably reflects the superior transport efficiencies for aqueous nebulization of DCP-AES to ICP-AES (15% to 2%) and the problems of ensuring complete atomization of the hydride given the geometry of the DCP. Most reports on vapor introduction use continuous flow systems; however, Ebdon and Sparkes [11] found the replacement of the conventional sample introduction chimney with a commercially available argon sheathed interface (Fig. 5) assisted in concentrating the analyte in the center of the analytical zone. The use of similar instrumentation but inserting a collection stage in the hydride generation procedure has been shown to achieve detection limits of approximately 1.5 ng/mL for Se, 5 ng/mL for Te [15]. A comparison of vapor techniques for mercury determination between atomic absorption spectrometry and DCP-AES has been made with good agreement between the techniques being found [16]. Other reports on vapor generation techniques followed by DCP-AES detection include the determination of arsenic by chloride formation [17] and the determination of mercury in iodine monochloride [18].



Chromatographic Detection

Atomic spectroscopy provides an interesting chromatographic detector. The coupling of chromatography (both GC and HPLC) to atomic spectroscopy offers the ability to quantify different elemental forms. Thus the separatory power of chromatography can be linked to the sensitivity of atomic spectroscopy to provide rapid trace element speciation. The role of DCP-AES in such coupled in gas chromatography [19-23], HPLC [2, 24-29], and gel filtration

Gas chromatographic (GC-DCP) applications reported for which a heated interface was advantageous [19] include the determination of organomanganese compounds in gasoline [29] and a selection of organometallic compounds of Cr, Various alkyl derivatives of Si, Ge, Sn, and Pb [21] and of Si in a silicone coupled with a vacuum u.v. spectrometer as a sulfur specific detector for gas chromatography has also been described [23].

The majority of reports concerning HPLC-DCP have used a direct interface between the HPLC column and the standard nebulizer. As mentioned earlier, Mazzo et al. [2] have described a modified sample introduction system for HPLC-DCP. A sample introduction chimney tip of 5 mm diameter was found to be optimal for a range of solvents with mechanical efficiencies of 20 - 95% depending on solvent characteristics. Boyko and Keliher [3] have described pulse nebulization

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techniques for the DCP, and these may be relevant in coupled HPLC-DCP-AES studies. High performance liquid chromatography has been used to separate various transition metal complexes [24, 25] with detection limits using DCP-AES in the sub-ng range. Reversed phase HPLC with DCP-OES detection has been shown to provide a viable method for the determination of Cr(VI) and Cr(III) speciation [26] with detection limits of 5-10 ng/mL using 100 μ L injections.

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An issue that is of much interest at present is the speciation of tin in natural waters in relation to the use of various organotin compounds in the formulation of antifouling paints. Krull and Panaro [27] have described procedures for the determination of tin and organotin species by HPLC-DCP including a hydride generation stage. Using this procedure, detection limits of 25 ng/mL were obtained for mono- and dimethyl tin and 40 ng/mL for trimethyltin using a 200 μ L injection. For comparison, Ebdon et al. [28] have developed a coupled HPLC-flame AAS technique with an instrument detection limit of 200 ng tributyltin, that in combination with sample pre-concentration is being used to monitor tin speciation in natural waters at levels down to 0.018 ng/mL. A major advantage of this type of procedure using coupled techniques is the minimal sample treatment required and the rapid separations achieved (<10 min). A separation of phosphorus species has been outlined with the technique reported [29] having a detection limit of 0.2 μ g P and RSD between 1-5%. Analyses were found to show good agreement with conventional procedures.

A growth area in the field of trace element speciation is the determination of element protein associations. The combination of gel filtration chromatography with DCP detection has been reported [30, 31]. Using simultaneous detection, protein bound copper, iron and zinc speciation was studied in serum and intravenous infusion fluids. The direct coupling of the two techniques was found to reduce contamination sources and increase sample throughput compared to fraction collection procedures. Detection limits using this coupled technique were 3.2 μ g/L Cu, 3.9 μ g/L Fe and 9.3 μ g/L Zn, considered adequate for the species of interest.

Conclusion

While reports of sample introduction studies in DCP-AES may not be as numerous as for ICP-AES, it is clear that the versatility of the DCP can be seen in the above work. It represents a robust excitation source capable of atomizing and exciting samples presented to it in liquid (both aqueous and organic), gaseous, or solid forms. Clearly more research in this area is likely to enhance still further the range of application of DCP-AES.

- [1] Decker, R.J. Some analytical characteristics of a three electrode d.c argon plasma source for optical emission spectrometry, Spectrochim. Acta 1980, 35B, 19-31.
- [2] Mazzo, D.J., Elliot, W.G., Uden, P.C., and Barnes, R.M. The design and characterization of an interface for high performance liquid chromatography with direct current argon plasma detection, Appl. Spectrosc. 1984, 38, 585-590.
- [3] Boyko, W.J., and Keliher, P.N. Some observations on the analytical utility of discrete sample introduction into a three electrode direct current plasma, Can. J. Spectrosc. 1982, 27, 51-57.
- [4] Zander, A.T. DC plasma emission spectrometry speeds elemental analysis, Ind. Res. Dev. 1982, (Feb), 146-150.
- [5] Mohamed, N., Brown, R.M., and Fry, R.C. Slurry atomization dc plasma emission spectrometry and laser diffraction studies of aerosol production and transport, Appl. Spectrosc. 1981, 35, 153-164.

ICP INFORMATION NEWSLETTER, Vol. 12, No. 1, 4 (June 1986)

- [6] Gilbert, T.R., and Penney, B.A. Determination of trace-elements in non-aqueous samples by d.c. plasma emission spectrometry, Spectrochim. Acta 1983, 38B, 297-302.
- [7] Brown, J.R., Saba, C.S., Rhine, W.E., and Eisentraut, K.J. Particle size independent spectrometric determination of wear metals in aircraft lubricating oils, Anal. Chem. 1980, 52, 2365-2370.
- [8] Kauffman, R.E., Saba, C.S., Rhine, W.E., and Eisentraut, K.J. Quantitative multielement determination of metallic wear species in lubricating oils and hydraulic fluids, Anal. Chem. 1982, 54, 975-979.
- [9] Eisentraut, K.J., Newman, R.W., Saba, C.S., Kauffman, R.E. Spectrometric oil analysis - detecting engine failures before they occur, Anal. Chem. 1984, 56, 1086A-1094A.
- [10] McCurdy, D.L., Wickman, M.D., and Fry, R.C. Rapid coal analysis Part II: slurry atomization DCP emission analysis of NBS coal, Appl. Spectrosc. 1985, 38 (6), 984-988.
- [11] Ebdon, L., and Sparkes, S.T. Studies on slurry atomization using a d.c. plasma, 1985 European Conference on Plasma Spectrochemistry, Leysin, Switzerland, 1985.
- [12] Comtois, R.R., and Kinsey, W.J. The spectrochemical analysis of refractory carbides by suspended sample introduction, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy 1982, Atlantic City, NJ.
- [13] Thompson, K.C., and Thomerson, D.R. Atomic absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by utilizing the generation of covalent hydrides, Analyst 1974, 99, 595-601.
- [14] Panaro, K.W., and Krull, I.S. Continuous hydride generation with direct current plasma emission spectroscopic detection for total arsenic determinations (HY-DCP), Anal. Lett. 1984, 17(A2), 157-172.
- [15] Häyrynen, H., Lajunen, L.H.J., and Perämäki, P. Determination of trace concentrations of selenium and tellurium in aqueous solutions by introduction of the gaseous hydrides into a direct current plasma source for emission spectrometry, At. Spectrosc. 1985, 6, 88-90.
- [16] Lajunen, L.H.J., Kinnunen, A., and Yrjänheikki, E. Determination of mercury in blood and fish samples by cold-vapour atomic absorption and direct current plasma emission spectrometry, At. Spectrosc. 1985, 6, 49-52.
- [17] Miyazake, A., Kimura, A., and Umezaki, Y. Determination of arsenic in sediments by chloride formation and DC plasma arc emission spectrometry, Anal. Chim. Acta 1979, 107, 395-398.
- [18] Smith, M.B. Determination of mercury in iodine monochloride by argon plasma emission spectrometry, Anal. Chem. 1980, 52, 583-585.
- [19] Lloyd, R.J., Barnes, R.M., Uden, P.C., and Elliot, W.G. Direct current atmospheric pressure argon plasma emission echelle spectrometer as a specific metal gas chromatographic detector, Anal. Chem. 1978, 50, 2025-2029.
- [20] Uden, P.C., Barnes, R.M., and Di Sanzo, F.P. Determination of methylcyclopentadienylmanganesetricarbonyl in gasoline by gas chromatography with interfaced direct current argon plasma emission detection, Anal. Chem. 1978, 50, 852-855.
- [21] Estes, S.A. Poirier, C.A., Uden, P., and Barnes, R.M., Gas chromatography with plasma emission spectroscopic detection of Friedel-Crafts catalyzed alkyl group redistribution products among Si, Ge, Sn and Pb atoms, J. Chromatog. 1980, 196, 265-277.
- [22] Riska, G.D., Estes, S.A., Beyer, J.O., and Uden, P.C. Plasma emission spectral detection for pyrolysis gas chromatography, Spectrochim. Acta

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1983, 38B, 407-417.

- [23] Treybig, D.S., and Ellebracht, S.R., Vacuum ultraviolet plasma atomic spectrometer as a sulphur specific detector for 288 emission chromatography, Anal. Chem. 1980, 52, 1633-1636.
- [24] Uden, P.C., Quimby, B.D., Barnes, R.M., and Elliot, W.G., Interfaced D.C. argon plasma emission spectroscopic detection for high pressure liquid chromatography of metal compounds, Anal. Chim. Acta 1978, 101, 99-109.
- [25] Uden, P.C., and Bigley, I.E. High pressure liquid chromatography of metal and d.c. argon-plasma emission diethyldithiocarbamates with u.v. spectroscopic detection, Anal. Chim. Acta 1977, 94, 29-34.
- [26] Krull, I.S., and Panaro, K.W., Trace analysis and speciation for Cr(VI) and Cr(III) via HPLC-direct current plasma emission spectroscopy (HPLC-DCP), J. Chromatog. Sci. 1983, 21, 460-472.
- [27] Krull, I.S., and Panaro, K.W., Trace analysis and speciation for methylated organotins by HPLC-hydride generation - direct currrent plasma emission spectroscopy (HPLC-HY-DCP), Appl. Spectrosc. 1985, 39, 960-968.
- [28] Ebdon, L., Hill, S.J. and Jones. P. Speciation of tin in natural waters using coupled high performance liquid chromatography - flame atomic absorption spectrometry, Analyst 1985, 110, 515-517.
- [29] Biggs, W.R., Gano, J.T., and Brown, R.J. Determination of polyphosphate distribution by liquid chromatographic separation with direct current plasma - atomic emission spectrometric detection, Anal. Chem. 1984, 56, 2653-2657.
- [30] Gardiner, P.E., Brätter, P., Negretti, V.E., Schulze, G. Ue of direct currrent argon plasma as a detector in gel filtration chromatography of biological fluids, Spectrochim. Acta 1983, 38B, 427-436.
- [31] Brätter, P., Gardiner, P.E., Negretti, V.E., Schulze, G., and Van Stockhausen, H.B. The determination and speciation of essential trace intravenous infusion solutions - importance in total elements in parenteral nutrition, Trace Element Anal. Chem. Med. Biol. Proc. Int. Workshop (2nd), 1982, Publ., 1983 Berlin, p. 45-59.

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AEROSOL FORMATION AND DC PLASMA EMISSION ELEMENTAL RESPONSE FOR MICELLAR HPLC MOBILE PHASES. P. C. Uden, C. M. Kirkman and S. A. Charvat, Department of 113. Chemistry, Lederle Graduate Research Center, University of Massachusetts, Amherst, MA 01003

Micellar high performance liquid chromatography is evaluated for the separation of metal-containing compounds and direct-current argon plasma emission spectroscopy (DCP) is considered for specific element detection. The effect of surfactants on the droplet size distribution in tertiary aerosols produced during pneumatic nebulization is investigated using polar nephelometry at 580 nm. Effects are small at or below the criticel micelle concentration but droplets produced from non-ionic surfactants are generally larger than those from water and other types of surfactant. The implications of these results as they relate to nebulization and atomization efficiency into the DCP are considered among other operating parameters for the system. Micellar solutions comprising various concentrations of sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 are examined for their effect on the emission intensities of metals in a range of cobalt, copper and nickel complexes. Emission enhancements are observed for SDS and Triton X-100 and possible mechanisms are considered.

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A Selected Bibliography and Review of Direct Current Plasma - Optical Emission Spectroscopy

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While the direct current plasma (DCP) enjoys considerable popularity as a multielement analysis technique, this has not been reflected in the amount of discussion in the scientific literature of this plasma source for optical emission spectroscopy. This is the first of a series of reports which are intended to help to correct this imbalance. It therefore seems appropriate to commence with a selected bibliography of recent publications with a guide to the area of work to which they refer.

The original two-electrode DCP has in recent years been supplanted by a much more stable three-electrode argon plasma, sustained between a single tungsten cathode and two graphite anodes. This arrangement produces a plasma in the shape of an inverted "Y" with the angle of the Y being the normal viewing zone. This development seemed the logical starting point for this bibliography. In the conventional commercial system argon flows through ceramic sleeves and around the electrodes. The arc is struck and the electrodes automatically assume their normal analytical configuration which allows the introduction of sample as an aerosol from the base of the inverted Y. A rugged ceramic nebulizer is used, and argon serves as the carrier gas with the sample being introduced via a peristaltic pump. The optical emission is observed using an echelle grating spectrometer which may be peaked manually onto the wavelength, or configured for computer-controlled rapid sequential operation or direct-reading simultaneous multi-element analysis. Most of the reports mentioned below have used this commercial instrumentation.

System characteristics and performance

Descriptions of the characteristics and performance of the DCP have centered in two areas; firstly, there are those accounts concerned with the evaluation of the source itself, and secondly, studies directly comparing the DCP with other techniques.

The capabilities of the source and the echelle grating spectrometer, with which it is commercially coupled, have been evaluated [2, 8, 20, 24, 53]. Applications of simultaneous multi-element analysis have produced interesting insights into spectral interferences and operation conditions [15, 56].

Data on the performance of the DCP in comparison to other atomic spectroscopic techniques is available showing the wide applicability of DCP-OES [17, 29, 32, 35, 41, 67, 83].

Fundamental studies

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An important area of study with the DCP has been excitation mechanisms, particularly in an attempt to explain enhancement of emission by easily ionized

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elements. Miller <u>et al</u>. [81] have reviewed the subject proposing a radiative transfer/collisional redistribution of energy model for analyte excitation. Many other papers have addressed these subjects [15, 16, 19, 25, 27, 30, 40, 48, 56, 57, 74].

In addition to the above, mainly concerning the effects of easily ionized elements, spatial studies of emission have been performed [25, 71, 73] providing data both on the distribution of emission intensity in the DCP and further information concerning excitation processes.

Other work has included a description of an Ar-N, direct current plasma [49] and a study of the vacuum ultraviolet emission spectra of the DCP [75].

Sample introduction

Sample introduction has been a popular area of investigation with DC plasmas. The introduction of liquid samples has been described in work considering the characteristics of DC plasma sources (see above). In addition, reports on discrete sample introduction [45] solute vaporization effects [16] and on the determination of trace elements in non-aqueous samples [58] have been published.

The use of a DCP as an element specific detector for chromatography has been described. The use of DC plasmas as a liquid chromatographic detector also has yielded information on solvent effects and sample introduction system characteristics and design [4, 10, 46, 80]. The use of DC plasmas as detectors for gas chromatography has not been neglected [6, 28, 68] using both conventional and vacuum uv spectrometers [34]. The use of gaseous sample introduction has been described for the determination of arsenic [18, 82] and sulfur [21].

The introduction of solid samples into the DC plasma has as yet attracted only limited attention, despite the advantages of the relatively high sample introduction gas flow rates and the robust construction of the nebulizer and sample introduction system of the conventional DCP. The use of an electrothermal atomizer for solid sample introduction into a DCP has been described by Wirz <u>et</u> <u>al.</u> [72]. The possibility of nebulizing aqueous suspensions ("slurry atomization") has been studied by Mohamed <u>et</u> <u>al</u>. [39] using a Babington-type nebulizer and a bovine liver sample. The use of the DCP in studying metallic wear particles in oils has also been described [23, 50, 76].

Recent publications have also included a study of nebulization using nitrogen in place of argon [79].

Applications

The DC plasmas have been used for elemental determinations in a wide range of samples. Trace element speciation using coupled chromatography has already been outlined. For clarity, illustrative applications have been tabulated below with a description of the element(s) determined and sample matrix.



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Table 1 Iron, Steel and Other Metallurgical Samples

ANALYTE Element(S)	MATRIX	REFERENCE .	
Various	Pb/Pb alloys	[14]	
Various	99.95 ZPa	[43]	
Various	Steels, Irons	[36]	
Various	Metals	[42]	
Nb	Ores, Steels	[59]	
Various	Steel	[77]	
W	Metals	[37]	

Table 2 Application to Rocks, Ores, and Sediments

ANALYTE	MATRIX	REFERENCE	
Various	Silicate Rocks	[12]	
major/minor Rare Earth Elements Various Various Ba, Sr	Ore Concentrates Estuarine Sediments Sediments Sediments	[51] [74] [32] [44]	

Table 3 Application to Clinical Samples

ANALYTE ELEMENT(S)	MATRIX	COMMENTS	REFERENCE
Na, K, Mg, Ca, Li, Fe, Cu, Zn Li Various Various Various	Human serum Serum Various Biological matrices Intravenous solutions	- Human metabolic study - - -	[22] [31] [41] [52] [46]
(trace) Various	Biologica <u>l</u> fluids	Chromatographic detection	[57]
Al, Ba, Si, Sr V	Amniotic fluid Urine, blood	- Comparison with ETA	[83]

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Table 4 Application to Oils, Chemicals and Industrial Materials

ANALYTE	MATRIX	COMMENTS	REFERENCE
Metallic wear particles	Aircraft lubricating	Uses particle size effect	:
	oils	Direct analysis	[20,23]
Merallic wear particles	Lubricating oils	As. [23]	[50]
Metallic wear particles	Lubricating oils	Review article	[71]
Various	Motor oils	-	[66]
Various	Organic solvents	Changes to sample	
		introduction system	[58]
Various (trace) Concentrated elec		olyte	
	solutions	Comparison of techiques	[70]
He	Iodine monochloride	-	[33]
Al. Fe. Ca. Mg	Wet process		
	phosphoric acid	-	[38]
Various	Industrial products	-	[63]
0	Phosphatic material	6 -	[64]
B	Glass	-	[13]
Various	Silicon nitride	-	[55]

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Table 5 Applications to Soil, Fertilizers, Plant and Animal Materials

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ANALYTE ELEMENT(S)	MATRIX	COMMENT	REFERENCE
Various (maj B Various Various Various Various Various	or) Soil Fertilizers Plant tissue Birch bark Orange juice Bovine liver (NBS SRM)	Simultaneous determination Comparison of techniques - Comparion of four techniques Slurry atomization with Babington nebulizer	[69, 64] [35] [26] [65] [17] [39]
Various Various B Ba	Horse hair Animal tissue Fertilizer Diatom ash	Selection of operating condition	[54] s [56] [3] [1]

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Table 6 Application to Air and Waters

ANALYTE	MATRIX	REFERENCE
V Be As, B, C, P, Se, Si Various (trace) Various (trace) Various Various Various Various	Workplace air Industrial aerosols Natural waters Natural waters Salt waters Saline waters Saline waters Sediments, waters, marine organisms	[67] [47] [83] [15] [19] [27] [48] [60]

REFERENCES

1977

- [1] Bankston, D.C., and Fisher, N.S., Anal. Chem. 1977, 49, 1017.
- [2] Kiers, C.D. and Vickers, T.J., Appl. Spectrosc. 1977, 31, 273.
- [3] Melton, J.R., Hoover, W.T., and Morris, P.A., J. Assoc. Off. Anal. Chem. 1977, 60, 873.
- [4] Uden, P.C. and Bigley, T.E., Anel. Chim. Acte 1977, 94, 29.

1978

[5] Fairless, C.M., Am. Lab. 1978, 101.

- [6] Lloyd, R.J., Barnes, R.M., Uden, P.C., and Elliott, W.C., Anal. Chem. 1978, 50, 2042.
- [7] Melton, J.R., Hoover, W.L., Morris, P.A., and Gerald, J.A., J. Asssoc. Off. Anal. Chem. 1978, 61, 504.
- [8] Skogerboe, R.K. and Urasa, I.T., Appl. Spectrosc. 1978, 32, 527.
- [9] Uden, P.C., Barnes, R.M., and Disanzo, F.P., Anal. Chem. 1978, 50, 852.
- [10] Uden, P.C., Quimby, B.D., Barnes, R.M., and Elliott, W.G., Anal. Chim. Acta 1978, 101, 99.

1979

- [11] Ball, J.W., Thompson, J.M., and Jenne, E.A., Anal. Chim. Acta 1979, 98, 67.
- [12] Bankston, D.C., Humphris, S.E., and Thompson, G., Anal. Chem. 1979, 51, 1218.
- [13] Burdo, R.A. and Snyder, M., Anal. Chem. 1979, 51, 1502.
- [14] Griffin, H. and McNulty, R., Environ. Meas. Lab. Environ. Q. (U.S. Dept. Energy) 1979, EML-356, 479.
- [15] Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., Spectrochim. Acta 1979, 34B, 197.
- [16] Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., Anal. Chem. 1979, 51, 2403.
- [17] McHard, J.A., Foulk, S.J., Nikdel, S., Ullman, A.H., Pollard, B.D., and

ICP INFORMATION NEWSLETTER, Vol. 10, No. 10, 801 (March 1985)

Winefordner, J.D., Anal. Chem. 1979, 51, 1613.

[18] Miyazaki, A., Kimura, A., and Umezaki, Y., Anal. Chim. Acta 1979, 107, 395.

1671

- [19] Nygaard, D.D., Anal. Chem. 1979, 51, 881.
- [20] Reednick, J., Am. Lab. 1979, 28, 383.

3

[21] Swaim, P.D. and Ellebract, S.R., Anal. Chem. 1979, 51, 1605.

1980

- [22] Berndt, H. and Messerschmidt, J., Fresenius Z. Anal. Chem. 1980, 301, 104.
- [23] Brown, J.R., Saba, C.S., Rhine, W.E., and Eisentraut, K.J., Anal. Chem. 1980, 52, 2365.
- [24] Coleman, G.N., Braun, W.P., and Allen, A.M., Appl. Spectrosc. 1980, 34, 24.
- [25] Decker, R.J., Spectrochim. Acta 1980, 35B, 19.
- [26] Debolt, D.C., J. Assoc. Off. Anal. Chem. 1980, 63, 802.
- [27] Eastwood, D., Schulz, M.H., and Sogliero, G., Spectrochim. Acta 1980, 35B, 421.
- [28] Estes, S.A., Poirier, C.A., Uden, P.C., and Barnes, R.M., J. Chromatogr. 1980, 196, 265.
- [29] Fujiwara, K., McHard, J.A., Foulk, S.J., Bayer, S., and Winefordner, J.D., Can. J. Spectrosc. 1980, 25, 18.
- [30] Johnson, G.W., Taylor, H.E., and Skogerboe, R.K., Appl. Spectrosc. 1980, 34, 18.
- [31] Mifune, M., Okayama Daiagaku. Onsen Kenkyusho Hokoku. 1980, 50,43.
- [32] Sinex, S.A., Cantillo, A.Y., and Helz, G.R., Anal. Chem. 1980, 52, 2342.
- [33] Smith, M.R., Anal. Chem. 1980, 52, 583.
- [34] Treybig, D.S., and Ellebract, S.R., Anal. Chem. 1980, 52, 1633.
- [35] Woodis, T.C., Hunter, G.B., Holmes, J.H., and Johnson, F.J., J. Assoc. Off. Anal. Chem. 1980, 63, 5.

1981

- [36] Belliveau, J., Griffin, H., and Salvolainen, A., ASTM Spec. Tech. Publ. 1981, 747, 77.
- [37] Czech, N. and Wunsch, C., Spectrochim. Acta 1981, 36B, 553.
- [38] Hunter, G.B., Woodis, T.C., and Johnson F.J., J. Assoc. Off. Anal. Chem. 1981, 64, 25.
- [39] Mohamed, N., Brown, R.M., and Fry, R.C., Appl. Spectrosc. 1981, 35, 153.
- [40] Nygaard, D.D. and Gilbert, T.R., Appl. Spectrosc. 1981, 35, 52.
- [41] Sutton, D.C., Rusa, W.C., and Legotte, P.A., Trace Subst. Envirn. Health 1981, 15, 270.
- [42] Urubleuskya, M.A., Talalaeva, A.V., Talalaev, B.M., Khim. Prom.-st. ser Azotn Prom-st 1981, 5, 16.
- [43] Worthington, M.A., ASTM Spec. Tech. Publ. 1981, 747, 91.

1982

- [44] Bowker, P.E. and Manheim, F.T., Appl. Spectrosc. 1982, 36, 378.
- [45] Boyko, W.J. and Keliher, P.N., Can. J. Spectrosc. 1982, 27, 51.
- [46] Braetter, P., Gardiner, P.E., Megretti, V.E., Schulze, G., and Von Stockhausen, H.B., Trace Element Anal. Chem. Med. Biol. Proc. Int. Workshop 2nd 1982 (publ. 1983), 45.
- [47] Chang, A.E., Morse, R., Harley, N.H., Lippmann, M., and Cohen, B.S., Am. Ind. Hyg. Assoc. J. 1982, 43, 117.
- [48] Eastwood, D.L., Schulz-Hendrick, M., and Miller, M.H., Spectrochim. Acta

ICP INFORMATION NEWSLETTER, Vol. 10, No. 10, 802 (March 1985)

1982, 37B, 293.

<u>د</u>

- [49] Fushiro, Y., Kubota, M., and Ishida, R., Anal. Chim. Acta 1982, 142, 173.
- [50] Kauffman, R.E., Saba, C.S., Rhine, W.E., and Eisentraut, R.J., Anal. Chem. 1982, 54, 975.
- [51] Johnson, G.W. and Sisneros, T.E., Rare Earths Mod. Sci. Technol. 1982, 3, 525.
- [52] Tempini, G., Pugleise, F., Franco, G., Riganti, V., Specchiarello, M., G. Ital. Med. Lav. 1982, 4, 83.
- [53] Zander, A.T., Ind. Res. Dev. 1982, 24, 146.

1983

- [54] Chandola, L.C. and Lordello, A.R., Microchem. J. 1983, 28, 87.
- [55] Czupryna, G. and Natansohn, S., Mater. Sci. Res. 1983, 15 (Adv. Mater. Charact.) 491-7.
- [56] Frank, A. and Petersson, L.R., Spectrochim. Acta 1983, 38B, 207.
- [57] Gardiner, P.E., Braetter, P., Negretti, V.E., and Schulze, G., Spectrochim. Acta 1983, 38B, 427.
- [58] Gilbert, T.R. and Penney, B.A., Spectrochim. Acta 1983, 38B, 303.
- [59] Griffin, H. and Savolainen, A., Spectrochim. Acta 1983, 38B, 183.
- [60] Grogan, W.C., Spectrochim. Acta 1983, 38B, 357.
- [61] Hall, G.S., Carr, M.J., Cummings, E., and Lee, M., Clin. Chem. 1983, 29, 1318.
- [62] Krull, I.S., Panaro, K.W., and Gershman, L.L., J. Chromatogr. Sci. 1983, 21, 460.
- [63] Natanshon, S. and Czupryna, G., Spectrochim. Acta 1983, 38B, 317.
- [64] Norman, J.D., Stumpe, L.A., Trimm, J.R., and Johnsonn, F.J., Assoc. Off. Anal. Chem. 1983, 66, 949.
- [65] Nurmesniemi, H. and Hayrynen, H., Pap. Puu. 1983, 65, 700.
- [66] Oreshkov, T. and Petrakiev, B., God. Vissh. Khim.-Teknol. Inst. "Prof.d-r. As. Zlatarov," gr. Burgas 1983, 17, 79.
- [67] Pyy, L., Lajunen, L.H.J., and Hakala, E., Am. Ind. Hyg. Assoc. J. 1983, 44, 609.
- [68] Riska, G.D., Estes, S.A., Beyer, J.O., and Uden, P.C., Spectrochim. Acta 1983, 38B, 407.
- [69] Shen Renshui, Zhen Chunrong, and Qian Qinwen, Fenxi Huaxue 1983, 11, 599.
- [70] Skidmore, R.R. and Greetham, S.S., Analyst 1983, 108, 171.
- [71] Williams, R.R. and Coleman, G.N., Spectrochim. Acta 1983, 38B, 1171.
- [72] Wirz, P., Gross, M., Ganz, S., and Scharmann, A., Spectrochim. Acta 1983, 38B, 1217.

1984

- [73] Blades, M.W. and Lee, N., Spectrochim. Acta 1984, 39B, 879.
- [74] Cantillo, Z.Y., Sinex, S.A., and Helz, G.R., Anal. Chem. 1984, 56, 33.
- [75] Carr, J.W. and Blades, M.W., Spectrochim. Acta 1984, 39B, 667.
- [76] Eisentraut, K.J., Newman, R.W., Saba, C.S., Kauffman, R.E., Rhine, W.E., Anal. Chem. 1984, 56, 1086A.
- [77] Fernando, L.A., Anal. Chem. 1984, 56, 1970.
- [78] Keliher, P.N., Boyko, W.J., Patterson, J.M., and Hersehy, J.W., Anal. Chem. 1984, 56, 133R.
- [79] Mangold, R.A. and Bastiaans, G.J., Appl. Spectrosc. 1984, 38, 377.
- [80] Mazzo, D.J., Elliott, W.G., Uden, P.C., and Barnes, R.M., Appl. Spectrosc. 1984, 38, 585.

ICP INFORMATION NEWSLETTER, Vol. 10, No. 10, 803 (March 1985)

[81] Miller, M.H., Eastwood, D., and Hendrick, M.S., Spectrochim. Acta 1984, 39B, 13. 24-2 hydr

[82] Panaro, K. and Krull, I.S., Anal. Lett. 1984, 17, 157.

[83] Pyy, L., Makala, E., and Lajunen, L.H.J., Anal. Chim. Acta 1984, 158, 297.

[84] Urasa, I.T., Anal. Chem. 1984, 56, 904.

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1984 Hungarian Plasma Spectrochemical Activities

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A new ICP spectrometer was installed at the Chemical Department of the University of Agriculture in Budapest under the leadership of Professor Dr. J. Paizs. Dr. Peter Fodor, who studied ICP techniques and performed research at the University of Massachusetts in 1981-2, is working with the Jarrell-Ash ICAP-9000 type spectrometer. The task of his laboratory is the analysis of agricultural and biological samples.

Scientific connections with the University of Massachusetts were continued as Dr. Zs. Horváth is performing ICP research in the ICP laboratory of Dr. Barnes.

Dr. J. Borszéki, senior Lecturer at the Institute of Analytical Chemistry of the Veszprém University, this year received a grant from the Technical University of Graz, where he is performing ICF research in the Institute of Analytical Chemistry, Micro- and Radiochemistry under the direction of Professor G. Knapp. On the basis of this work, the following poster presentation was made at the 1985 European Winter Conference on Plasma Chemistry in Leysin, Switzerland: G. Knapp, J. Borszéki, B. Schreiber, "High pressure asher and ICP-OES - a combined analytical method for the rapid determination of metals in organic industrial products."

A Symposium on the Application of Spectrochemical Analysis Methods in Agriculture and Environmental Protection was held April 2-3, 1984 at the University of Agrar Sciences in Gödöllö. The following lectures were presented: O. Boldis, "Use of ICP technique in agrochemical investigations," Sz. Bálint, "Simultaneous analysis of nutritive element content of aqueous and ammonium lactate soil extracts using ICP spectrometry," P. Fodor, "Sample preparation problems in the spectral analysis of agrochemical solution samples," A. Mészáros and A. Lásztity, "Results of electrothermal atomic absorption determination of Pb and Cd content in regional air above Hungary."

The 27th Hungarian Annual Conference on Spectral Analysis was held June 4-7, 1984 in Szombathely. A wide range of spectrochemical topics were considered in 81 lectures. The following papers were related to plasma chemistry: Abo Bakr M. El-Nady, K. Zimmer, Gy. Záray, and E. Kultsár, "ICP investigation of mediaeval glasses," P. Fodor, "Experiences with a Jarrell-Ash ICAP-9000 spectrometer," E. Bertalan and P. Zentai, "Geological application of a double arc method," K. Percsich and Gy. Heltai, "Comparison of various soil extracts by ICP and AAS trace analysis," and L. Paksy, "Determination of trace elements in airborne dusts in a high-current d.c. arc."

The Symposium on problems of sample introduction in AAS was held September

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