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A THESIS ENTITLED

GEOCHEMICAL ANALYSIS BY INDUCTIVELY-COUPLED PLASMA

OPTICAL EMISSION SPECTROSCOPY

USING SLURRY ATOMIZATION

Presented by

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in part fulfilment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

OF THE

COUNCIL FOR NATIONAL ACADEMIC AWARDS

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Geochemical Analysis by Inductively Coupled Plasma

using Slurry Atomization

ABSTRACT

Elemental analysis by the nebulization of slurries of geological materials into an inductively coupled plasma has been investigated.

High-solids nebulizers, spray chambers and torches have been designed and optimized for aqueous slurry introduction. The influence of particle size on sample introduction and atomization efficiency was shown to be paramount. Kaolin particles greater than 8 μ m were not atomized in the plasma. When the plasma operating parameters were optimized by simplex only the injector gas flow-rate and viewing height were critical.

Clay suspensions of known concentration, varying particle size distributions, and concentrations of 0.2 to 20% w/v were prepared and major, minor and trace elements determined by slurry atomization. Equivalent atomization efficiencies were obtained for slurries containing particle size of 8 μ m. For slurries containing larger particles the use of silicon in the kaolin as an internal standard corrected for variable atomization efficiency.

The addition of dispersants greatly increased slurry atomization by decreasing flocculation. Aqueous ammonia (0.35% m/v) was optimal. For high concentration slurries (>8% w/v) nebulization was affected by viscosity and an added internal standard was used to correct this.

Slurry atomization was successfully applied to a variety of kaolin analysis and showed promise for on-line monitoring. Dolomite and basalt samples were ground prior to application of the technique, due to problems with dispersion an internal standard correction provided best results. Preliminary investigation of partial dissolution and equal density slurry approaches suggested the former to be more promising.

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1. INTRODUCTION

1.1 Geochemical Analysis

The determination of the abundance of trace elements in geological materials has long been of major interest to geochemists. With the introduction of instrumental methods, the application of major, minor and more importantly trace element data has lead to greater understanding of geological processes such as weathering processes, ore formation and magma generation. In applied geochemistry the most important application is in mineral exploration. Geochemical prospecting commonly involves the determination of trace metal abundances in systematically collected samples from large areas of land, with a view to the identification of small areas (anomalies), where particular elements have unusually high concentrations and hence justify further investigation.

Exploration geochemists generally attach greater importance to relative, rather than absolute, metal abundances. (1) This will therefore have a considerable influence on the approach taken to the analysis and choice of analytical method, tending to emphasize sample throughput and batch analysis.

One of the many applications of analytical instrumentation in geology is the 'complete' analysis of silicate rocks and minerals. Complete or 'whole' rock analysis is used both in the applied and pure research fields of geology, with heavier emphasis on the range of elements to be determined together with the need for reasonable precision. Traditionally, complete analysis has been the concern of academically orientated studies, rather than for use in quality control, in the industrial processing of geological materials. Knowledge of mineralogical

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composition is frequently needed before and after industrial processing so precautions can be taken in production to ensure the geological material comforms to constituent specifications, to satisfy the often stringent technical and commercial requirements of the user industry.

The conventional 'complete' analysis of silicate rocks requires the determination of SiO₂, Al_2O_3 , Fe_2O_3 , CaO, MgO, Na_2O , K_2O , TiO₂, MnO, P_2O_5 , as percentage constituents (quoted as oxides) together with a number of the more abundant and diagnostic 'trace' elements which are measured at $\mu g g^{-1}$ levels. Concentrations of trace elements in geological material can range from their typical crustal abundances and grades, so that there is considerable variability in both chemical and physical characteristics of the samples. Suitable analytical methods must therefore combine adequate sensitivity with freedom from interferences over a wide range of compositional variability. The need to handle large numbers of samples, at a minimum cost, imposes further constraints in the choice of methods and also requires careful organization in laboratory operations.

1.1.1 Instrumentation

Analytical methods in geochemical prospecting have been discussed in a recent text by Fletcher (2). Several methods are currently available for the determination of one or more elements (including X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), and to a lesser extent colorimetric and gravime tric methods etc). However the large number of elements required and the substantial variations in bulk composition found in silicate rocks, would suggest inductivelycoupled plasma-optical emission spectroscopy (ICP-OES), could offer considerable potential advantages as a method for the analysis of

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geochemical samples. X-ray fluorescence (XRF), which has found wide acceptance as a solid sampling technique for the determination of the major constituents of rocks, is also capable of determining many trace elements in geochemical matrices. It is also a non-destructive technique so that the sample analysed can be retained. Moreover, sample preparation can be extremely simple. For general analysis, pelletized samples (or powders) are analysed against standards of similar composition. Precision is considered better than ICP-OES although accuracy is severely hampered by matrix interference. XRF, however, suffers from a number of disadvantages including lack of sensitivity, with detection limits being in the μg g region rather than the ng g^{-1} region (3), and also the need to correct data for matrix effects. The detection limits for elements of low atomic number, notably Na, Mg, Al and Si, are severely curtailed by the 'Auger effect', which involves the internal re-absorption of fluorescence radiation and causes a serious reduction of X-ray intensity for light elements. Many of the trace elements of interest in exploration samples have been reported by Leake et al. (4,5) and Levison (6). However, because of the wide compositional variations of geochemical samples and differential excitation of different components of individual samples as a result of textural and mineralogical effects, it is only possible to obtain reliable results if sample preparation is designed to minimize textural variations and if corrections are made for mass absorption differences between samples and standards. For the need of very accurate whole rock analysis in petrography, fusion of the sample to give a homogenous glass disc is required, in which mass absorption coefficient variations are greatly reduced (7).

As detection limits for many elements are somewhat poorer than can

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be attained with ICP-OES or AAS and the need to correct for matrix effects, XRF is considered best suited to analysis of materials for minor element determinations or in Walsh's opinion (8), for major element analysis of rocks where the samples are of limited compositional range and can be closely matched by standards.

The flame atomic absorption technique is probably the most widely employed method for analysing soil solutions. Atomic absorption spectrometry can be subdivided into two categories, flame AAS and electrothermal. Historically a flame has been the means of atomization for AAS and is still the basic source for the majority of AAS measurements Flame atomic absorption spectroscopy is a simple, rapid and relatively inexpensive technique for determining minor and trace levels and has the advantage of being relatively free from interferences if precautions are taken. In AAS, the flame is only required to produce ground state atoms (c.f. AES, where a hot flame is preferred as atoms must also be excited). Most elements can be easily atomized by the commonly used air-acetylene flame. For those elements which form more refractory compounds or where solutions having high sample matrices are encountered, a nitrous oxide-acetylene flame is preferred. The use of flame atomic absorption spectrometry in geochemical analysis for the determination of major and minor elements, is widely reported (9,10,11). Of the trace elements often sought in geochemical analysis the majority are detectable with routine operating conditions and dilution factors in the range 20 - 50 after complete or almost complete sample dissolution. The remaining elements are usually only detectable after preconcentration or by using special techniques such as hydride generation for the determination of elements forming gaseous hydrides eg As, Bi, Sb, Sn and Te (12). For simplicity and rapidity, solvent extraction,

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whereby an uncharged ion association or metal chelate is extracted from an aqueous phase into an immiscible organic solvent, has found many analytical applications in the concentration and separation of trace elements from interferences in geological materials. Hannaker and Hughes (13) and Viets et al. (14) have reported multi-element extraction schemes to reduce interferences and increase sensitivity for the determination of trace elements in geological material. Fortunately, providing background absorption is corrected for, interferences in flame AAS are seldom sufficiently troublesome to warrant use of solvent extraction for those elements with adequate sensitivity for their direct determinations in acid extracts. Most interferences could be overcome either by careful matching of sample and standard solutions or by simple modification to the composition of the sample solution by adding various releasing, compensating, and/or complexing agents to samples and standards alike. Electrothermal atomization or furnace techniques have also been reported for trace element determination in geological materials (15). Furnace techniques offer better sensitivity than conventional flame AAS, but cannot compete, either in productivity or freedom for interferences with flame AAS for the rapid routine determination of most of the elements of interest in soils and sediments. For those elements readily determined in the flame use of electrothermal furnaces offers no advantages.

Nevertheless one of the major disadvantages of AAS is that it is conventionally a single element method, whereas ICP-OES has the ability to perform sequential and/or simultaneous multi-element analysis. Furthermore ICP-OES is clearly superior to AAS in dynamic range covered, which is advantageous in multi-element work. The source is optically thin and linear calibration ranges of 4 - 5 orders of magnitude are

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widely reported, this allows a large range of elements to be determined on a single solution preparation without any dilution. This is not the case in AAS, where only 2 - 3 orders of magnitude can be covered and dilutions are very often required in practice.

The inductively-coupled plasma offers several advantages in atomic spectroscopy. The range of elements that can be excited is large, and includes many of the 'difficult' elements such as refactory elements, the rare earth elements and also light elements such as lithium, beryllium and boron. Therefore ICP-OES has a considerable potential for the analysis of different types of geological samples, and the range of elements that can be determined. Detection limits are also low, due to the high temperatures experienced by the analyte passing through the plasma (6-7000k) and the inherently low background of the source. The detection limits quoted for single elements determined in aqueous solution cover the range from <u>ca</u> 0.1 μg ml $^{-1}$ eg K, P and U down to 0.0005 μ g ml⁻¹ eg Ba, Be, Ca, Mg, Mn and Sr (16). The ICP enjoys relative freedom from chemical interferences compared with other techniques, particularly arc and spark sources and also atomic absorption spectrometry. Chemical interferences as observed in flame atomization, do not occur. Interferences due to easily ionizable elements can occur, but their effect is to modify the excitation mechanism, particularly its spatial character, rather than to produce a simple shift in ionization equilibrium, as occurs in flames. This can be reduced to insignificant levels by correct optimization of the plasma. However the principal cause of inaccuracy in ICP-OES, as encountered with other emission techniques, is spectral interferences. Good resolution monochromators and the choice of the correct one of the many wavelengths available for the determination of any one element,

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may help to overcome these problems. Precision is good for an instrumental method. In routine use precisions of 1 - 5% may be expected depending upon the concentration range and the sample matrix. One of the most important assets of the ICP is the potential to deal with liquid, slurries, solid and gaseous samples. Since this work deals with the use of ICP for the analysis of slurries, it is considered separately in section 1.3 of this chapter.

1.2 ICP

The ICP developed in the 1960's has gained much popularity in recent years. The inductively coupled plasma, a high temperature excitation source, is formed by the coupling of ionized argon with a powerful radio-frequency (RF) field. When the sample, usually in the liquid form, is introduced to the plasma, as an aerosol mist via nebulization, the aerosol particles undergo various processes such as desolvation, decomposition, atomization/excitation and ionization/excitation. The atomic/ionic emission signals of the analyte elements are received by a spectrometer and transformed into measurable signals.

Since this work uses the ICP, a summary of the theory of emission, development and spectroscopic analytical properties of this source will follow.

1.2.1 Emission Theory

Emission spectrometry is based on the principle that an atom in an excited state, j, of energy Ej, may spontaneously undergo a radiational transition to a lower energy state, Ei, with emission of a photon of energy,

$$hvji = Ej - Ei$$
 1.1

where h is Plank's constant (6.6 x 10^{-34} Js)

When the lower of the two levels is the ground state (i = o, Eo = o), the emitted spectral line is known as a resonance line. The process was described by Einstein in terms of the transition probability Aji, which is the probability per second that an atom in the state j will spontaneously radiate its energy and return to a lower state. The intensity of a spontaneous emission line is related to Aji by the equation

For a system in dynamic equilibrium the number of atoms in the excited state, Nj, is given by the Boltzmann Distribution Law:

	NJ = NO	gi go	exp - (Ej/kT)	1.3
Where	Ņj	5	number of atoms in	state j per unit volume
	No	=	number of atoms in	ground state per unit volume
	gj	=	statistical weight	of the jth state
	go	=	statistical weight	of the ground state
	k	=	Boltzmann constant	
	Т	=	thermodynamic temp	erature

Thus
$$\frac{Nj}{No} = \frac{gi}{go} \frac{exp(-Ej/kT)}{exp(-Eo/kT)}$$
 1.4

To make this formula useful to the analytical spectroscopist it is necessary to relate the number of atoms in the excited state to the total number of atoms present <u>i.e.</u> the concentration of analyte species.

The total number of atoms present, N, is expressed as the sum of the population of all levels <u>i.e.</u> N = Σj Nj-

$$Nj = \frac{gj \exp \left[-(Ej/kT)\right]}{\sum j gi \exp \left[-(Ej/kT)\right]}$$
$$= gj \exp \left[\frac{-Ej/kT}{F(T)}\right]$$
1.5

where F(T) is known as the partition coefficient, which expresses

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the population of states as a function of temperature.

For a system in thermodynamic equilibrium and neglecting self absorption

Iem = Aji . hvji . $\underline{\text{Ngj exp } [-Ej/kT]}_{F(T)}$ 1.6 F(T) Thus the intensity of atomic emission is critically dependent on temperature. The number of excited atoms, and hence the intensity of emission, increases very rapidly with increasing temperature. Also at low concentrations of analyte concentrations (<u>i.e.</u> negligible self absorption) the plot of emission intensity against sample concentration is a straight line.

A number of texts concerning the rules governing the transition which give rise to observed atomic spectra are available. A detailed study of this area is outside the scope of this work but the reader is referred to the work of White (17), Mandelshtam (18) and Sharp (19) in particular.

1.2.2 History and development of the Inductively Coupled Plasma

It is generally agreed that Babat's work first published in 1942 in Russian (20), and later in English (21), was the forerunner of the ICP used today. The importance of Babat's papers are that they document the first successful operation of ICPs at atmospheric pressure. Babat's work was concerned only with static non-flowing plasmas and it was not until 1961, with the work of Reed (22), that ICP discharges in flowing, atmospheric pressure gases *were* generated. Reed described an ICP torch operating at atmospheric pressure on argon alone or mixed with other gases and powered a 10 kW HF heating unit operating at a frequency of 4 mHz. The torch consisted of a quartz tube, with a brass base having a tangential gas entry, placed within the work

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coil of the generator. The plasma was first formed by the insertion of a carbon rod into the torch, thus producing thermal electrons by the Joule heating effect of the alternating magnetic field. This provided the initial ionization of the argon, enabling coupling to occur and a plasma to form. Reed thought that a tangential gas entry was necessary in order to create a vortex which would cause some of the plasma to flow counter-current to the gas flow and so maintain the plasma. Reed followed this paper by another (23) in 1961, in which he describes a torch with three concentric tubes with a centre powder feed which he used for crystal growing. This torch has formed the basic design for ICP torches used today, which have changed little from the Reed design. Although the potential for producing emission spectra was recognised the plasma was not used for analytical purposes.

A patent application was made in 1963 (24,25) by Greenfield and coworkers for the torch design adopted for use as a spectroscopic source. It was Greenfield who made the next important modification of the plasma by forming an annular shaped discharge. The torch is described in detail by Greenfield <u>et al.</u> (26,27) and consists of three concentric tubes. The outer two quartz tubes were used to contain the plasma and the inner tube, made of borosilicate glass, was used to introduce the sample aerosol which punches a hole in the flattened base of the plasma. Initially there was disagreement about the desirability of an axial channel through the plasma. In 1965 Wendt and Fassel (28) used a laminar flow torch which produced a 'solid' ellipsoidal plasma for which was claimed the advantage of less turbulence and perhaps greater stability than was obtained with the vortex flow.

In 1969 Dickinson and Fassel (29) achieved improved powers of detection

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using a three-tube torch similar to that of Greenfield design but smaller and an ultrasonic nebulizer for sample introduction into the torroidal shaped plasma. They attributed their greatly reduced detection limits to the development of the plasma shape to torroidal, to allow more efficient introduction of aerosol into the plasma, and the addition of a remote tuning facility for optimal coupling of the generator to the plasma which greatly assisted in stablization of the plasma.

In the late 1960's and continuing in the 1970's, Fassel and co-workers and Greenfield and co-workers continued their extensive in-depth studies of ICPs. The acceptance of ICP-OES today must, to a very large extent, be ascribed to these studies.

Since the availability of commercial instrumentation in the early 1970's, optimization, modification and refinement of the system have led to a variety of instrumental configurations in common use today. The ICP discharge has been widely applied in fundamental and practical applications, as an emission spectrochemical source. It also has been developed successfully as an atom cell for atomic fluorescence spectroscopy (AFS) (30,31), an ion source for mass spectrometry (32,33) and as a detector for chromatography (34,35) giving advantages of increased sensitivity and reduced matrix effects.

In recent years, the ICP has been extensively reviewed. Barnes (36,37) has produced two extensive literature reviews up to 1978, followed more recently (38,39) with reviews on the progress in inductively coupled plasma analytical spectroscopy. Sharp's review (19) contains some theoretical considerations of emission spectrometry. The historical development, basic properties and limitations and recent applications

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and developments have been reviewed in some detail, which include reviews of Fassel (40), Boumans (41), Boulos <u>et al</u>. (42), Ohls (43), Greenfield (44,45) and more recently Robins (46), which illustrate the growing popularity and application of ICP as an excitation source for multi-element analysis.

1.2.3 Plasma description

The arrangement for plasma production consists, typically, of a 3 tubed quartz torch coupled in a spray chamber and nebulizer. The diameter of the torch is usually either 27 or 18 mm, based on Greenfield (27) and Fassel designs (47). A schematic diagram of a conventional system is given in Figure 1. Three separate gas flows are employed to operate a conventional ICP for OES. The outer gas flow, namely coolant or plasma support gas (~10-20 $lmin^{-1}$), is introduced tangentially to the annular gap between the two outer quartz tubes. Argon or nitrogen is usually used, the latter which can only serve to cool the plasma and protect the torch. The resulting vortex flow produces a low pressure region at the end of the inner tube, where the plasma is ultimately located, and the high velocity of the flow cools and physically separates the outer tube from the plasma core. The plasma or auxially gas flow is tangentially introduced into the intermediate tube, to propagate the plasma. This may be omitted if argon is used in the outer flow. The nebulizer or injector gas (innermost flow $0.5 - 3 \text{ lmin}^{-1}$) transports the sample aerosol to the plasma, the high velocity flow produced 'punches' the sample into the centre of the plasma. A copper induction coil, through which coolant water is passed, surrounds the top end of the quartz tube. The coil, typically two to three turns, is coupled to an RF generator producing 1 - 30 kW output at betwen 5 - 50 mHz. (The usual combination being a few

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kilowatts at 27.1 mHz). When the power is switched on, an alternating magnetic field is established having field lines running axially through the coil. No plasma results, however, as there are no charged particles to which power can be coupled. Therefore for initiation of the plasma a telsa coil or graphite rod is used to ionize the argon gas stream by providing a 'seed' of electrons which become thermally excited in the alternating RF field. The magnetic field induces the ions and electrons to flow in closed circular horizontal paths, so producing eddy currents. The eddy currents heat the neutral argon by collisional energy exchange to give temperatures in the order of 7000 - 10000 K and develop and maintain the flame-like discharge. After the plasma has formed the sample aerosol is injected into its centre, creating a torridal shaped plasma in which the sample passes through the hole without penetrating the skin of the plasma. This impenetrability of the plasma results in it being relatively insensitive to injection of aerosols. The field does not penetrate uniformly, and the largest currents flow in the periphery of the plasma, this is the socalled 'skin-effect'. The existance of this phenomenon fundamentally influences the shape of the plasma and its analytical potential. The inside portion of the plasma is heated indirectly, resulting in a lower-temperature channel running through the centre. Although temperatures in the axial channel of the plasma fireball are lower than those within the plasma, they are still much higher than temperatures attainable in flames or arcs and more than adequate to vaporize the solute and dissociate molecular species. However, the background continuum in the plasma fireball is intense and for analytical purposes it is necessary to view the spectrum at some point in the tail flame where the background is low but temperatures are still sufficiently high to prevent recombination of atoms. As the axial channel is cooler

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than the surrounding plasma the problems of self-absorption, encountered with flames and arcs in which the temperature decrease towards the • out fringes, are virtually absent and the plasma behaves as an optically thin source.

The actual excitation mechanisms is not fully understood. Among the most important properties of the ICP which can be used to characterize the "plasma state" are 'temperature' and electron density. In recognition. of the fact temperature and electron density are important parameters of interest to ICP spectroscopists, a number of workers have measured and reported values of the parameters for ICP systems (48,49,50,51,52,53). Spatial distributions of the spectroscopic measurements have been made, using the mathematical technique of the Abel Inversion integral to convert lateral intensity to spatially resolved information (49,51, 54,55). Recently, Winefordner et al. (56,57) proposed two methods based on a saturated absorption spectroscopic and laser induced fluorescence method to allow the direct determination of spatial distributions in the plasma. Unlike previous emission and absorption methods reported above, these methods can be used regardless of the plasma symmetry and therefore without the need of the 'Abel Inversion'. The results from these studies show that there is no doubt that the plasma is, on the whole spatially inhomogenous and that local thermal equilibrium (LTE) does not exist in the all argon plasma. It is now generally accepted that the inductively coupled plasma operated in argon is not in LTE, at least not in the region used for analytical observations between 5 - 30 mm above the RF coil (49,51,52). The reported observations can schematically be written as:-

 $T_{ion} > T_{ex} > T_{g}$

where T = the temperature required to explain the ionization ion

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of the argon on the basis of the Saha equation.

 T_{exc} = excitation temperature which characterizes the population of various energy levels (on the basis of the Boltzmann equation).

 T_g = kinetic temperature of the moving atoms. Basically four mechanistic models have been proposed:-

a) the non-thermal excitation model (58,59,60) involving collisions of the second kind with argon meta-stables, known as "Penning ionization".

 $A^{meta} + m \qquad Ar + m^{+*} + e Ar + m + e$

This is particularly attractive since the excitation energies of the metastable argon levels of 11.55 and 11.71 eV correspond with the excitation energies of singly ionized species found in the plasma. This mechanism, however, is not considered efficient enough, especially with regard to atomic emission.

- b) The radiation trapping model (61,62) that attempts to explain the overpopulation of high energy levels emitted by the hot outer plasma ring where Ar species are trapped and are rapidly transferred to the metastable levels. Although postulated, recent papers (63) make it unlikely.
- c) Reaction rate model (64) where the level populations are derived from the excitation and de-excitation reactions occurring in the plasma.
- d) The ambipolar diffusion model, where the kinetic temperature of atoms and ions is significantly lower than the (kinetic) temperature of the electrons. Electrons created in the hot plasma

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ring inside the coil region, migrate into the cooler zones inside and above the plasma ring through axial convection and ambipolar diffusion.

De Galan (66) has suggested that the various mechanisms are complementary and that the plasma should be viewed as decaying from conditions of heterogenous equilibrium to a homogenous thermal equilibrium. Thus the ICP is now commonly regarded as a recombining plasma in partial thermal equilibrium.

Water has also been shown to play an important role in connection with atomization of aqueous samples (67). It has been suggested that introducing water into the plasma brings the ICP closer to local thermal equilibrium.

1.2.4 Application of ICP to geological analysis

The application of ICP-OES to major and trace element determinations in soil, sediments and geological material is now beginning to attract great interest, not only for its analytical speed and lack of chemical interferences but also because of the ability to detect refractory metals and rare earths at levels usually not achieved by AAS. The application of ICP-OES for the analysis of geological samples has been recently reviewed in a book by Thompson and Walsh (8).

In one of the earliest published studies Scott and Kokot (68) compared the determination of Cu, Pb, Zn, Co and Ni by ICP-OES and AAS. One gram of soil samples were digested with nitric-perchloric acids and diluted to 50 ml with water for aspiration at 1 ml min⁻¹ into a 27 mHz 1 kW argon plasma. No problems were encountered in the determination

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of Cu, Zn, Ni and Co which had linear calibrations over four orders of magnitude, although Ni and Co results were lower than those obtained by AAS. This appeared to be due to interferences in the flame rather than the plasma. In the case of Pb, high Ca content of the soils caused spectral background in the vicinity of the line used and it was found necessary to apply a correction.

Walsh (69) evaluated an ICP spectrometer for the simultaneous determination of a range of a major and trace constituents in silicate materials, using routine sample pretreatment procedures. The results were evaluated by the analysis of international rock standards and acceptable detection limits and precision obtained. Other workers (70,71,72,73) have discussed problems encountered in the analysis of minor and trace elements in geological materials, using different dissolution techniques. Wavelength scans indicated that broad recombination emission and spectral overlaps, caused by varying amounts of major components, gave rise to interferences for most elements at low concentrations.

Recombination of ions and electrons in the plasma can result in the emission of continuum radiation which causes an upward shift in the background intensity over a relatively wide wavelength region. Recombination of magnesium and/or aluminium ions and electrons can cause a significant background shift in the region from 200-300 nm if either or both of these elements are major constituents of the sample, as they are in many geological materials. If these do cause significant error then background correction and/or matrix matching of the standard solutions is required.

As reported by other workers, the effects of chemical and ionization

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interferences in the plasma were generally found to be insignificant. Acid concentration in sample solutions and standards should, however, be reasonably matched to avoid apparent interferences from the effects of changing viscosity on nebulization rates. The influence of optical dispersion and stray light on the analysis of geological samples by ICP-OES was reported by Walters <u>et al</u>. (74).

The consequence of stray light is a general rise in the plasma background which in the analytical situation corresponds to a positive bias in the results. Stray light is the general term applied to spurious spectroscopic interferences which arise from optical imperfections in the spectrometer. Intense calcium ion lines at 393.37 nm and 396.85 nm and magnesium lines at 279.55, 280.27 and 285.21 nm have been identified as major contributors to stray light in ICP-OES. Walters (74) reported that holographic gratings (75) and rejection filters (76) should minimize such problems.

The determination of rare earth elements in geological samples has been investigated by several authors (77,78,79), using digestion, ion exchange and concentration techniques. Although these techniques have been successful in determining the rare earths, a major disadvantage of these procedures is the limit they impose on sample throughput, which is a major consideration for laboratories involved in highvolume routine analyses.

Brown and Biggs (80) reported the determination of platinum and palladium in geological samples by ion exchange chromatography with ICP spectrometric detection. By separating Pt and Pd, from the base metals (large concentrations of non-platinum group elements) using a cation exchange

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resin in the H $^+$ Form spectroscopic interference effects could be eliminated. The chlorocomplex anions of Pt and Pd, obtained by digestion in aqua regia and then by HF and HClO₄, were not retained by the cation exchange resin while the base metal cations were efficiently removed from the eluent. Good agreement with conventional fire assay techniques was obtained for sulphide ores, however unexplained discrepancies arose in the analysis of several other geological materials.

Another approach to separate trace elements of interest from major

elements in geological samples is by selective extraction techniques. Mot ∞ ka et al. (81) described a multielement extraction procedure utilizing a 10% Aliquot 336 - MIBK solution for the analysis of Ag, Au, Bi, Cd, Cu, Pb and Zn in geological materials. Direct spectral interferences, matrix and interelemental effects carried by the major elements in geological materials were reported to be effectively eliminated and the sensitivity increased by concentrating, the trace metals in the organic phase. Results were obtained without any attempt to correct for background or spectral interferences, and consequently were only semi quantitative. A similar technique was employed by Thompson and Lang (82) who determined molybdenum in 6 M HCl, after extraction by heptan - 2 - one. Major and minor elements originally present in the samples were found to cause no measurable effect on the extraction and furthermore were all but iron which needs to be absence in the heptan - 2 - one extract. Practical detections masked limits better than $0.1 \mu g g^{-1}$ were obtained.

Rather than aspirating solutions into the ICP, Thompson et al. (83,84)

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determined As, Sb, Bi, Se and Te by generation of their gaseous hydrides, using 5 m hydrochloric acid - 1% sodium borohydride as the reductant and direct introduction of the hydride into the ICP. Detection limits of 1 ng g^{-1} or better in solution were obtained but it was necessary to control the interference of Cu, on, Bi, Se and Te by their coprecipitation and separation in lanthanum hydroxide. Using the same ICP system, Pahlavanpour <u>et al</u>. (85) separated Sn from interfering elements by sample decomposition with ammonium iodide fusion. The sublimate was leached with a 1% solution of tartaric acid; sodium borohydride was added to generate stannane (SnH₄). Direct introduction of stannane into the ICP gave a working range of 0.02 - 50 µg g⁻¹.

A recent paper by Thompson (86) discusses the capabilities and the limitations of ICP with particular emphasis in geochemistry. Most aspects reported, are discussed elsewhere in this thesis. From the paper it can be seen that sample dissolution problems are one of the major limitations of ICP for use in geochemical analysis and is discussed separately in the following section.

1.2.5 Present limitation of ICP-OES for geochemical analysis

A disadvantage of both AAS and ICP-OES in geological application is that they are both primarily techniques which are applied to samples in solutions whereas most geological samples are solids. The conventional method of sample introduction by nebulization of the dissolved samples, has several limitations in the analysis of geological materials, the most important of which is the problem of devising a truly multi-element dissolution. The literature on the available methods for the dissolution of silicates is extensive, as can be seen in a recent text by Jeffrey and Hutchinson (87). The two major methods,

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based on fusions or on the dissolution of samples using acids, give incomplete dissolution of some minerals, as well as large dilution factors, risk of contamination and loss of certain elements by volatization and other processes. Dissolution can also be tedious and timeconsuming and can incorporate the use of hazardous chemicals <u>e.g.</u> HF, $HClO_{\mu}$. Clearly the direct introduction of solids or slurries without sample pretreatment would avoid these problems and markedly reduce analysis time by combining matrix destruction and analyte atomization or excitation into one step. The ICP having a kinetic temperature considerably higher than conventional combustion flames offers much promise for the analysis of solid samples by a slurry atomization technique.

1.3 Analysis of solid samples

1.3.1 Direct solid introduction

Traditionally arc and spark emission spectrometry has been an important technique for solid sample analysis. An arc is a continuous electrical charge of high energy between two electrodes in gas. Gas molecules and atoms in the discharge are ionized to form a thermal plasma from which radiation is emitted. The technique is most successful analytically when analysing conductive material, the sample is usually packed into an anode electrode, or in the case of metallurgical analysis, the sample itself becomes the anode.Non-conducting materials have also been analysed, the sample is usually mixed with carbon powder to make it conducting. When the arc is struck between the two electrodes, the sample is vapozrized and atoms sputter into the discharge region where excitation and emission occur. Relatively large amounts of samples are excited and hence detection limits are low, but the relatively unstable nature of the discharge, due to random temperature fluctuations

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of the arc caused by selective volatization is a disadvantage. Additionally, it is usually necessary to standardize using samples of closely approximating composition, as the intensity of emission is highly dependent upon the matrix. Samples admixed with graphite and spectroscopic buffer such as alkali salts, are used to improve and maintain arc conditions. Avni <u>et al</u>. (88) found matrix effects, in standard rocks, were appreciably reduced when samples were mixed 1:5 with graphite. A disadvantage is the greatly increased cyanogen (CN) band emission caused by the combination of carbon and atmospheric nitrogen in the arc.

The light from the discharge is dispersed by a prism and a camera is used to record spectral intensity on a photographic plate or film and is usually used for rapid qualitative identification of the elements in an unknown sample. Direct reading spectrometers are available, where the photographic plate is replaced by photomultipliers, the output from which is fed to a voltmeter or other electronic readout system. The polychromator system, together with computer control of the data acquisition and calculation of the several corrections needed because of inter-element effects and spectral interferences, enables quantitative measurements. Various aspects of the application of direct reading spectrometers to the determination of trace elements in geochemical matrices have been discussed by Foster (89) and Timperly (90) and Fletcher (2).

If an intermittant discharge is used, as in the spark source, precision can be greatly improved, but detection limits are slightly degraded due to the relatively small amounts of sample volatized Modern electrical discharges combine the characteristics of both the arc and spark to

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optimize both detectability and precision. Further improvements have been made by sheathing the electrodes in inert gas helping to stabilize the discharge and reduced background. Barnes (91) in an extensive bibliography discusses the theory, use and applications of both arc and spark sources.

(XRF is well suited to solid samples and is discussed elsewhere.)

In contrast to arc and spark techniques, atomic absorption and ICP-OES offer better sensitivity, precision and more importantly reproducible conditions. It is not surprising therefore that there has been gradually increasing interest in the application of these techniques to the analysis of solid samples, especially for the use in geochemical analysis.

A comprehensive review by Langmyhr (92) described various approaches to the direct analysis of solid samples using atomic absorption spectrometry with reference to practical applications. Van Loon (93) dealt more generally with atomic emission and atomic fluorescence as well as absorption spectrometry.

Methods using flames for atomization of solid samples have tended to produce unsatisfactory results, lacking in sensitivity and precision. An attempt at the AAS analysis of a powdered sample mixed with a solid dispensing agent was made (94), with a miniature Archimedian screw for introducing the sample into a gas stream. Another procedure was based on mixing the sample with NaCl, depositing the mixture between the threads of the screw (95) and atomizing the analyte by moving the screw into the flame. Venghiattis (96) determined various metals

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in their ores by mixing the powdered sample with a solid propellant and introducing the pellitized sample into a flame. Reproducibility with this method was generally unsatisfactory. Such methods are not widely reported.

Since the early experiments of L'Vov (97,98) on the analysis of solid samples using electrothermal atomization with AAS, this technique has been successfully used for a variety of solid samples (99,100,101). Disadvantages of this technique include problems from excess background absorption signals, difficulties in standardization, relatively poor precision and restriction of sample size to only a few milligrams. Also techniques of this type are limited by the relatively low temperatures available and hence only the more volatile elements can be determined.

Powdered samples have also been analysed directly using the ICP, this approach has recently been reviewed (102). The very high temperatures achieved in the inductively coupled plasma make this device particularly attractive as an atomizer for solids. Hoare and Mostyn (103) placed powdered solid sample into a borosilicate cup at the base of a plasma torch. The cup was then vibrated. A relatively low argon flow rate through the vibrating powder carried the solid into the plasma. This device was used for the analysis of trace impurities in powdered nickel alloys, lithium salts and alumina. The results obtained proved only marginally better than those of the traditional AES method of solid sample analysis in a graphite arc. Precision of 5 - 10% was obtained.

Another technique to introduce solid sample powders by an argon flow was described by Dagnall <u>et al</u>. (104). A fluidized bed chamber was

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used to entrain powders into an argon carrier gas flowing into a plasma. In this device, powdered sample was placed on a sintered glass disc through which argon was flowing. A cyclone chamber was placed above the fluidized bed chambers to separate large particles. Ng <u>et al</u>. (105) recently described a simple powder injection device to pulse coal fly ash into an ICP, however in this paper little consideration was given to calibration and particle size and the technique also necessitated the plasma being extinguished between sample runs.

Subsequent investigators chose to separate and to optimize independently the solid sample evaporation process and the sample excitation process in the ICP in order to reduce irregularity in sample introduction rate, sample inhomogeneity and incomplete volatilization and atomization of the analyte observed with previous studies. Spark discharges (106,107,108) have been employed for the vaporation of solid samples. Promising results were obtained by Markset al. (107) for the analysis of alloys, with comparable precision achieved with the solid analysis technique as with the conventional solution method. In this method the sample after spark elutriation was transported from the spark sampling chamber not to the ICP directly, but first to an intermediate chamber where the aerosol was nebulized together with water and introduced into the injection tube of the torch by another argon flow, thus a more homogenous aerosol was achieved. Microarcs (109) have also been used in a similar manner to the spark elutriation techniques described above. The sample gas flowed over the microarc electrodes and carried vaporized sample rapidly into the ICP through the sample tube of the plasma torch. A rubber septum was attached to the arc stand at a right angle to the plane of the electrodes to allow the

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sample to be applied to the cathode without disruption of the sample gas flow. The microarc ICP combination exhibited detection limits and working curves comparable to those of other methods of sample introduction but functioned with sample volumes in the 0.5 to $1.0 \ \mu$ l range. Matrix and ionization interference effects were absent or trivially overcome. However precision, 1 to 5%, was found to be affected by the sample electrode material and shape.

More recently laser ablation has been used to volatilize samples for subsequent analysis using ICP-OES (110,111,112) and ICP-MS (113). Thompson et al. (111) employed a laser system, together with a glass chamber where the solid sample was located. After laser ablation the sample products were transported by an argon flow in a PVC tube to the ICP. Detection limits in the steel samples analysed were reported to be not as good as those obtained by macrotechniques. This was attributed by the very small laser ejection mass (some micrograms) of the sample analysed. In general, poor reproducibility for some elements has been reported using these laser ablation techniques, which is probably due to sample inhomogeneity (such a small area is vaporized). However these combined methods undoubtedly have certain advantages in comparison with the conventional methods of direct analysis of solid samples using spark and arc sources which include reduced interelemental effects and because of the high temperatures achieved by the laser, the ability to albate refractory materials with the same ease as volatile ones.

Another approach of direct introduction of solids into ICP has been reported by Salin and Horlick (114) who used a graphite rod, as a

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sample elevator, to introduce sample directly into the plasma and thus combining the evaporation and excitation source. Similar rod and cup devices have been investigated by a number of workers including Zil' bershtein (115), Ohls <u>et al</u>. (116), Kirkbright and co-workers (117), Abdullah <u>et al</u>. (118) and Lorber and Goldbart (119). These direct ICP-OES methods yield low detection limits and wide dynamic concentration ranges. However problems of poor reproducibility (RSD >5 - 10% in most cases) were again observed. The values of the analytical signals are very sensitive to the position in the plasma and especially with respect to the torch axis, of the sample being analysed.

Another approach is by using ETA-ICP-OES. Graphite rod electrothermal devices combined with ICP have been used for sample solutions (120,121, 122) and has recently applied to the analysis of microlitre solution volumes, inorganic powders, botantical solids and coal (123).

An alternative option for introducing solid into the ICP is by slurry atomization. This method has the advantage of being simple, with minimal sample pretreatment, ease of calibration and can be used with the existing ICP instrumentation.

1.3.2 <u>Slurry introduction</u>

Of increasing interest is the analysis of slurries, <u>i.e.</u> powders suspended with or without agitation in either aqueous or organic solvents, by ICP,flame AAS systems, or graphite furnaces.

Following the lead of Gilbert (124), who obtained flame emission spectra from a soil sample by aspirating a suspension of the soil in 1:1 isopropanol-glycerol, several workers have measured alkali metals

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in plant materials (125) and rocks (126) by analogous techniques. In atomic absorption early work was applied to the analysis of tin in tin ore concentrates (127), but closely matching of samples and standards appeared to be necessary. A few papers appeared on the determination of suspended metal particles in lubricating oils (128,129). Fuller (130) determined trace metals in titanium oxide pigments employing a combination of flame and electrothermal atomization of suspended samples. A significant contribution to the field of slurry analysis was the paper by Willis (131). A study was made of the factors influencing the atomization efficiency of several metals when suspensions of geological material were sprayed into the flame for analysis by atomic absorption spectrometry. He concluded that only particles below about 12 µm in diameter contributed significantly to the observed absorption and the atomization efficiency increased rapidly with decrease of particle size. He found that the results for one particular element could vary by a factor of two between rocks of widely differing types and recommended the technique for such purposes as geochemical prospecting where this accuracy could be accepted. Several workers (132,133) have studied the line of soil suspensions in the determination of trace elements by flame atomic-absorption spectrometry. Particle size, flame temperature and position in the flame were found to be critical in determining the fraction of particular elements atomized. Since these studies it has become apparent that the potential for the direct analysis of slurried samples may be limited by the complexity of the untreated matrix. Also blocking of the sample capillary or burner slot are problems encountered when using conventional burner/nebulizer assemblies. Much work has been performed on the development of nebulizer and burner systems capable of handling samples with high salt content and high levels of suspended

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solids. Development and subsequent characterization of a unique nebulization principle by Babington (134) has revolutionized sample introduction techniques (see Chapter 2). Using this type of nebulizer in combination with a wide-slot high-solids burner, Fry et al. (135) have determined copper and zinc in whole blood, milk, urine and seawater using atomic absorption spectrometry. Slurries of homogenized animal tissue samples (136) and Hogdogs (137) have been nebulized using similar apparatus. Despite the obvious advances, flame atomization efficiencies in slurry nebulization techniques are still low, typicaly 20% of those of aqueous solutions of equivalent concentration. Fuller, Hutton and Preston (138) compared the use of flame, electrothermal and inductivelycoupled plasma atomization techniques for the analysis of slurries. The authors conclude for flame atomization pulsed nebulization must be used and for inductivey-coupled plasma atomization a high solids nebulizer is essential. The results show that atomization efficiency in nebulizer based systems is dependent on sample transport efficiency, particle size, atomization temperature and sample matrix. For analytical determinations it is necessary to grind the sample to less than $10 \text{ } \mu$ m particle size and to use standards which are closely matched to the samples. For electrothermal atomization particle size effects only become significant above 25 µm when sampling becomes the major source of error. Langmyhr and Aadalen (139) reported the direct determination of copper, nickel and vanadium in coal and petroleum coke, whilst Ebdon and Pearce (140) proposed a direct method for the determination of arsenic in coal by AAS using solid sampling electrothermal atomization with aqueous solution calibration. A similar apparatus was used by Jackson et al. (141) for the determination of lead in soils.

To date few workers have published work on a slurry atomization

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technique using ICP. Sugimae and Mizoguchi (142) described a direct method for ICP determination of iron in airbourne particles collected on polystyrene fibre filters. A suspension prepared by dissolving the filter material in xylene, was directly nebulized into the ICP. Precision of < 5% were obtained, which were considered acceptable for large scale air pollution survey work. Some recent work (143) has been performed on the simultaneous multi-element analysis of clays by ICP using suspension aspiration. Clay suspensions were prepared over a concentration range of 2% to 0.5% (particle size <2 $\mu m)$ to evaluate the effect of colloidal concentration on the analyte nebulization rate. Preliminary experiments indicated that suspension at a higher concentration gave a 25% or greater reduction in aspiration rate as compared with equivalent aqueous samples. The authors concluded this decrease in aspiration rate appears to be directly responsible for the analytical variation observed and once corrected for by use of a correction factor satisfactory results can be obtained. Watson and Moore (144) concentrated Au, Pd, Pt, Rh and Ry on an ion-exchange resin, formed a slurry by mixing with H_20 , and nebulized the slurry into an ICP. It was suggested that the ICP-resin technique was adequate for the analysis of trace noble metals in ores and tailings if a sample of 500 g was taken.

Analytical methods based on slurry atomization techniques have several advantages to offer, particularly in terms of simplicity and speed in analysis. However, the complexities of this approach are apparent. If these limitations can be eliminated or reduced to tolerable leve/s:, either by the refinement of existing methods, or by the development of new techniques, then such methods could be of particular interest to those involved in geochemical analysis.

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The inductively coupled plasma offers an atom cell of higher temperature (relative of flame) and, under certain conditions, longer residence times. These effects should combine to promote complete matrix destruction and analyte atomization. Hence it may be possible using the inductively-coupled plasma, to achieve equivalent sensitivity for slurry and aqueous concentrations.

1.4 Objectives of this work

The aim of this study was to identify means of introducing and atomizing solid samples in an inductively coupled plasma and to develop these for the analysis of geological samples using simple aqueous calibration.

It has recently been demonstrated that torches (145) and nebulizers (146) can be designed and optimized by the simplex optimization routine (147), to enable introduction of aqueous slurries of finely ground material into the plasma. This approach has been applied with promising initial results to the determination of trace metals in coal slurries (148). Work has been directed to this approach to more refractory geological samples such as silicates. Kaolin slurries provide almost ideal examples of finely divided silicate materials obtainable with well defined particle size ranges. Several physical and chemical parameters are now known to affect the degree of atomization when nebulizing slurries into the plasma, i.e. three gas flows, power and height of observation. Clearly the velocity of the particles in the plasma and height of observation are crucial and because these are affected by several parameters simplex optimization is ideally suited to these studies. This work has concentrated on kaolin samples with a view to designing nebulizers for slurry nebulization, identifying optimal particle size ranges and plasma optimization. From previous

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studies (131,138) particle size is known to be a critical factor in determining atomization efficiency. Particular attention was given in this work to the investigation of the relationship between particle size and atomization efficiency, and the influence of the sample introduction parameters on the emission signal intensity and stability. As a suitable analytical method developed for major and trace elemental analysis of kaolin samples by slurry atomization, this approach was applied to a range of sample types, following preliminary grinding where necessary.

2. INSTRUMENTATION AND NEBULIZER EVALUATION

2.1 Introduction

In this study two different ICP instruments were used. Initially an in house designed system (Radyne/Jarrell-Ash) was used which was later updated by a more sophisticated sequential, computer controlled, fully integrated plasma spectrometer (Kontron S35 plasmakon, Kontron spectroanalytical, Eching, West Germany). A brief description of equipment for both systems is given below, together with a detailed study on the evaluation of nebulizer design used for this work.

2.2 Initial instrumentation

Figure 1 is a schematic diagram of the instrumentation.

The ICP torch, (Figure 3; see reference (145) for details of construction) was mounted concentrically in a three turn, water-cooled copper induction coil. The radio-frequency (RF) power was supplied to the coil by a 5 kW, 27 mHz free-running generator (Radyne R50P, Radyne, Workingham, England).

The gas was supplied to the torch by a purpose built 'gasbox'. Five rotameters in this box allowed direct switching of the plasma from 'start up' to 'running' conditions. All three gas flows (coolant, plasma and injector) were controlled from the gas-box allowing the optimum operating conditions to be selected.

The analyte was introduced into the plasma in the form of an aerosol, produced using a glass and plastic 'high-solids' nebulizer (Figure 4; see reference(146) for details of construction). The nebulizer was force-fed using a small peristaltic pump (60 r.p.m. 'Schuco mini

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pump mark IV', Schuco Scientific, Halliwick Court Place, London). This was necessary as this type of nebulizer has no natural uptake action. The nebulizer produced a fine mist of analyte solution droplets. The larger droplets produced were removed using a laboratoryconstructed double-pass spray chamber and the resulting aerosol was transported through the central injector tube of the torch into the plasma.

An inverted image of the plasma was projected 1:1 on to the 25 μ m. entrance slit of the monochromator using a quartz lens, 7.5 cm focal length. The spectroscopic emission lines of interest were isolated using a 0.5 m Ebert scanning monochromator (Jarrell Ash (Europe), Le Locle, Switzerland). The radiation was then focused <u>via</u> a 25 μ m exit slit into a photo-multiplier tube (Hamanatsu R106). The signal from the photomultiplier was amplified using a linear picoammeter (LM 10, Chelsea Instruments Ltd, London), and fed into a three-pen potentiometric chart recorder (Type MC 641-32, Watanabe Instrument Corporation, Japan).

2.3 Kontron instrument

A schematic diagram of the instrumentation is shown in Figure 2.

This instrument operates on a similar principle to the above instrumentation, however increasing computer sophistication in the field of instrument control has permitted important developments in ICP technology <u>e.g.</u> the introduction of scanning monochromator ICP systems, such as the Kontron system. An additional benefit is also the improvement in data handling.



The Kontron ICP torch (Figure 3b) based on the larger Greenfield design (149), consists of three interchangeable round quartz tubes fitted into an all PTFE base by a series of O-rings. It is mounted in a four turn water-cooled induction coil. The RF generator which supplies the power to the coil via a motor-driven automatic turning circuit, is crystal controlled and operates at a fixed frequency of 27.12 mHz. The maximum output of 3.5 kW permits operation of both argon and nitrogen cooled argon plasmas.

The ignition, by a high voltage spark from a telsa coil, is automatic, with output and gas-flow rate set to pre-selected values. After ignition the instrument resets to the running parameters selected by the user. The individual gas flow rates are controlled by massflow controllers and the flow rates are displayed on LED columns.

The sample was initially introduced into the plasma by the plastic and glass high solids nebulizer (Figure 4, reference (146)), used in the former system but this was later replaced by a more robust all PTFE Babington type nebulizer (P S Analytical, Westerham, Kent) (Figure 5).

The plasmakon S35 was purchased with a Meinhard nebulizer (TR-30-A3, J E Meinhard Associates, California), a concentric-pneumatic glass nebulizer and could be used in conjunction with a carrier gas humidifier for solutions with high salt content. However, this nebulizer was prone to blockages as is discussed in more detail later in this chapter.

A rapidly scanning Czerny-turner monochromator, with an optical resolution

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3a For Radyne System

3b Kontron torch

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Fig. 4 Glass and plastic high solids

nebulizer



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Figure 5(b)

Nebulizer/Spray Chamber Connector for Nebulizer No 2



of 0.015 nm, is used to isolate the selected wavelengths. The unique feature of this monochromator is the angle encoder. This is rigidly connected to a 2400 lines/mm holographic grating. The instantaneous grating position and the corresponding wavelength is established by the angle encoder. An optoelectronic counting system transmits the grating position to the computer. The actual grating position can be selected to an accuracy of 1 - tenthousandth of a degree, corresponding to 0.0015 nm. The angle encoder ensures precise and reproducible adjustment of the grating position without excessive software requirements. The 'housed-in' spectrometer system is temperature controlled at 37 ± 0.1 °C to minimize wavelength drift.

The computer controls the operations of the optical system. It operates the grating and hence wavelength of the monochromator, the voltage applied to the photomultiplier tube and the periscopic mirror arrangements of the imaging optics which can automatically select the viewing height in the plasma giving best signal to background ratio. The computer based on a Z80A microcomputer, receives the emission signal from the optical system and performs mathematical and statistical calculations to allow line calibration <u>etc</u>. Each step in an analysis can be followed on the visual display unit, including graphs of signal levels and individual results on the entire spectrum which provides the user with general information on the complexity of the sample. A printer-plotter is used for processing analytical protocols.

2.4 <u>Nebulizer development</u>

2.4.1 Introduction

Nebulizers are devices for introducing liquid samples into the ICP, in the form of a fine aerosol transferred by the injector gas flow.

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Nebulization devices for the introduction of liquid samples into the ICP have been reviewed by Barnes (150) and more recently Boumans (151) cited 39 references to a wide variety of nebulizers proposed for ICP-OES. The conventional concentric pneumatic nebulizers, made generally from metal, as used in AAS, are of limited use in ICP work because the high flow of gas required to operate them is too high for the optimum operating conditions of the plasma.

The two most commonly employed pneumatic nebulizers for ICP work are the glass concentric nebulizer (152) (Figure 6a) and the cross-flow nebulizer (79) (Figure 6b). The former, commonly named after the most successful manufacturer, Meinhard, is probably the most widely used ICP nebulizer of any type. Meinhard nebulizers are built with a variety of performance specifications (152) and operate at modest pressures of ca 30 p.s.ig with an uptake rate of 2 - 3 ml per minute. They consist of a narrow annulus ($\sim 10 - 35 \mu m$ gap), surrounding a narrow (~0.5 μ m) sample capillary. The high velocity flow of nebulizer gas produces reduced pressure at the capillary tip, drawing sample solution through the capillary, where it is shattered into a fine aerosol by the high velocity gas flow. Satisfactory precision is obtained and they can be used for most solutions except those which attack glass, e.g. HF. The cross flow nebulizer operates in a similar manner, the nebulizer gas flow in this case is at 90° to the sample uptake capillary. Reliable construction of a cross-flow nebulizer suitable for ICP-OES has proved difficult. Individual workers have had good results, but the mass-produced article of guaranteed specifications has until recently remained elusive.

Kniseley et al. (153) (Figure 6b) designed a nebulizer which had adjustable

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(c) Modified Cross-flow

capillaries for both gas flow and sample uptake (allowing the performance to be optimized. However the setting up of a cross flow nebulizer is extremely critical and long-term stability and replaceability are of major concern. This problem was overcome by two sets of workers Novak <u>et al</u>. (154) and Meddings <u>et al</u>. (155) (Figure 6c) who made fixed cross-flow nebulizers. In this modified design the capillary tubes are positioned so that a given solution uptake rate is obtained at the required gasflow and pressure. The tubes are then fixed together by a glass bar so that, once constructed, the nebulizer required no further adjustment. Cross-flow nebulizers of various designs, are now a popular alternative to the concentric nebulizers and many ICP manufacturers supply the cross-flow as a standard nebulizer.

The main disadvantage with the above mentioned nebulizers is that the sample solution has to pass through a narrow capillary (~0.5 mm i.d.), so that care has to be taken that sample solutions contain no small particles which can block the nebulizer. It has been found that solutions containing high salt content (5 - 10%), particularly with the concentric nebulizer, can cause build up of material at the capillary tip, impairing nebulizer performance and eventually causing a blockage. The deposition of analyte to solids in the concentric and too a lesser extent the cross-flow design nebulizers still seems to be a problem despite the availability of tip-washing devices and gas humidifiers. Gas humidifiers, however, increase the water loading in the plasma. Introducing water into the plasma brings the ICP close to local thermal equilibrium (see Chapter 1) and as a result loss in sensitivity of the analyte emission signal has been observed.

A recent study by Meinhard and Baginski (156) described some effects

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of high-solid matrices on the sample delivery system and the Meinhard concentric nebulizer during ICP emission analyses. Whilst Thompson <u>et al</u>. (157) reported on a modified concentric glass nebulizer with minimal dead volume for reduction of memory effects in inductively-coupled plasma spectometry.

Obviously these types of nebulizers are unsuitable for slurry nebulization. Their narrow sample orifices lead to one of the primary limitations of both devices for slurry nebulization, the ease with which they can be partially or totally blocked by the presence of particulates or fibres in the solution, let alone high concentration or large particle slurries e.g. greater than 1%.

Development and subsequent characterization of a unique nebulization principle by Babington (134) has advanced sample introduction techniques. The advantage of this nebulizer is that unlike concentric or crossflow nebulizers, the sample is no longer required to pass through a very narrow capillary and therefore the presence of particulates does not cause blockage. Instead the sample flows through a relatively broad tube (up to a few mm i.d.) and then forms a film. High velocity gas issues from a hole beneath the film and disrupts the sample stream allowing direct generation of high density, finely-dispersed aerosols from a variety of complex materials. Nebulizers based on this design are the most successful to date at nebulizing slurries. There is however, a danger of torch blockage when nebulizing high-solid solutions and slurries over a long period of time. This can be minimized by using a wide inner bore injector tube and is discussed in Chapter 5.

Using this type of nebulizer, in combination with a wide-slot burner. Fry and Denton (158,159) determined copper and zinc in whole blood, milk, urine and seawater using atomic absorption spectrometry. The characteristics of Fry and Denton's nebulizer (158) were evaluated with the carrier gas flow rates $(9 - 12 \ \text{min}^{-1})$ required for flame atomic absorption spectrometry. These flow rates are not consistant with the operational requirements of ICP $(0.5 - 31 \text{ min}^{-1})$, therefore design characteristics were then re-evaluated based upon these substantially different operating conditions (160). Also, as the sphere in their nebulizer was totally coated in liquid, the device was prone . to memory problems. This was alleviated in the v-groove approach which also promoted an even flow and conserved sample volume. The v-groove nebulizer, as shown in Figure 5a, is a derivative of the original design by Babington. The argon used for nebulization is discharged from a narrow orifice located in a 'v' groove which is cut along the face of the nebulizer body. The sample is allowed to trickle down the groove and a greater contact established between sample and gas results in more efficient nebulization. Suddendorf and Boyer (161) devised a high-solids nebulizer for the ICP, using the Babington principle with a v-groove (or slot)/orifice combination rather than the Babington sphere for analysis of biological samples. Their design consisted of a plexiglass base, gold plated stainless steel block unit, a v-groove and a small gas orifice, a sample feed tube, a shield and impactor rod. Sample flow rate was 5 ml min⁻¹ and the gas flow rate was compatible with ICP systems. Wolcott and Sobel (162) devised a similar nebulizer consisting of a PTFE base and glass nebulizer and capillary tube which replaced the metal components which were considered a potential source of contamination. The advantages of glass and metal nebulizers are that they are easily

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wettable but glass nebulizers are difficult to construct and a disadvantage of metal nebulizers is the potential of contamination. Therefore there has been a move to fluorocarbon polymer based nebulizer systems. Although a PTFE Babington nebulizer is poorly wettable, it is potentially easier to construct than one of glass, less likely to yield contamination than one of metal and more durable and corrosion resistant than one of either glass or metal construction. Plastic or PTFE Babington type nebulizers have been described by a number of workers (163,164,165).

However one of the main difficulties with devices described above is that they consist of separate components, all of which require alignment, particularly after cleaning and the components may suffer mechanical movement with respect to one another particularly where different materials are employed in the construction. One piece nebulizers would overcome this problem and have been reported by several workers (146,164). Walton and Gouter (164) recently described a slotted one piece design constructed from PTFE which has good corrosion resistance (including HF). A 2 mm channel or groove was cut in the face of the nebulizer as a flow guide and the face was rounded to prevent condensation being sucked back into the channel. Although these nebulizers are not widely used yet, they are very rapidly growing in popularity and they may ultimately prove to be the most suitable in the geological and slurry field.

Various other types of nebulizer, in particular the ultrasonic (166,167) and Frit nebulizer (168,169) have been reported. The ultrasonic nebulizer uses mechanical means for aerosol production. A piezoelectric device operating at radio frequency disperses the sample solution

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into fine droplets. Unlike pneumatically driven nebulizers, ultrasonic generation do not require nebulization gas. In addition there are no restrictive orifices to effect blockage. A carrier gas effectively transports the aerosol to the plasma discharge. Since the carrier gas flow rate is independent of nebulization mechanism it can be adjusted to very low flows, which result in longer aerosol residence times in the discharge, thereby increasing the sensitivity. The nebulization efficiency of the ultrasonic nebulizer is approximately compared to 2% usually obtained for the pneumatic nebulizers. 80% (29) At nebulization rates of $0.5 - 1 \text{ ml min}^{-1}$, the large amount of aerosol produced cool the plasma excessively, reducing the spectral sensitivity to a point such that detection limits may be improved only by a factor of two (166). In order to overcome this limitation, desolvation is used in conjunction with the ultrasonic nebulizer. However, desolvation often enhances chemical interference effects resulting from solute vaporization. Also ultrasonic nebulization is usually limited too low matrix samples, as the transfer rate of an interferent element will be increased by the same factor as that of the analyte and therefore may reduce sensitivity caused by matrix interference effects.

With the glass frit nebulizer (169) gas is passed through convoluted passages in a fine porosity glass frit as solution is pumped to the frit surface. The solution spreads over the frit surface to form a very thin sheet before being disrupted by the exiting gas. Nebulization gas flow rate may be adjusted, of which the rate at which the sample can be introduced is dependent. Using this combination leads to reduced droplet size (<1 μ m) greater transport efficiency (90%), and using low nebulization gas flow rates, lower residence times in the plasma but do however suffer from undesirable long wash-out times. Although

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both offer significant improvements in efficiency, they have not gained wide acceptance, mainly due to operational and reliability problems largely related to memory effects due to insufficient cleaning out times between samples and sample changeover and as yet none have been successfully developed as serious competitors for the types described above.

2.4.2 Evaluation of nebulizer systems for this work

Several nebulizers were designed in order to produce, pneumatically, fine aerosols from kaolin slurries for introduction into the ICP. The constraints being that the nebulizer must accept liquids with particulate content, and produce an aerosol of size <10 μ m (as larger particles are excluded by the associated nebulizer cloud chamber) (138) it was felt any nebulizers built on the Babington principle would meet these criteria.

The first nebulizer (No 1) (Reference 146) (Figure 4) was built from glass and plastic and included an impact bead. A 'high solids' nebulizer of similar design was machined from a single block of PTFE (No 2) (Figure 5a and b). The evaluation of the nebulizer systems were carried out in two stages. Firstly the transport efficiences (i.e., the ratio of sample delivered to the plasma to the ratio of sample uptake, per unit time) of these devices was measured. The PTFE fixed geometry (high solids nebulizer No 2) was compared with nebulizer No 1 and with a commercial Meinhard all glass concentric nebulizer (TR-30-A3) (Figure 6a).

Secondly, the nebulizer systems were then connected to the plasma and the signal to background ratios for

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each nebulizer, operated under identical conditions, were measured for 1.2 μg ml $^{-1}$ magnesium at 280.270 nm.

2.4.3 Experimental

The efficiency experiment was carried out by measuring the uptake rate of the nebulizer over a given time and by collecting the aerosol produced by the nebulizer/spray chamber combination. The outlet of the plasma torch tube was connected to dry silica in two 'u' tubes in series. The 'u' tubes were weighed beforehand and afterwards to determine the amount of water collected. The performance of each of the nebulizers was then compared by measuring the signal to background ratio (SBR) at the same plasma conditions for a 1.2 μ g ml⁻¹ magnesium solution. All nebulizers were pumped at 1.6 ml min⁻¹.

Plasma operating conditions: -

Injector Ar flow/1 min ⁻¹	1.9
Plasma Ar flow/l min	2.8
Coolant Ar flow/lmin	16.2
Net forward power/kW	1.8
Height/mm above load coil	24

*Forward power minus reflected power.

2.4.4 <u>Results and discussion</u>

The results of these experiments are summarized in Table 1.

It can be seen that nebulizer No 2 is more efficient in terms of fluid transport than nebulizer No 1, and the commercial all glass concentric nebulizer. However, no serious consideration was given to droplet size distribution in this part of the experiment.

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Table I '

Comparison of Nebulizers

Nebulizer Design	Efficiency (%)	SBR
Meinhard	1.9	50 - 51
*Babington No 1	1.4	67 - 67.5
**Babington No 2	2.2	30 ^a 50 ^b

* Babington No 1 See Figure 4.

** Babington No 2 See Figure 5a and b in this section. A series of nebulizers subscripted a - j based on design of Babington No 2, Figure 5a, have been evaluated. The SBR^a reported in the table was the result obtained from the first prototype used in the initial experiments. SBR^b denotes best performance nebulizer.
It can be seen from the SBR results obtained from the nebulizers that the best emission signals do not correlate to the order of best transport efficiencies suggesting that nebulizer No 2 produces an aerosol of larger droplets which are not atomized in the plasma, hence giving a poor SBR. The character of the aqueous aerosols produced by nebulizer No 1 and the all concentric nebulizer appeared on visual inspection to be finer and more uniform that that produced by nebulizer No 2. The good performance of nebulizer No 1 was probably due to the secondary impaction surface of the bead, shattering the larger droplets produced by nebulizer itself. However with slurry nebulization (as discussed in Chapter 5) for both nebulizers, with and without impact bead, no variation in particle distribution was observed.

Other techniques to measure efficiency have been suggested, but the choice of method is a controversial area(170). There have been arguments in the literature (171,172,173,174) for and against direct and indirect methods for the measurement of transport efficiency. Most authors now accept that different methods including direct filter methods, silica-gel trapping and indirect method such as waste collection, determine different quantities and the question is therefore what do we want to measure, not which method to use.

With direct methods, the aerosol itself is collected, whilst the indirect method collects the liquid going to waste from the system. With indirect methods, the fraction of analyte passing to the plasma (or flame) is calculated by taking the differences between the amount of analyte aspirated and that passing to waste. Although indirect methods have been most widely used (175) as they are simple to perform and require no specialized aerosol collection equipment, they are

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however prone to significant error, because of the sensitivity of the measurement to even very small recovery losses, particularly with ICP. These losses may occur in the spray chamber, on impactors or plasma torch and therefore because the lack of accurate comparable values this method makes evaluation of new aerosol generation and transport systems difficult. With the direct methods, different quantities are measured. Cascade impacters and membrane filters (172) collect solute, and are considered to have superior accuracy and precision to other techniques, whereas, the silica gel trapping method (173,174) collects solvent and is prone to inaccuracy and generally gives positive bias in its results. This method, as with the solute waste collection, rely for their accuracy on assumptions about the nature of solute and solvent transport processes. Water vapour collected at the torch arises mainly from two sources, namely, from evaporation of the aerosol which passes through the spray chamber and reaches the collection trap and from solvent evaporation from the chamber wall. Browner and Smith (174) suggested that water vapour from the liquid jet of the nebulizer as it is disrupted by the gas and from the air stream prior to loss on the chamber walls, also make a major contribution to the total water vapour loading and although are not directly related to aerosol transport properties, will register on the trap as if it were and hence values will give a positive bias. Although these techniques described above, determine different quantities of aerosol associated with transport efficiency, they do not however compare what is actually atomized in the plasma and therefore our experiments suggest that SBR measurement is a more practical criterion for nebulizer system evaluation and was therefore adopted for the rest of this work.

Several further prototypes with varied geometry, based on design of the PTFE Babington, have been evaluated to investigate the factors controlling nebulizer performance. Of the nebulizers considered the SBR values obtained varied from less than 1 (i.e. the nebulizer produced little or no aerosol) to a SBR of 50. The best performance nebulizer, with a SBR 50, had a gas office close to 0.2 mm (compared with 0.35 mm for the nebulizer which gave a SBR 30 in the previous experiments) and a more even flow of sample down the v groove. Other parameters controlling nebulizer performance were identified on the distances marked 'a' and 'b' on diagram 5a. Distance 'a' should be as short as possible to ensure that all the available gas pressure is used for nebulization. Pulsation effects are reduced if the gas orifice is placed near the sample entry i.e. short distance 'b', however, if the gas orifice is actually placed in the sample entry large droplets are produced. It appears necessary to form a film of solution in the 'v' groove over the gas orifice. The optimum distance for 'b' was found to be 1 + 0.5 mm. To summarize, the factors controlling nebulizer performance seemed to be dominated by the size of gas orifice, and the associated gas pressure drop within the nebulizer body and to a lesser extent depth and angle of the 'v' groove and the relative position of the two orifices.

One of the main disadvantages of the use of PTFE for the nebulizer construction is the hydrophobic nature of the surface presented to the sample aerosol. Some aerosol particles collect on the nosepiece of the nebulizer and on the walls and sides of spray chamber/ nebulizer connector. As these small particles do not wet the surfaces they eventually coalese into large droplets and fall down under gravity and are excluded by the spray chamber. They may also be sufficiently close to the nose-piece of the nebulizer to be re-nebulized causing

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fluctuations in the optical signal and thus cause poor reproducibility.

An advantage of the nebulizer being constructed from PTFE is that it is chemically inert and can be used for a variety of chemicals inducing HF and furthermore decreases wash out times between sample runs.

2.4.5 Conclusions

Our own design PTFE nebulizer demonstrated competitive performance with established nebulizers and additionally has the ability to handle samples containing high salt content and more importantly slurries, without blockage. The 'fixed capillary' construction also makes the nebulizer more robust than other commercially available nebulizers, is without the need of capillary alignment, easily machinable, and more importantly for commercial aspects, fabrication is simple and can be easily reproduced. 3. PRELIMINARY STUDIES OF THE ANALYSIS OF KAOLIN BY SLURRY ATOMIZATION

3.1 Introduction to kaolin

As the majority of the work in this thesis deals specifically with the analysis of kaolin (known as 'china clay' in the UK) it has been thought necessary to give some background to kaolin and its mineralogy, in this thesis, so interpretation of results can be considered to the full.

3.1.1 Structure and mineralogy

Of the minerals containing silicon, the four important layer clay minerals are as follows:

1. Kandite group (including kaolinite)

2. Illite group

3. Smectite group (including montmorillonite)

4. Vermiculite group

Kaolinite belongs to the kandite group and the essential features of the structures of kaolinite minerals were first described by Pauling (176).

The fundamental unit in the building of silicate minerals is the $\operatorname{SiO}_{\mu}^{-}$ tetrahedra in which the silicon atom (or more strictly, cation) is situated at the centre of a tetrahedron whose corners are occupied by four oxygen atoms (Fig 7a). A sheet structure is formed when the $\operatorname{SiO}_{\mu}^{-}$ tetrahedra are linked by three of their corners and extend indefinitely in two-dimensional 'sheet' (Fig 7b). Aluminium and hydroxyl ions similarly form an octahedra (Fig 7c). The composite layers built from components with these tetrahedrally and octahedrally coordinated cations form the basic units. Classification of the

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silicates is based on the different ways in which the SiO_4 tetrahedra occur, either separately or linked together and by the actual atom composing the layers. Chemical composition may vary according to the extent of replacement of Si, Al and Mg by other cations, the nature and quantity of interlayer cations and the water content.

Kaolinite is formed by a series of sheets containing the octahedral and one tetrahedral layer; in the linkage certain of the hydroxyl groups in the Al-OH octahedra are replaced by oxygen from the tetrahedral layer and the layers join, as in Figure 8 and then stacked one on top of the other in the kaolinite crystal with the inner layers always on the same side.

The empirical formula for kaolinite is $Al_4Si_4O_{10}(OH)_8$. Other members of the kaolinite group are dickite and nacrite (two rarer polymorphs which yield well formed crystals) and halloysite, a hydrated form of kaolinite with a single layer of water molecules between its structural sheets.

The chemical composition of kaolinite itself is subject to little variation. Small amounts of various ions may substitute in the structure, but because of the fine-grained nature of clays it is difficult to be certain that impurities have been eliminated, so that the limits of substitution cannot easily be defined. Of the minor constituents, titanium, iron and magnesium probably substitute for aluminium while calcium, sodium and potassium are present either as absorbed (exchange) cations, or in impurities of other clay minerals such as illite or montmorillonite. The cation exchange capacity of the kaolinite minerals is quite low and usually amounts to 1 to 10 meq per 100 grams. Since the basal spacing of kaolinites

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Silicon-oxygen tetrahedra (7a) join to form a tetrahedral layer (7b). Aluminium hydroxyl octohedral (7c), by sharing oxygens with the tetrahedral layer form an octahedral layer (7d). These shared oxygens serve to unite the two layers, giving the unit layer of kaolinite (see Figure 8).



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does not leave room for interlayer cations, all the charge-compensating cations must be absorbed on the exterior surfaces of the stack of unit layers representing a particle.

The size, shape and nature of the surfaces of the particles are important factors in the distinction between clay-minerals and non-clay mineral components of natural materials. Particle size in particular is a significant factor, and particle sizes in the micron and sub micron range are commonly encountered in clay minerals; it is possible for the impurities to be as fine as this and for the clay mineral itself to be as coarse at 1 mm, but these are the exceptions rather than the rule and it can be said that impurities are generally coarser than the clay mineral. The size and shape of kaolin is discussed in more detail in subsequent chapters.

3.1.2 Diagenesis of kaolin

Kaolin mainly results <u>in situ</u> from the alteration of the feldspars of granites and other silicates.(Granite is a loose term covering a type of acidic rock composed of several distant mineral species, such as quartz, mica and feldspar). This alteration may be caused by two processes a) the ordinary weathering of the feldspar, first into a clay-like mineral allied to kaolinite, but with less water, and then into kaolin, or b) by hydrothermal action on the feldspar. The former produces secondary deposits as the clay has been transported by surface water and deposited elsewhere. The latter, produces primary deposits, in which the clay is located in its original place of formation. The second mode of origin has been held to account for the Cornish occurrences, although the reaction is not fully understood.

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In the Cornish granites the reaction was probably proceeded, at high temperatures and under great pressures, though the agency of water containing free acids and the solution having been forced up from below, penetrating the granite through joints. As the feldspar broke down, the granite mass became porous and more powdery thus yielding china clay rock. This theory is that of Exley (177) who also holds the view that the decomposition of feldspar was a two stage process, with montmorillonite first being formed as an intermediate.

The main constituent of commercial china clay is kaolinite although impurities, such as mica, quartz tourmaline and feldspar, at trace levels may be present. The extraction of clay for commercial use and the analysis of impurities are discussed in Chapter 7 (monitoring of abrasives).

3.1.3 The uses of kaolin

The main uses of china clays are in the paper and ceramics industries. In the paper industry, clays are used both for paper filling and coating because it improves the paper gloss, smoothness and opacity, and hence improves printability. The improvement in gloss and smoothness

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are very marked indeed in coated paper. For paper filling, a comparatively coarse grade is used, whose content of particles finer than 2 μ m is unlikely to be above 40% and may well be very much less, whereas coating requires a much finer grade of clay, with a 2 μ m content of at least 75%. Equally fine clays are generally used for ceramics. Kaolin is also used as a filler or extender for rubber and paints etc.

General aspects of clay and its mineralogy have been well documented by a numbr of authors, including Deer <u>et al</u>. (178), Grimm (179), Grimshaw(180), and recently by Wilson:(181).

3.2 Feasibility of study

The possibility of introducing kaolin slurries into an ICP for the determination of major elements was first investigated at Plymouth Polytechnic by Ebdon and Ward (182) in a short communication with ECLP (St Austell, Cornwall). Plasma conditions used for this work were those reported previously by Wilkinson (148) for the analysis of coal slurries. The initial results were sufficiently encouraging to suggest a more detailed investigation <u>e.g.</u> into plasma conditions, particle size and sample introduction design. It was felt that improvements in slurry atomization efficiencies could be obtained by re-optimizing the plasma for kaolin slurries and to identify, if possible, those conditions which would enable standardization of kaolin slurries by aqueous standards for a range of major and trace elements.

3.3 Application of simplex optimization

To obtain a true optimum in the ICP it is obviously necessary to optimize all the operating parameters, these are: the power in the

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plasma, observation height above the load coil, the outer, intermediate and injector gas flows, but as these parameters interact with each other, they must be optimized together. The modified simplex procedure (183) is an elegant and well proven method for optimizing the ICP (147). (A simplex is a geometric figure defined by a number of points equal to the number of parameters considered in the optimization plus one i.e. one more than the number of dimensions of the factor space). The simplest criterion of merit for ICP optimization is the signal to background ratio, SBR. Greenfield and Burns (184) have shown this to be a figure of intrinsic merit independent of the spectrometer. Other criteria of merit, e.g. signal to noise ratio, SBR/% interference are also helpful. The simplex method was first devised by Spendly et al. (185). In this original method the step size is fixed. If the initial step size is too small compared to the factor space the optimum will be approached slowly; if it is too large, the optimum is determined with insufficient precision. In the latter instance a new simplex with a smaller step size can be started at the provisional optimum. This was the method used by Long (186). However, a modified simplex method in which the step size is variable throughout the whole procedure offers a more elegant, and efficient, solution. The principal disadvantage is that the simplicity of the calculations in the original simplex method no longer exist, this can however, be outweighed by the reduction in the number of steps required to reach the optimum. Nelder and Mead (183) formulated a method for introducing variable step size in the simplex procedure. This modified simplex method also avoids the identification of false optima. More recently there have been further modifications to the variable step size simplex in an attempt to improve its efficiency (187,188) but increases in efficiency are not always apparent and any gains may be outweighed by complicated

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time-consuming calculations. The choice of the initial step-size is critical. It is desirable to start with a large simplex and collapse in upon the optimum. Yarbro and Deming (189) have described a matrix for a 5 dimensional system which can be used to design the initial simplex. The modified simplex procedure is usually terminated when successive simplexes give no significant improvement in SBR. The centroid of the final simplex is then taken as the optimum, when the optimum is obtained this may be checked using univariate searches. Four parameters are held constant at the optimum and the fifth varied. Clearly it should peak at the previously optimized position. The univariate search and convergence allows the investigation of the influence of parameters on plasma optimization.

In this study the plasma operating conditions were optimized for:

- (i) magnesium SBR in kaolin slurries using the initial instrumentation, this enabled a study of slurry analysis for determining major and minor elements in clays;
- (ii) magnesium SBR in aqueous solution using the Kontron instrumentation at the magnesium 280.270 nm ion line;
- (iii) magnesium SBR in kaolin slurries using the Kontron instrumentation, this enabled a study of slurry analysis for determining minor and trace levels in clays.

The variable step-size simplex method, as previously applied to the inductively-coupled plasma by Ebdon <u>et al</u>. (147), was used to optimize plasma performance.

The procedure was initially performed by hand, but was a rather laborious and tedious task. This was later replaced by a software package written

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for the Apple computer to perform all the numerous and logical processes of the simplex procedure.

Kaolin samples supplied by ECLP (St Austell, Cornwall) were used to prepare slurries and attempts were made to determine selected major and trace metals by directly atomizing these slurries in an inductively coupled plasma.

3.4 Slurry analysis for major and minor elements

3.4.1 Introduction

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The modified simplex procedure was used to indentify the optimum conditions for slurry analysis performed on the initial instrumentation. Clay samples were characterized by referee methods and then analysed by slurry atomization to evaluate the procedure. Particle size data was also obtained on the kaolin samples.

3.4.2 Analysis of a bulk kaolin sample

3.4.2.1 Introduction

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A sample of kaolin light BP (the Boots Co Ltd, Nottingham, England) was mixed, dried and analysed for several elements both by ourselves and ECLP, this sample referred to elsewhere as 'BP kaolin' being used as a bulk sample for the preliminary studies described above.

This clay was analysed by ECLP, using XRF and chemical analysis and by ourselves on solution samples obtained following a lithium metaborate fusion procedure, by using atomic absorption spectrometry (AAS) using a nitrous oxide/acetylene flame and ICP-OES.

3.4.2.2 Fusions

3.4.2.2.1 Experimental

Into a platimum crucible kaolin powder (0.5g) was weighed accurately and LiBO₂ (2.0g) was added. The powders were mixed carefully with a thin platinum rod and fused on a meker burner for 30 min, while the fused mixture was gently swirled. The crucible was allowed to cool to room temperature and then placed into a 250 ml polythene beaker containing 200 ml of cold 5% vv⁻¹ nitric acid. The crucible was wholly immersed in the dilute nitric acid, and magnetic stirring was commenced without delay. Dissolution of the bead took 1-2 hr, and the solution was then diluted to 250 ml.

This method, with various modifications has been used extensively to prepare silicate solutions since it was introduced by Suhr and Ingamells (190) and Ingamells (191,192). The advantages of using a lithium metaborate fusion for major and minor constituents in silicate rocks instead of acid attack have been discussed by a number of workers including Verbeek <u>et al</u>. (11). Advantages are that: (a) it is faster; (b) it readily dissolves minor refractory minerals which are not adequately attacked by hydrofluoric acid mixtures (191); (c) it needs no special equipment such as pressure vessels; and (d) it provides a clear aqueous solution suitable for a variety of analytical prcedures.

3.4.2.2.2 Instrumentation and analytical procedure

The analytical system used in this study was the initial instrument, a Radyne source unit and 1/2 m Ebert monochromator (details discussed in Chapter 2, section 2).

The instrument's parameters are summarized in Table II.

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Parameter

Injector gas flow/1 min ⁻¹	0.37
Plasma gas flow/l min ⁻¹	12.0
Coolant gas flow/1 min ⁻¹	5.0
Power /kW	0.54
Height of observation/mm	21

Kaolin solutions were also analysed for the major elements using an atomic absorption/flame emission spectrometer (IL 151, Instrumentation Laboratories Inc, Lexington, Massachusetts, USA).

3.4.2.2.3 Standard solutions

For the elemental analysis of the kaolin fusion, 3 multielement standards in 5% v/v nitric acid were used. Single-element stock-solutions (1000 μ g/ml) which originated from either high purity metals or salts were used for the preparation of the multi-element standard solutions.

3.4.2.2.4 Results of referee analysis and discussion

A comparison of results is given in table III.

	Table III	I Ma	jor and u	minor e	lements	(% w/w)	
Technique	• Si0 ₂	A12 ⁰ 3	^{Fe} 2 ⁰ 3	Ti0 ₂	Ca0	MgO	к ₂ 0	Na ₂ 0
XRF	47.5	37.9	0.58	0.03	[.] 0.05	0.19	1.2	0.1
Chemical Analysis	46.6	37.2	0.69	0.10	0.08	0.12	1.23	0.18
AAS	48.2	39.0	0.80 ¹	0.03	0.05	0.19	1.5 ²	0.28 ^{1,2}
ICP-OES	48.0	39.0	0.64	0.03	0.08	0.19	N.D.	0.27 ¹

¹contamination of sample suspected

²flame atomic emission spectrometry result

There is reasonable agreement between the results obtained using the different techniques. The observed spread of results is very small, although AAS and ICP-OES both report a high result for Na_2^{0} . This discrepancy may be due to the fact that contamination of the fusion sample was suspected.

3.4.3 Direct kaolin slurry analysis without sample pretreatment

3.4.3.1 Optimization of plasma operating conditions for slurry atomization

With this instrument 5 plasma operating parameters, namely radiofrequency power, height of observation, coolant, plasma and nebulizer gas flow rates have found to affect the analytical performance. Optimization of plasma operating procedure was used in attempt to identify those conditions in which magnesium in a kaolin slurry might by atomized with the same efficiency as in an aqueous solution (magnesium was chosen as a representative element). This would enable aqueous solutions to be used to calibrate slurry atomization. The criterion of merit for the optimization was chosen to maximise the ratio of the Mg signal in the slurry to the Mg signal in an aqueous solution. While workers (147) have had considerable success in optimizing plasma for signal to background ratio (and has been used subsequently for simplex work in this study), it must be acknowledged that there was no theoretical justification to suggest a suitable response surface for the ratio chosen. While the simplex procedure moved rapidly into a region where slurry atomization appeared to be 47 to 52% efficient compared to aqueous solutions, it did not identify a clearly defined optimum.

The simplex procedure was terminated when no further improvements in the ratio were obtained. The conditions are shown in Table IV

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below.

Table IV

Parameter	Optimal Range	<u>Centroid</u>
Coolant gas/l min ⁻¹	8 - 11.7	9.4
Plasma gas/ 1 min ⁻¹	9.7 - 12.9	11.2
Nebulizer gas/l min ⁻¹	0.1	0.4*
Power in plasma/kW	0.63 - 0.88	0.73
Height/mm	37 - 35	36

For Mg (II) 280.2 nm line

*not centroid figure, but was used as 0.11 min⁻¹ was impractical for analysis as signal was too small.

A univariate search, in which four of the five parameters were held constant at their optimum values and the fifth varied as the ratio of the Mg signal in the slurry to the Mg signal in an aqueous solution was measured, was used to investigate the response surface about the centroid. The univariate search results in Figures 9,10,11, 12 and 13 for coolant, plasma, injector gases, power and viewing height respectively, show that the ratio of slurry to aqueous atomization efficiently remains constant over large volumes of factor space. The shaded area on each graph correspond to the region identified as optimum range by the simplex procedure. Both the solution and slurry exhibited similar trends in emission signal. Of the five parameters studied, power, viewing height and injector gas flow rates are known to play a decisive role in determining the analyte emission signal (147). For the power variation study (Figure 12), element emission intensity for both slurry and solution increased with increasing power. Increase in power results in a rise in plasma

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Figure 10



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Figure 11







Power (kW)

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temperature and volume, and a corresponding rise in plasma background. The increase in signals observed can be attributed to the longer residence times available for the analyte in the plasma as a result of increased plasma volume, thus allowing a longer time for excitation to occur. For the viewing height univariate study (Figure 13) slurry and solution signals decreased with increase in height above the normal analytical zone (NAZ), 15 - 30 mm above the load coil, as expected. At positions near the coil (observation region approximately 0 - 10 mm above the coil), the plasma temperature is high and the argon continuum background is intense. This region is not usually favourable for observing analyte emission on account not only of the background but also because the relatively short residence time is insufficient to vaporize and excite the analyte. On moving up the plasma the temperature gradually decreases and as a result, together with the presence of molecular interferences at the plasma/air interface, observation zones high in the plasma e.g. 40 - 60 mm are also not usually favoured.

Of the five parameters investigated, the only ratio (i.e. signal in slurry to the signal in aqueous solution) increase observed was at very low injector gas flow rates (Figure 11), where little signal was observed for both slurry and solution, which is impractical for real analysis but this seems to help slurry atomization. The poor analytical performance obtained at low carrier gas flow rates was due to insufficient aerosol droplet velocity to penetrate the plasma and instead the droplets formed around the outer regions of the plasma.

As the simplex procedure failed to find the optimum conditions for slurry atomization using the slurry/solution signal ratio as the criterion of merit, it was decided at this point to take SBR as the criterion

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of merit for subsequent applications of the simplex procedure.

3.4.3.2 Direct kaolin slurry analysis

(a) 'BP Kaolin'

Total metal levels (as for the fusion samples) were determined in the 'BP Kaolin' by ICP-OES using direct slurry nebulization. The 'BP Kaolin' was made up to a 3% w/v slurry and a magnetic stirrer was used to reagitate the sample prior to and during pumping. The sample was pumped via a small peristaltic pump (at a rate of 1.5 ml/min^{-1}) so as to flow down the slit of the plastic and glass 'Babington type' nebulizer (see Chapter 2, Figure 4). The pumped slurry was nebulized pneumatically by a flow of argon issuing from a pin-hole. The sample mist travelled through a double-pass cloud chamber before injection into the centre of the plasma. The plasma operating conditions were the centroid conditions shown in Table IV.

The high aluminium and silicon content entering the plasma caused considerable elevation of spectral background in certain regions through ion recombination effects. Therefore spectral lines were scanned by recording the emission spectra continuously across a few nanometers either side of the analyte line, using a chart recorder and the instrument wavelength scan at 2 nm min⁻¹ performed.Scanning also helped in the identification of any spectral interferences. The following wavelengths were selected as giving best signal to background ratios, consistant with linearity of calibration over the concentration range of interest and freedom from spectral line interferences by other components of the sample.

Element	Wavelength/nm	AtomI/Ion II lines
Silicon	288.1	I
Aluminium	309.3	I
Iron	371.9	I
Magnesium	280.27	II
Sodium	589.56	I

3.4.3.2.1 Results and discussion

The results in Table V compare the direct 'BP Kaolin' slurry analysis without sample pretreatment with the XRF figures reported by ECLP for the specified components. Aqueous standards were used for the slurry analysis.

Table V	Major and minor elements results i	for 'BP Kaolin'
Component	'BP Kaolin' slurry (% w/w)	'BP Kaolin' XRF(%w/w)
Si0 ₂	22.7	47.5
A1203	20.3	37.9
Fe203	0.45	0.64
MgO	0.093	0.19
Na ₂ 0	0.14	0.18

The results were disappointing. If all the discrepancy was attributed to atomization efficiency, this appeared to be 48 - 78% compared to the aqueous fusion solutions obtained previously in the 'BP Kaolin', using ICP-OES and confirmed by ECLP. Sodium results are relatively high, probably due to contamination.

(b) ECLP Kaolin samples 1 - 8Kaolin samples 1 - 8, from various sources and of varying particle

sizes, together with XRF analysis figures were supplied by ECLP. The same experimental conditions as those used for the 'BP Kaolin' were employed for the ECLP samples. These samples were similarly made up to 3% w/v slurries and analysed directly by ICP-OES without sample pretreatment.

Particle size distributions were also determined on the kaolin samples using a coulter counter (model TA II multi-channel particle counter, Coulter Electronics, Northwell Drive, Luton, Beds.). Proprietory coulter electrolyte and dispersant were used to suspend the samples.

The particle size distribution of the batch of kaolin samples Nos 1 - 8 supplied by ECLP is shown in Figures 14 - 21.

A direct correlation between the figures obtained by direct slurry atomization and those supplied by ECLP are shown in Figures 22,23,25,27 and 29 (see Table VI). The lines drawn on the graphs were calculated from linear regression analyses and the correlation co-efficients are given.

The correlation co-efficient for silicon, Figure 22, was the poorest, as expected, as the levels of this element and relatively constant. The importance of particle size in slurry atomization is however emphasized. Similar arguments as to the poor applicability of linear regression analysis apply to aluminium (Figure 23). If the results for individual elements are ratioed to those obtained for silicon the situation is much improved, presumably because of the compensation for varying atomization efficiencies arising from particle size effects. Thus, while the results in Figure 25,27,29 for Fe, Mg and Na respectively

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show poor correlation, the corresponding graphs Figures 26,28 and 30 where the silicon ratio has been used show much improved correlations. The graph in Figure 28 of Mg levels is particularly encouraging with a good spread of points and a correlation coefficient of 0.74.

The results for Sample 2 have been omitted from these graphs, as it was clearly in appearance and coarse nature, different to the other samples, giving extremely low results. From preliminary studies it has been found that slurry particles should preferably be less than 10 μ m in size (138) and the particle greater than 25 μ m in size, of which sample 2 greater consists (see Figure 15) contribute very little to the observed atomic emission. Thus, there is a definite relationship between particle size and atomization and therefore there is clearly a need to control particle size. As particle size is so critical in slurry atomization it is discussed further in Chapter 5. The possibility of adjusting for unequal atomization efficiences by using a correction factor based on relative silicon appears promising.

Table VII shows the numerical results achieved when this approach was used. The aluminium values now show considerable positive errors, as frequently do the iron figures. Iron is known to preferentially occur in the smaller particles and hence it is likely to have a higher atomization efficiency. Interestingly iron does show a better correlation when aluminium figures are used for the normalization - see Table VIII.

Unfortunately the figures for sodium have to be larger discounted because of contamination problems. The figures for magnesium as shown in Table VII give considerable encouragement. In no cases, apart

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Figure 22 Correlation of %w/w results silicon by slurry atomization ICP-OES with ECLP silicon figures

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Figure 24

CORRELATION OF & RESULTS; RATIO OF ALUMINIUM TO SILICON BY

SLURRY ATOMIZATION ICP-OES WITH ECLP ALUMINIUM TO SILICON FIGURES





% Fe₂O₃ ECLP

- 88

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Figure 26



% Fe₂0₃/Si0₂ ECLP

Figure 27

CORRELATION OF & RESULTS, MAGNESIUM BY SLURRY ATOMIZATION ICP-OES WITH ECLP MAGNESIUM FIGURES



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- 90 -

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Figure 28

CORRELATION OF & RESULTS, RATIO OF MAGNESIUM TO SILICON BY SLURRY ATOMIZATION ICP-OES WITH ECLP MAGNESIUM TO SILICON FIGURES



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CORRELATION OF & RESULTS RATIO OF SODIUM TO SILICON BY SLURRY

ATOMIZATION ICP-OES, WITH ECLP SODIUM TO SILICON FIGURES



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Sample	sio ₂ 1	sio ₂ 2	A12031	A12032	Fe203	Fe203	MgO ¹	MgO ²	Na201	Na202
1	49.5	20.0	35.5	20.0	0.56	0.28	0.28	0.098	0.09	0.114
2	49.3	0.2	34.1	6.7	1.66	0.03	0.28	0.007	0.16	0.015
3.	47.9	7.3	36.5	12:2	0.95	0.23	0.21	0.026	0.09	0.07
4	51.0	8.7	32.9	12.7	0.79	0.14	0.31	0.041	0.13	0.048
5	. 47.4	8.0	37.5	13.7	0.48	0.10	0.13	0.027	0.07	0.028
6	45.7	16.0	38.2	20.2	0.32	0.33	0.09	0.03	0.08	0.15
7	47.1	28.7	38.0	25.0	0.45	0.43	0.14	0.07	0.07	0.062
8	47.3	14.0	36.9	15.7	0.84	0.34	0.32	0.095	0.04	0.054

COMPARISON OF ECLP RESULTS OBTAINED BY VARIOUS METHODS WITH RESULTS OBTAINED BY SLURRY ATOMIZATION

TABLE VI

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LECLP Results by various methods in % w/w

Slurry results in % w/w

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			8 w/w		
SAMPLE		A1203	^{Fe} 2 ^O 3	MgO	Na20
1	a b	35.5 49.5	0.56 0.69	0.28 0.24	0.09
3	a	36.5	0.95	0.21	0.09
	b	80.0	1.51	0.17	0.46
4	a	32.9	0.79	0.31	0.13
	b	74.4	0.82	0.24	0.28
5	a	37.5	0.48	0.13	0.07
	b	81.2	0.59	0.16	0.17
6	a	38.2	0.32	0.09	0.08
	b	57.7.	0.94	0.09	0.43
7	a	38.0	0.45	0.14	0.07
	b	41	0.71	0.12	0.10
8	a b	36.9 53.1	0.84 1.15	0.32 0.32	0.04
BP Kaolin	a	37.9 ⁺ 0.9	0.64 ⁺ 0.06	0.19 [±] 0.04	0.18 ⁺ 0.09
	b	42.5	0.94	0.19	0.29

TABLE VII

COMPARISON OF ECLP ANALYSES FOR ALUMINIUM, IRON, MAGNESIUM AND SODIUM AND SLURRY ATOMIZATION ANALYSES USING NORMALIZATION BASED UPON THE RATIO OF SILICON FIGURES

a ECLP results by various methods

b Slurry atomization results normalized

TABLE VIII

COMPARI	ISON	OF	ECLP	ANALYSES	FOR	SILICON,	IRON,	MAGNES	IUM A	ND S	ODIUM	AND
SLURRY	ATO	41Z2	ATION	ANALYSES	USI	NG NORMAL	IZATION	BASED	UPON	THE	RATIC	OF
ALUMINI	LUM I	FIG	JRES									

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	€ ₩/₩									
Sample		SiO ₂	Fe203	MgO	Na20					
1	a	49.5	0.56	0.28	0.09					
	b	35.5	0.50	0.17	0.20					
3	a	47.9	0.95	0.21	0.09					
	b	21.8	0.69	0.078	0.21					
4	a	51.0	0.79	0.31	0.13					
	b	22.5	0.36	0.11	0.12					
5	a	47.4	0.48	0.13	0.07					
	Þ	21.9	0.27	0.07	0.077					
6	a	45.7	0.32 .	0.09	0.08					
	b	30.2	0.62	0.57	0.28					
7	a	47.1	0.45	0.14	0.07					
	b	43.6	0.65	0.11	0.09					
8	a	47.3	0.84	0.32	0.04					
	b	32.9	0.80	0.22	0.13					
BP Kaolin	a	47.5 ⁺ 0.9	0.64 ⁺ 0.06	0.19 ⁺ 0.04	0.18 ⁺ 0.09					
	b	42.4	0.84	0.17	0.26					

a ECLP results by various methods

b Slurry atomization results normalized.

from the already eliminated sample 2, is the difference of the Mg0% by normalized (to SiO₂) slurry atomization and the ECLP figure greater than the spread of results obtained by established methods for 'BP Kaolin' reported in Table III. In three cases, sample 6,8 and 'BP Kaolin' the results are identical, only in the case of sample 4 is the difference likely to be statistically significant.

From preliminary studies it has been seen that the capillary necked tip injector tubes (Figure 31b, used in this work) are unsuitable for slurry introduction to the plasma. Solid materials tended to collect where the injector tube necks down to the capillary and this deposition was especially severe when high solid solution such as kaolin slurries were continually nebulized. As the construction was near the top of the injector tube, the radiation from the plasma tended to bake the deposits, affecting the performance of the injector. The jet injector tube (sometimes known as the taper tip injector) (Figure 31a) was also investigated for the introduction of slurries to the plasma. However this type of tube is prone to ablation, caused by progressive devitrification, and as a result it gradually changed the performance of the torch. The jet injector also produced a cone shaped sample, which did not penetrate through the centre of the plasma. Since the base of the injector tip must be small to allow the injector gas to puncture the plasma, the straight capillary injector (Figure 31c) seems to be the most promising for slurry introduction to the plasma, and a 2.2 mm i.d. bore tube was adopted for the trace analysis work. Evaluation of various variations of the 'straight capillary' injector tubes have been discussed in Chapter 5.

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INJECTOR TUBE DESIGN



Three variants of injector tube design: (a) with a jet injector tip; (b) with a capillary necked injector tip; (c) with a 'straight capillary' injector tube.

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3.5 Slurry analysis for trace elements

3.5.1 Introduction

The modified simplex procedure was used to identify the optimum conditions for slurry analysis performed on the Kontron instrumentation. This enabled trace element analysis of solid kaolin samples by direct slurry atomization. Both digests and kaolin solid samples were supplied by ECLP. The samples were digested by the HF/perchloric procedure described in Chapter 5. The HF was added to remove the silica as the volatile silicon tetraflouride and the remaining residue was digested by perchloric acid and extracted using HC1 (see section 5.6.2.1.1).

3.5.2 Digest samples

3.5.2.1 Experimental

Plasma operating conditions were those identified as optimal for aqueous solutions at the Mg (II) 280.270 nm line by the variable step-size simplex procedure. With this instrument, the 5 plasma operating parameters reported before, with the addition of peristaltic pump speed were optimized for the signal to background ratio as the criterion of merit. The results are presented in Table IX. The univariate searches are presented graphically in Figures 32,33,34,35,36 and 37, for coolant, plasma, injector gas flow-rates, power, viewing height and sample uptake respectively. Optimum values were successfully identified for all the operational parameters within the normal range of instrumental settings. The shaded area on each graph corresponds to the region identified as optimum by the simplex procedure.

In the sample uptake variation study (Figure 37), no gain in SBR was observed above 1 ml min⁻¹. However, the pump rate was found to effect the noise of the analytical signal due to pulsation effects of the

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Figure 32





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pump and as a result was omitted from further simplex optimization procedures. Instead, the best results were achieved by using a finebore uptake capillary tube (0.5 mm i.d.) with a high pump speed in order to minimize pulsation effects due to the separate action of each pump rollers to give an uptake rate of 1 - 1.5 ml min⁻¹.

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Table IX

Optimal solution	conditions for	Mg (II)	<u>280.27 nm line</u>
Parameter	Optimal range		Centroid
Coolant gas/1 min ⁻¹	15.1 - 17.6		16.2
Plasma gas/l min ⁻¹	2.5 - 3.3		2.8
Injector gas/l min ⁻¹	1.7 - 2.2		1.9
*net forward power/kW	1.6 - 2.1		1.8
Height/mm above load coil	23 - 25.4		24
Sample uptake/ml min $^{-1}$	1.26- 1.4		1.3

*incident-forward power minus reflected power

3.5.2.2 <u>Wavelength selection</u>

The following wavelengths lines in Table X were selected as giving the best signal to background ratio, consistent with linearity of calibration over the concentration range of interest and freedom from spectral line interferences by other components in the samples. The spectral lines were scanned and automatic correction of background performed using the Kontron S 35 background correction procedure, written into the software. In this particular procedure the element line is carried and the background wavelengths at either side of the peak are defined by the operator. The spectrometer locks onto the defined lines and the computer automatically locates and holds these

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exact grating positions for integration. The background intensity value is calculated as the mean of the background signal either side of the peak position. The computer calculates the concentration from the net intensity (peak intensity - background intensity) via a calibration curve.

<u>Table X</u>

	Wavelength selecti	on for trace elements	
Element	Wavelength/nm	Atom I/Ion II line	* <u>Sensitivity</u>
		·	ranking
Cd	228.802	I	· 2
Cu	324.754	I	1
Mn	260.569	II	. 3
РЪ	216.999	I	2
Zn	206.200	II	3
Cr a	261.710	II	3
Cr b	205.552	II	1
Ni	231.604	II	3

*Ranking of ICP line sensitivity as published by Winge, Peterson and Fassel (193).

3.5.2.3 <u>Results and discussion</u>

The results in Table XI compare the ICP-OES results for the digest samples with the AAS figures reported by ECLP for the specified components.

The results were encouraging. Agreement with the AAS results was good for elements, Cu, \cdot Mn, Zn and Ni. The agreement for Cd and Pb

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Clay type		Cđ	Cu	Mn	РЪ	Zn	Cr	Ni
S	a	0.40	16	17	16	20	13	3.0 ·
	b	1.0±0.1	20	17	<2.5	21	8±1	3.2
с	a	O.24	40	64	20	33	2	3.0
	b	4.9±0.5	43	50±1	<2.5	30	· 13±1	3.7
D	а	0.05	46	-	23	35	14	3.0
	b	<0.1	46	91±2	<2.5	36	3	3.0
SP	a a	<0.01	28	100	6	33	10	2.0
	b	<0.1	32	121±1 .	<2.5	30	4	1.0
	a	0.21	27	25	44.5	42	5 94	30.0
Baliciay .	d	<0.1	28	27	<2.5	41±1	195±8(i) 188 (ii)	31.8

TABLE XI Digest samples: Comparison of Results in µg/g

a ECLP results by Atomic Absorption spectrometry

Cr (i) 267.71 ion line

b Results by ICP-OES

(ii) 205.552 ion line

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was not so good, ICP-OES generally gave lower Pb results than AAS whereas the results for Cd were generally higher by ICP-OES. Neither Cd nor Pb are elements for which ICP-OES is particularly sensitive and in each case spectral interferences in these samples forced the use of lines other than the most sensitive. Most notably levels for Pb and Cd were below the limit of detection for this matrix for several samples. The comparison of results for chromium was more puzzling, the analysis was repeated at an alternative line, similar results were obtained bringing into question the AAS results.

3.5.3 <u>Direct kaolin slurry analysis without sample preparation</u> Solid kaolin samples were obtained from the same batch of samples used in section 3.4 for the digests. The results obtained by direct slurry analysis without pretreatment was compared with the AAS figures

3.5.3.1 Optimization of plasma operating conditions for slurry atomization

reported by ECLP and ICP-OES for the equivalent digests.

The plasma was optimized for kaolin slurry nebulization using the modified simplex procedure and SBR of magnesium was taken as the criterion of merit.

3.5.3.2 Experimental

The simplex procedure was used to identify the optimum conditions for a magnesium ion line as being representative. The BP light kaolin was made up to a 0.5% w/v slurry and pumped at a rate of 1.6 ml min⁻¹. To confirm that optimum conditions were achieved a series of univariate searches were performed, holding each of the other operating parameters at the indicated optimum.

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3.5.3.3 <u>Results and discussion</u>

Optimum ranges and centroid values of the operating parameters for the introduction of kaolin slurries into the ICP are given in Table XII.

Table XII

Optimal values	for kaolin slurry fo	r Mg (II) 280.270 nm
Parameter	Optimum range	<u>Centroid</u> values
Coolant gas/l min ⁻¹	14.5 - 17.5	16.0
Plasma gas /l min ⁻¹	3.3 - 3.9	3.6
Nebulizer gas/l min ⁻¹	2.5 - 2.7	2.6
Power/kW (forward)	1.23- 1.68	1.48
Height/mm	22 - 25	23

The univariate search results, in Figures 38,39,40,41 and 42 for coolant, plasma, nebulizer gas flow, power and viewing height respectively, show that the simplex procedure was successful in identifying the optimal operating conditions for slurries.

3.5.3.4 Analysis of kaolin slurries

Specified total trace elements (as above) were determined in the solid samples by ICP-OES using direct slurry nebulization. Particle size data for the kaolin samples was also determined.

3.5.3.5 Experimental

The solid samples were dried at 80° C in an oven overnight, and then made up to 20% w/v slurries with distilled water. The plasma operating conditions were those identified by the variable step size simplex procedure in section 3.5.3.3. Aqueous standards were used for the

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Figure 41 Mg 280.2 nm univariate search-power

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slurry analysis.

3.5.3.6 Results and discussion

The particle size distribution of the ECLP kaolin samples, determined by coulter counter, are shown in Figures 43,44,45,46 and 47 for S, D, C, Sp and Ballclay respectively. The coulter counter is not directly comparable to other methods of particle size but does however give an indication of sample particle size distribution (see Chapter 5 for further discussion).

The results in Table XIII compare the direct slurry analyses without sample pretreatment with AAS figures reported by ECLP and ICP-OES results for the digest samples, for the specified components. The use of slurry nebulization allowed the aspiration of 20% w/v slurry, <u>i.e.</u> ten times more concentrated than the 2% w/v corresponding digest solutions. Unfortunately this increase in concentration was insufficient to allow measurement of lead and cadmium, any increase in sensitivity being more than offset by increasing background from the aluminosilicate matrix now also present in high concentration. This further emphasises the difficulty of determining lead and cadmium by ICP-OES.

For the other trace elements, Cu, Mn, Zn, Cr and Ni the results were disappointing. The poor correlation with the digest figures presumably was caused by variable atomization efficiency. The atomization efficiency, however, was reasonably constant within the sample type, indicating the variation is probably due to the particle size-effects as noted before or dispersion effects.

As previously, plots of the individual element results ratioed to

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PARTICLE SIZE DISTRIBUTION



		Cu	۶E	M	n %E	Zn	&E	Cr	۶E	Ni	€E	Si mgg ⁻¹	ŧЕ
S	a b c	16 20 8.2	51 41	17 17 6.5	38 38	30 21 7.8	26 37	13 8 3.7	29 46	3.0 :3.2 1.2	40 38	*21.8 108	
с	a b c	40 43 12.9	32 30	64 50 10.5	16 21	30 30 8	24 27	2 13 2.5	125 19	3.0 3.7 1.0	33 27	*22.1 8.0	36
D	a b c	46 46 12.1	26 26	- 91 12.0	- 13.2	35 36 6.2	18 17	14 3 2	14 67	3.0 3.0 1.0	33 33	*22.1 9.1	41
Sp	a b c	28 32 10.4	37 33	100 121 15.0	15 12	33 30 6.3	19 21	10 4 1.5	15 38	2 1 0.83	42 83	*22.1 9.6	43
Ballclay	a b c	27 28 8.9	33 32	25 27 11.3	45 42	42 41 8.8	21 22	94 195 112.5	120 58	30.0 31.8 13.3	44 42	*26.7 11.7	44

We Atomization efficiency ratio of g signal in the slurry to g signal in an aqueous solution (as a percentage). * Typical results mg q^{-1} .

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those obtained for silicon, have been used in order to correct for the varying atomization efficiency arising from particle size effects (referred to in section 3.4.3, slurry analysis for major elements).

The Si levels supplied by ECLP for the kaolin samples were typical levels and were not actually determined by AAS for this work. The Si levels were therefore determined by direct slurry atomization using a 0.5% w/v slurry. All investigated silicon lines, at that time, were too sensitive for the silicon determination with a 20% w/v slurries resulting in overloading of the photomultiplier. Using a 0.5% w/v slurry overcame this problem.

These correlation graphs using ratios showed significant improvement and are shown in Figures 48 to 52 for elements Cu, Mn, Zn, Cr and Ni respectively for both AAS and solution ICP-OES results versus normalized slurry ICP-OES results.

The possibility of adjusting for unequal atomization efficiency by using a correction factor based on relative silicon results appears promising for all elements. The graphs for Cu and Ni levels were particularly encouraging. Table XIV shows the numerical results achieved when this approach was used.

An investigation to establish why there was a failure to achieve equal atomization efficiency for aqueous and slurry nebulization was the obvious next stage in the project.

From the preliminary studies, all the samples, including slurries

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with 90% of their particles less than 2 μ m, had given low atomization efficiencies when compared to aqueous standards. This was disappointing as previous work with coal and coal ash (148) had suggested that if particles were sufficiently small (>8 μ m) complete atomization of slurries was possible. This suggested that the fine particles may have flocculated together and passed through the plasma as conglomerates. Work on dispersants to overcome this problem is described in the next chapter, together with an investigation into viscosity effects which are also thought to affect the atomization efficiency, especially when using high concentration slurries as with the trace analysis work discussed in this chapter.







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Figure 49b



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Sample	Cu	Mn	Ni	Zn _	Cr
S _	a 16	17	3.0	20)	1.3
	b 20	17	3.2	21	8
	c 16.6	13.1	2.4	16	8
С	a 40	64	3.0	33	2
	b 43	50	3.7	30	13
	c 36	30	2.8	22	7
. D	a 46	-	3.0	35	14
	b 46	91	3.0	36	3
	c 30	30	2.6	15.4	5
5P	a 28	100	2.0	33	10
	b 32	121	1.0	30	4
	c 24	34.5	1.9	14.5	4
Ballclay	a 27	25	30.0	42	94
	b 28	27	32.0	41	195
	c 20	26	30.0	20	256

TABLE XIV Comparison of trace element digest results and slurry atomization analysis using normalization

based upon the ratio of silicon figures ($\mu g g^{-1}$)

a. ECLP digest results by AAS

b. Our digest results by ICP-OES

c. Slurry atomization results normalised i.e. ICP slurry results x $\frac{Si \ ECLP \ typical \ figure}{Si \ slurry \ result}$

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4. EFFECT OF DISPERSANTS AND VISCOSITY ON SLURRY ATOMIZATION

4.1 <u>Dispersants</u>

4.1.1 Introduction

Dispersion methods are used for the preparation of suspensions of preformed particles. The term dispersion, according to Tadros (194), is used to refer to the complete process of incorporating the solid into a liquid such that the final product consists of fine particles distributed throughout the dispersion medium. The role of surfactants in the dispersion process can be seen from a consideration of the stages involved (195). Three steps have been considered by Parfitt (196,197): wetting of solid powder by the liquid; breaking of the aggregates and agglomerates, usually with the use of mechanical methods such as ultra-sonic baths or high speed mixers; and comminution of the resulting particles which involves the rupturing of chemical bonds to create new surfaces and, therefore, will facilitate size reduction.

4.1.1.1 Flocculation and deflocculation in clay slurries

There are many schools of thought on the explanation of flocculation and deflocculation processes in clays which are of great importance in the field of rheology (198,199,200).

The distribution of atoms on the surface of kaolinite crystals gives rise to a differential distribution of charges on the surfaces. One interesting, relevant experiment in this respect was performed by Thiessen · (201). He mixed a kaolinite suspension and a negative gold suspension and prepared an electron micrograph of the mixture. It appeared that the small negative gold particles were exclusively absorbed at the edge of surfaces of the large kaolinite plates indicating that the edges carried available positive sites. It seems likely that a

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positive edge double layer is responsible for the absorption of anions acting as counter-ions (<u>i.e.</u> the accumulated ions of opposite charge). Simultaneously the observed small cation exchange capacity may be attributed to a negative double layer on the flat surfaces which results from slight isomorphous substitution in the kaolinite lattice. This two-site hypothesis was confirmed by Schofield and Samson (202) who showed that pure kaolinite absorbs exchangeable Na⁺ ions from solution, demonstrating the presence of negative sites on the flat kaolinite surface. Electron microscope examination also showed negatively charged montmorillonite particles adhering to the kaolinite particle edges. From the results it was deduced that a kaolinite crystal, which is a hexagonal flake shaped particle, has positively charged edges and negatively charged faces.

On standing, particles in clay suspensions will flocculate together. Schofield and Samson (202) visualized flocculation as arising from the negatively charged face of one crystal attracting the positively charged edges of another, a 'house of cards' structure being formed by the particles throughout the suspension. To achieve deflocculation the positive-edge charge can be reversed and thus creating a welldeveloped negative-edge double layer. Then the positive-edge-tonegative-face attraction would be eliminated and a strong edge-to-edge as well as edge-to-face repulsion would be created, resulting in a breakdown of the 'floc' structure. The clay particles are free to move as individuals. This charge reversal effect can be achieved by the addition of chemicals known as deflocculants or dispersants. Various chemicals behave as dispersants, such as tetrasodium pyrophosphate or polyphosphates which reverse the positive edge charge into a negative one as a result of anion adsorption at the edges.

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As the absorption capacity of the clay for anions is usually rather small only a small amount of dispersant is needed to build a negative double layer on the small edge surfaces. The anions are attracted by the positive edge surface and the electrostatic attraction of the anions alone would lead to the neutralization of the edge charge only. In order to create a stabilizing negative edge charge, the anions must be adsorbed in excess. The cation (usually Na⁺) accumulates in the liquid in the neighbourhood of the negatively charged particles in a cloud of so-called 'counter-ions'. The counter-ions are electrostatically attracted by the oppositively charged surface but at the same time these ions have a tendency to diffuse away from the surface to the bulk of the solution; where the concentration is lower. This diffuse character of the counter-ion 'atmosphere' was recognised by Gouy (203) and Chapman (204). Charge distribution for kaolinite particles having been dispersed by the use of a polyphosphate dispersant (200) is shown in Figure 53. The cloud of counter-ions is a three dimensional cloud, and is not, as shown in the diagram for simplicity, restricted to the particle edge region. Deflocculation then originates in the forces of repulsion existing between one double layer and another.

An alternative method of deflocculation would be to reverse the negative-face charge into a positive one by the addition of small amounts of alkali resulting in the formation of complex anions. In kaolinites, the reversal of the edge charge by alkalies has been demonstrated by the decrease of chloride ion absorption with increasing pH (202).





Anionic polyphosphate chains

Sodium counterions (outside kaolinite plate)

Charged sites on kaolinite crystal

4.1.2 Effect of dispersants on slurry atomization

Preliminary studies had shown that there is a definite relationship between particle size and atomization. Slurry particles greater than 10 µm in size have been shown to contribute very little to the observed atomic emission (138). Since these particles have not been reported to be atomized in the plasma and only contribute to noise, nebulizers are operated in conjunction with cloud chambers. The cloud chamber acts as an order sorter removing any larger particles and preventing them reaching the plasma. With homogenous solution samples this creates no analytical bias but with kaolin slurries problems arise if elements are preferentially associated with large particles (see Chapter 5). This was thought to have been a problem during previous slurry analyses. The particle size distribution of clays, before nebulization, can be seen to have extremely wide particle size ranges. The particle size distributions of a typical ECLP sample and 'BP Kaolin' determined by coufter counter are shown in Figures 54a and 55a. However after nebulization, as previously mentioned, the presence of a spray chamber modifies the range considerably, typically removing the large particles from the stream and allowing only particles of less than a certain size to pass to the plasma to be atomized. Samples collected by trapping

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the particles in the aerosol at the injector tube and subsequently measured using a couter counter, show as expected, that the original size distribution is different to the sample actually delivered to the plasma. The bias towards lower size particles is most noticeable when there is a wider range of particle size e.g. ECLP sample, Figure 54b and less noticeable in refined clays where the majority of particles are less than the critical $8 - 10 \mu m$ size <u>e.g.</u> 'BP Kaolin', Figure 55b. In fact from the results obtained it can be seen that particles greater than 5 µm are not actually delivered to the plasma and are removed by the spray chamber. This 'cut-off' effect by the spray chamber can explain the poor atomization efficiencies obtained so far for the slurry samples with large particle size ranges. The effect of particle size on atomization efficiency and the influence of the sample introduction system is detailed in the following chapter). However a few samples supplied by ECLP contained 90% of their particles <2um, and still low atomization efficiency had been observed. This suggests that the fine kaolin particles have flocculated together and pass through the plasma as conglomerates or are removed prior to this, by the spray chamber.

The addition of dispersants to the kaolin slurries should help to overcome this problem and at the same time provide a more homogenous sample, improving signal reproducibility.

4.1.2.1 Experimental

Three candidate dispersants were chosen from literature, Calgon (sodium polyphosphate and sodium carbonate), Dispex (sodium polyacrylate) and ammonium hydroxide solution. Of these, aqueous ammonia was chosen to investigate the effects of dispersant on slurry atomization, as it

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PARTICLE SIZE DISTRIBUTION



PARTICLE SIZE DISTRIBUTION



is readily available in analytical grade purity and also allows the determination of sodium, if requested. Aqueous ammonia has previously been reported as a suitable dispersant for kaolin suspension (205).

To determine the optimum concentration of the dispersant to be added, the emission signal intensity was obtained for a 0.5 w/w 'SR' clay in a range of ammonia solution concentrations. The 'SR' clay (with the majority of its particles <2 μ m) was supplied by ECLP, together with XRF figures. Analysis by ICP-OES solution and ICP-OES slurry atomization procedures, using the previous methods are reported in the following chapter. The aqueous ammonia concentrations, in the range 0.035 to 3.5% m/v, were prepared by the dilution of a 35% m/v 0.88 specific gravity, high purity grade aqueous ammonia solution. Aqueous ammonia concentrations greater than 3.5%, at the operating conditions used for study, were found to affect the plasma stability. The resultant molecular species appear to have a quenching effect and excess ammonia can extinguish the plasma. The element magnesium was chosen for illustration for comparison with previous studies. A11 analytical results were obtained using slurry plasma operating conditions (see Table XII). It was considered necessary to match the ammonia concentrations of the standard solutions (by which the slurry was calibrated) and blank to that of the samples in order to correct the effects of possible differences in sample transport efficiency and plasma excitation mechanisms. The samples and standard were left to stand overnight and then placed in an ultrasonic bath to aid the dispersion before introduction into the ICP.

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4.1.3 Fluxes

By addition of large concentrations of flux it was hoped that on leaving the spray chamber the slurry particles would be coated with fusion mixtures. This should have dried and been heated in the preheating zone of the plasma. This could possibly constitute an approach to the situation in conventional fusions. Even partial fusion would help to destroy the refractory matrix and assist in atomization.

4.1.3.1 Experimental

Initially the following fluxes were tried, lithium metaborate, sodium peroxide, sodium carbonate and potassium pyrosulphate.

4.1.4 <u>Results</u> and discussion

The results in Table XV compare the atomization efficiencies <u>i.e.</u> the ratio of Mg signal in the slurry to Mg signal in an aqueous standard of equivalent concentration (as a percentage), for direct 'SR' clay slurry, 'SR' clay and dispersant, and 'BP Kaolin' and flux determinations.

a) <u>Dispersants</u>

The addition of a dispersant such as aqueous ammonia (0.35% m/v optimal) appeared to have markedly improved the atomization efficiencies for kaolin slurries <u>e.g.</u> the atomization efficiency had increased from approximately 50\% to 70\% for magnesium in 'SR' clay. This has in effect dispersed the fine kaolin particles which previously coagulated together and passed through the plasma as conglomerates, or were removed by the spray chamber.

The graph in Figure 56 shows the effect of aqueous ammonia as a dispersant on the atomization efficiency. The slurry signal intensity increased

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Table XV Atomization efficiency (aqueous/slurry) for Mg II 280.270 nm in a kaolin slurry

a) <u>Dispersant</u>

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b) <u>Fluxes</u>

0.5% w/v SR clay	Atomization efficiency/%	0.5% w/v 'BP Kaolin'	Atomization efficiency
+ 0% m/v ammonia	50 <u>+</u> 1	+ O w/v Flux	45 <u>+</u> 4
+ 0.35% m/v ammonia	70 <u>+</u> 2	+ 2% w/v lithium metaborate	60 <u>+</u> 5
: + 0.35% m/v ammonia	90 <u>+</u> 4	+ 10% w/v sodium hydroxide	37 <u>+</u> 6
(standards and		+ 5% w/v sodium carbonate	62 <u>+</u> 3
0.35% m/v)		+ 20% w/v sodium peroxide	35 <u>+</u> 5
		+ 10% w/v potassium	70 <u>+</u> 10
		pyrosulphate	

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Effect of the addition of aqueous ammonia as a dispersant on the atomization efficiency

(Aqueous/Slurry %) for Mg II 280.270 nm in a kaolin slurry

Figure 56

rapidly with increased dispersant concentration, until an optimum effect was observed (approx 0.35% m/v ammonia). The signal levelled off upon further additions of ammonia with no improvement in the slurry signal. However, at high ammonia concentrations (>3% m/v) a slight decrease in signal was observed. This effect is called 'over-treatment' and flocculation of the clay slurry with the dispersant occurs.

The apparent atomization efficiency can be improved further by the addition of ammonia to the aqueous calibration standards used in slurry atomization. This is presumably due to the formation of the hydroxide species and the resultant colloidal effect is thought to be responsible for the supression in the aqueous standard signal (Figure 61). Almost equivalent aqueous and slurry atomization efficiencies for Mg in kaolin were obtained and the potential for slurry work was investigated further (see Chapter 7).

b) Fluxes

As mentioned previously, large amounts of various fluxes were added to the slurries in order to try to simulate the conventional fusion techniques to help destroy the refractory matrix and assist in atomization. From Table XV it can be seen that improvements in atomization efficiencies were achieved with the addition of lithium metaborate, sodium carbonate and potassium pyrosulphate. However poor results were obtained for sodium hydroxide and sodium peroxide. Although this might be attributed to the fact that the optimum concentrations of flux to be added had not been identified. At this point, although the addition of fluxes seemed promising in assisting slurry atomization it was felt that further investigation was unfounded as the addition of aqueous ammonia as a dispersant had already proved to have markedly assist in the

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atomization efficiency.

4.1.5 Conclusions

The addition of dispersants and fluxes have been shown to assist in improving slurry atomization efficiencies. However aqueous ammonia was considered to be the most suitable dispersant for the analysis of slurries as it only includes the simple addition of small volumes of ammonia (0.35% m/v) to the slurry, as opposed to the addition of flux in which large weighed amounts are necessary and therefore on a routine basis would not be considered cost-effective. Furthermore such fusion agents preclude the determination of particular elements used in the flux, whilst aqueous ammonia would allow the full elemental analysis of the clay slurries.

4.2 Viscosity effects on slurry atomization

4.2.1 Introduction to viscosity

Viscosity is generally defined as 'resistance to flow' and is a measure of fluid friction. It may be considered as the internal friction resulting when a layer of fluid is made to move in relationship to another layer. A highly viscous material is one possessing a great deal of internal friction.

Isaac Newton defined viscosity by considering the model shown below:



Two parallel planes of fluid of equal area 'A' are separated by a

distance 'dx' and are moving in the same direction at different velocities 'v1' and 'v2'. Newton assumed that the force F required to maintain this difference in speed was proportional to the velocity gradient <u>i.e.</u> the difference in speed through the liquid.

 $\frac{F}{A} = \eta \frac{dv}{dx}$ where η is constant for given material and is called its viscosity

The velocity gradient $\frac{dv}{dx}$

is a measure of the speed at which the intermediate layers move with respect to each other. It describes the shearing the liquid experiences and can thus be called 'the rate of shear' (s)

therefore $\frac{dv}{dx} = s$

The term $\frac{F}{A}$ indicates the force per unit area required to produce the shearing action called 'shear force' or 'shear stress (F') therefore viscosity = $\eta = \frac{F'}{s} = \frac{shear \ stress}{rate \ of \ shear}$

Newton further assumed that, at a given temperature, the viscosity that is independent of rate of shear <u>i.e.</u> the relationship between shear force (F') and rate of shear (s) is a straight line and the viscosity remains constant as the rate of shear is changed. Such a fluid is called "Newtonian" and are best exemplified by materials such as water and thin oil. However, not all fluids are newtonian and high concentration slurries are a good example of this. These are called 'non-newtonian' where $\frac{F}{s}$ would not be constant <u>i.e.</u> when the rate of shear is increased, the shear stress does not increase in the same proportion and viscosity changes with a change of shear rate.

4.2.2 <u>Viscosity effects on slurry atomization</u>

4.2.2.1 Introduction

Degradation of the atomization efficiency can be attributed to changes in transport efficiency, rate of desolvation of the drops and the rate of vaporization of the dry aerosol. It is now considered common practice to match acid concentration of standard solutions to that of the sample in order to eliminate differences in the sample transport efficiency or plasma mechanism for the two solutions, caused by physical interference effects.

Greenfield et al. (206) was the first to report on the physical interferences which occur when mineral and organic acids are injected into the plasma and of these, considered aspiration rate and nebulizer performance the most important factors in the analysis of solutions. The effect of high acid concentrations in the sample solution on signal intensity was investigated with a high power plasma as the excitation source. With mineral acids the intensity was reduced by increased viscosity. With organic acids such a reduction was outweighed by other enhancements which were represented as a function of the viscosity, surface tension and density of the solution. With such a dependence of all the effects on solution properties Greenfield suggested that they should be attributed to the aspiration and nebulization system rather than the plasma. To prove conclusively that signal reduction could be largely explained in terms of changing viscosity for acid solution of different concentrations each solution was pumped through the nebulizer in such a way that a constant volume flowed irrespective of viscosity. Comparison of results indicated change of signal intensity was considerably reduced when the force-feed system was used instead

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of the conventional non-forced feed system for the concentric nebulizer. Similar results were obtained by a number of workers (207,208). Dahlquist and Knoll (207) further reported excitation effects due to physical properties of the test samples, such as changes in solute and/or solvent composition, were minor after nebulization and transport effects were taken into account. Although increased water loading in the plasma has been reported to affect the plasma mechanism (67), by substantially increasing the electron density in the central channel of the ICP which essentially 'thermalyses' the plasma and variation in sensitivity results for atom and ion lines according to the excitation mechanism.

Moore <u>et al</u>. (209) reported on the effects of acid strengths on the transpoørt efficiency of a GMK Babington nebulizer in emission spectrometry, using an ICP. The authors concluded that the variation in transport efficiency with acid concentration depends directly on the density of the solution irrespective of the type of acid used. The viscous sulphuric and phosphoric acids have the greatest effect on transport efficiency, in spite of the fact that the solution is as pumped to thenebulizer. Concentrations of hydrochloric and nitric acids up to 30% v/v were found to have little effect.

A factor which must be considered when dealing with kaolin suspensions is the influence of the shell or hull of absorbed water that each clay particle carries around it. The water is held tightly on the kaolinite particle surfaces but gets more loosely bound with increasing distance from the particle until it is indistinguishable from 'free water' or water in bulk (200). That such water exists is shown by the fact that about 1% by weight cannot be removed at 110°C, but requires a

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much higher temperature and hence greater energy to remove it. The shell of absorbed water has a viscosity greater than that of free water and whose viscosity decreases with increasing distance from the particle. Hence it would be reasonable to speculate that higher concentrations (20% w/v) slurries would expect to have a greater viscosity than, say, a 0.5% w/v slurry.

4.2.3 Experimental

Magnesium and iron were chosen as test elements in the investigation of the linear working range and the influence of viscosity in slurry atomization. 'SR' clay slurries were prepared over a wide range 0.5 - 20% w/v and made up with 0.35% m/v aqueous ammonium solutions. Equivalent concentration aqueous standards were prepared and the plasma operating conditions were those identified by the simplex procedure for slurry atomization (Table XII).

4.2.4 Results and discussion

Emission signals for both magnesium and iron were plotted against increased slurry and aqueous concentration to establish whether their respective calibration graphs were linear within the range of interest for this particular study. These are shown in Figures 57a and 58a for magnesium and iron respectively.

For magnesium and iron, signal increased linearly with aqueous elemental concentration within the range of interest. However the signal increased linearly with slurry concentration only up to approximately 7 - 8% w/v. The deviation of the slope was considered to arise from increasing viscosity of the suspensions whereas aqueous was constant, irrespective of solution concentration.







Figure 57b Emission signal for Magnesium (280.270 nm II line) plotted against increased slurry







concentrations with slurry figures corrected by the use of internal standard



Viscosity is known to influence both the aspiration rate and nebulization process and this alters the nebulizer yield. Nukiyama and Tanasawa (210) produced an empirical relationship between the droplet diameter and solution properties in conjunction with nebulizer parameters.

$$d_{o} = \frac{585}{\nu} \left[\frac{\sigma}{p} \right]^{0.5} + 597 \left[\frac{\eta}{(\sigma p)} 0.5 \right]^{0.45} \left[10^{3} \frac{Q_{lig}}{Q_{gas}} \right]^{1.5}$$

Where d_0 is the mean droplet diameter in µm, v is the velocity of gas in ms⁻¹, σ is the surface tension in dyne cm⁻¹, p is the density of the liquid in g ml⁻¹, η is the viscosity in poises, and Qliq and Q_{gas} are the volume flows of the liquid and gas. Although it is doubtful that this empirical equation is an accurate description of aerosols generated by all nebulizers, nevertheless it has been shown by some workers to be useful in predicting trends for aerosol generation (this equation refers to the aerosol emerging from the nebulizer, not to the aerosol reaching the plasma).

Changes in viscosity of solutions/slurries give different volume uptake into the nebulizer, according to Poiseuilles' equation. With concentric nebulizers, the sample solution is introduced into the plasma by surrounding a capillary with a high velocity argon gas stream parellel to it. The pressure differential created draws the sample solution through the capillary. The Poiseuille equation may be applied:

$$Q = \frac{\Pi R^4 P}{8 \eta L}$$

where Q is the rate of flow in mls^{-1} , R the capillary radius in mm, P the pressure differential in pascals, n the viscosity in poise and L the capillary length in mm.

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Spiers <u>et al</u>. (143) reported that kaolin suspensions at 2% w/v concentrations gave a 25% or greater reduction in uptake rate as compared to aqueous samples, using a meinhard nebulizer. However reduction in uptake rate does not arise with the system used in this work as samples were always pumped so that a constant volume flows, irrespective of viscosity. However there still remains the need to correct for nebulizer effects arising from viscosity according to Nukiyama and Tanasawa equation. Such an effect would cause a decrease in the number of atoms reaching the plasma. These nebulizer effects appear to be responsible for the analytical variation observed and the low atomization efficiencies obtained for the trace element analysis in which a 20% w/v slurry was used.

This theory was confirmed by semi-quantitative viscosity results obtained for the different percentage slurries using two different techniques. Initially a Brookfield syncho-lectric viscometer, model LVT (Brookfield Engineering Laboratories Inc., Stoughton, Massachusetts) was used to measure the viscosity. The viscometer measures viscosity by measuring the force required to rotate a spindle in a fluid. The instrument was only sensitive enough to measure the 20% w/v slurry and was prone to a number of problems associated with measuring slurries of relatively low concentrations. One of the major problems is that a continuous system cannot be maintained due to particles settling out of suspension, and hence decreasing viscosity readings are obtained.

Another technique employed was a controlled-stress viscometer (Carri-Med, Dorking, Surrey). This consists of a cone and plate system. The cone which rotates subject to a magnetic field, is placed above a stationary plate, on which the sample is placed so that surface

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contact is just broken. The apparatus provides a constant rate of shear throughout the material and the viscosity is measured by measuring the displacement of the turning cone as it reacts to the stress in the suspension. Several problems were encountered using this technique, namely, settling out of particles, keeping the slurry sample between the plate and cone, as it tends to 'creep' towards the plate edge, and thirdly, as with all thin materials, only small displacement values are measured and consequently these small changes are subject to large errors.

Estimations of viscosity values for 10,15 and 20% w/v slurries, using this technique, are shown in Table XVI.

Table XVI Variations in viscosity with slurry concentration

% slurry	viscosity, in -1-1 centpoise µg cm ⁻¹ s ⁻¹		
O (Blank)	1*		
10	2.9		
15	3.4		
20	4 - 4.6, (4 - 5) **		

* Taken from Handbook of Chemistry and Physics (211) ()** Measured using Brookfield viscometer

The 10 and 15% slurries exhibited 'newtonian' behaviour <u>i.e.</u> viscosity was independent of rate of shear, whereas the 20% exhibited 'nonnewtonian' behaviour <u>i.e.</u> showed a decrease in viscosity which increased shear rate, this effect is called shear thinning and is typical of

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a pseudo-plastic material. From these results it can be concluded that viscosity increases with slurry concentration and this viscosity effect is responsible for the analytical variation observed. These effects can be corrected by the use of an internal standard. This was accomplished by the incorporation of La (500 $\mu g\ \text{cm}^{-3}),$ as an internal standard, into the slurry samples prior to analysis and the emission signal measured at 394.910 m and the 403.169 nm ion lines. A problem with internal standards is that elements do not behave in the same manner in the ICP, and consequently it was necessary to match the internal standard spectral line to those of the analyte elements, by using all ion lines. As a known concentration of lanthanum was added to the slurry samples, any analytical bias for lanthanum in the slurry results, due to the viscosity effects could then be calculated. The increased viscosity of the clay slurries was found to inhibit the nebulization process and hence produced a reduction in La emission signal, by 6.4% for a 10% w/v slurry, 15% for 15% slurry and 28.8% for 20% w/v slurry. All analyte results then were ratioed to that of the internal standard for a particular slurry concentration. Often accuracy can be degraded if the internal standard and analyte emission transitions (i.e. differences in excitation potentials) are not closely matched (212). However this was not found to be too critical as similar reduction in slurry signals, as for La, was observed for both the Mg and Fe and therefore the use of La as an internal standard, adequately corrected for the differences in viscosity effects observed, and thus increased the linear working range for slurries. (Figures 57b and 58b for magnesium and iron respectively). Similar results were obtained for subsequent minor and trace elemental analyses (Figure 59, Titanium, Figure 60, Manganese, and Figure 61, Copper).

increased slurry and aqueous concentrations





increased slurry and aqueous concentrations

1

aqueous concentrations



4.2.5 Conclusion

Viscosity has been shown to increase with increase in slurry concentration and this viscosity effect was found to be responsible for the reduction in analyte slurry signal and hence atomization efficiency for slurries greater than 7 - 8% w/v, due to variations in nebulization and aerosol transportation. This was successfully corrected by the use of La as an internal standard. On the basis of these findings, for major and minor element analysis <u>e.g.</u> the clay separates work discussed in the next chapter, 0.2 - 0.5% w/v slurries were used to produce minimal nebulization effects and thus eliminated the need for internal standards. However for minor and trace element analysis, where a higher concentration slurry is necessary to maintain levels above the instrumental detection limits, the use of internal standard correction would obviously be beneficial.

5. EFFECT OF PARTICLE SIZE ON ATOMIZATION EFFICIENCY OF CLAYS

5.1 Introduction

Certain size fractions may be relatively enriched or depleated in one or more of the analyses. Thus under identical experimental conditions the response per unit concentration of analyte may vary from sample to sample. The results of analyses of different particle size clay fractions by routine dissolution procedures were compared with those obtained following slurry atomization. This also facilitated an investigation of the relationship between particle size and atomization efficiency and the influence of sample introduction design parameters on the emission signal.

5.2 Variation of elemental composition with particle size

5.2.1 Experimental

Particle size fractions were separated from suspensions by a gravity sedimentation technique. For particle sizes in the range $0.5 - 4\mu m$ the Andreasen technique was used and the 'Repeated Decantation' method for coarser particle size in the range 4 - 40 μm (213). Both methods are based on Stokes Law which defines the constant velocity (V) reached by a sphere falling, without turbulence, through a viscous fluid.

$$V = \frac{gD^{2}(\Delta d)}{18\eta}$$
(5.1)

From (5.1) time for sedimentation for a given size is then given by:

$$t = \frac{18\eta h \times 10^8}{g D^2 (\Delta d)}$$
(5.2)

where

t = time (seconds)

 η = viscosity of the fluid (poise)

h = settlement depth (cm)

g = gravitational constant (cm/sec²)

D = Diameter of sphere (um)

 $\Delta d=$ the difference in density between the sphere and the fluid (g/cm^3)

V = constant velocity (cm/sec)

 η is temperature dependent so that if the temperature is kept constant $\eta \Delta d$ and g are constants and V is proportional to the square of the diameter of the particle. (η is known to be associated with concentration (see Chapter 4) and therefore will change during the settling process. This presumably is assumed to be negligible in this particular case).

Using this relationship the time required for all particles greater than a certain size to settle through a given distance, can be predicted. This is the basis of these methods, in which particles of a certain size can be removed or decanted from a known depth in a cylinder after a predetermined time.

Samples were prepared and supplied by ECLP.

Clay separates (CS) samples were filtered using a millipore filter (pore size 0.45 μ m) and washed three times to ensure freedom from previous reagent contamination during the sedimentation process. The filtrates were dried in an oven at 110°C.
5.2.1.1 <u>Conventional analysis by fusion</u>

A fusion procedure for each clay separate portion was carried out using the lithium metaborate fusion procedure described previously (Chapter 3).

Particle size data for the clay separates were also determined by Coulter counter.

Major and minor elements, Si,Al, Ti, Ca, Fe and Mg were determined by ICP-OES. The operating conditions selected were reported previously for solution analysis (see Table IX) and the following wavelengths were chosen for both solution and slurry analysis.

Element	Wavelength	Atom I/Ion II	Sensitivity
•			ranking (193)
Si	212.412	I	2
Al	396.152	I	3
Ca	393.366	II	1
Mg	280.270	II	2
Ti	334.270	II	1
Fe	259.940	II	1

The same sample experimental conditions were also employed for the 'SR' clay. Particle size data was also obtained.

5.2.2 <u>Results and discussion</u>

From Figure 62 it can be seen that the order of particle size from coarse to the fine particles size is CS 1, >CS 2, >CS 3, >CS 4,>CS 5 clay. Particle sizes were in the range 50 - 8 μ m (mean approx 25 μ m), 25 - 5 μ m (mean approx 12 μ m), 13 - 2.5 nm (mean approx 5 μ m),





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8 - 0.8 μ m (mean approx 2.5 μ m) and 5 - <0.3 μ m (mean approx 0.5 μ m), respectively. Both CS 5 and the 'SR' clay (Figure 63) exhibited similar particle size distributions.

Results are shown for SiO_2 , Al_2O_3 , MgO, Fe_2O_3 , TiO_2 and CaO in Table XVIII for the clay separates. Similar trends were observed for SiO_2 , TiO_2 and Fe_2O_3 , with a preferential bias in favour of the coarser particle sizes. Whilst Al_2O_3 and MgO are more associated with the finer particle sizes, although MgO showed a slight reverse in this trend in the very finest of the clay particles. After discussion with ECLP it was suggested that this rise of MgO concentration at the very fine particles was typical, as Mg is mainly associated with the micas which also are found to show this slight reverse in trend. Calcium, however, was not strongly associated with particle size.

A comparison of results by ICP-OES of solutions and XRF (supplied by ECLP) for the 'SR' reference clay is given in Table XVIII. There is excellent agreement between the results obtained using the two different techniques. Elemental composition is similar to the CS 5 sample which was not surprising as they both exhibited similar particle size distributions.

From these results it can be seen that certain size fractions are relatively enriched or depleted in one or more of the elements analysed. As previously discussed in Chapter 3, small amounts of various ions may substitute, particularly with aluminium, in the kaolin structure or maybe present in impurities, such as micas, feldspar and quartz which are generally associated with the larger particle sizes. This was diagramatically shown by Clark (214) (Figure 64) and element association

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	Sample	Si0 ₂	A12 ⁰ 3	Ca0	MgO	Ti0 ₂	^{Fe} 2 ⁰ 3
25 µm	CS1	50.7	27.5	0.067	0.50	0.220	1.95
(coarse)	CS2	48.5	35.5	0.070	0.33	0.093	1.13
	CS3	49.5	35.7	0.055	0.28	0.045	0.79
	CS4	47.3	36.9	0.09	0.27	0.032	0.67
0.5µm	CS5	46.7	38.3	0.070	0.33	0.028	0.56
(fine)							

Table XVII Results by Fusion ICP-OES For Clay Separates (% w/w)

Rable XVIII Results by Fusion ICP-OES 'SR' Clay (% w/w)

Element	XRF	ICP
	(ECLP)	
SiOo	46.6	46.5
Al ₂ ⁰ 3	38.5	38.4
Fe203	0.49	0.49
Ti0 ₂	0.03	0.03
Ca0	0.05	0.04
MgO	0.20/0.19	0.19

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Figure 63



PARTICLE SIZE DISTRIBUTION



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of impurities are discussed in detail in a following chapter. This apparent mineral/particle size relationship might explain the slight variation in atomization efficiency observed between elements of a single sample type obtained from the preliminary kaolin analysis.

Portions of each of the clay fractions were then used to access the effect of particle on atomization efficiency.

5.3 Effect of particle size on atomization efficiency by analysis

of kaolin slurries using existing sample introduction system

5.3.1 Experimental

The solid clay separate samples, together with the two previous used bulk samples ('SR' and 'BP Kaolin'), were made up to 0.2% w/v slurries with aqueous 0.35% m/v NH₃ and major and minor elements (as outlined in section 5.2.1.1) were determined by slurry atomization. The plasma operating conditions were those identified by the variable size simplex procedure for slurry atomization in Table XII. Aqueous standards were used to calibrate the slurry analysis.

5.3.2 Results and discussion

The results in Table XIXa and XXa compare the direct 'clay separates' and reference clay slurry analyses, without sample pretreatment, with the ICP-OES figures obtained from the fusion technique.

The results were disappointing, again indicating the effect of particle size as a major influence on slurry atomization, although the atomization efficiency has markedly improved since previous studies, with the use of aqueous ammonia as a slurry dispersant, <u>e.g.</u> the atomization efficiency has increased from 50 to 70% for Mg.

Major and minor element data for clay separates by

(a) ICP solution (b) ICP slurry atomization (% w/w)

using double pass spray chamber and 2.2 mm i.d. injector

<u>tube</u>

Sample		S102	A1203	MgO	T102	Fe ₂ 03
CS1 (Coarse sample)	a	50.7.	27.5	0.50	0.22	1.95
	ъ	1.14	0.52	0.004	0.0008	0.006
	\$E	2.25	1.9	0.86	0.34	0.47
CS2	a	48.5	35.5	0.33	0.093	1.13
	Ъ	0.98	0.82	0.005	0.001	0.00
	\$E	2.02	2.3	1.6	1.17	0.49
CS3	a	49.5	35.7	0.28	0.045	0.79
	Ь	2.34	1.36	0.002	0.002	0.028
	\$E	4.7	3.8	5.4	4.59	3.48
CS4	а	47.3	36.9	0.27	0.032	0.67
	b	11.0	8.19	0.056	0.008	0.136
	\$E	23.3	22.2	20.7	25.78	20.3
CS5 finest sample)	a	46.7	38.3	0.33	0.028	0.56
	ъ	33.4	21.25	0.24	0.020	0.376
	≸E	71.5	55.5	72.7	71.8	67 1

% E atomization efficiency

Table XIXbComparison of major and minor element (a) ICP solutionresults and (b) slurry atomization analysis usingnormalization based upon the ratio of siliconFigures (% w/w)

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Sample		\$10 ₂	A1203	MgO	TIO ₂	Fe203
081	а	50.7	27.5	0.50	0.22	1.95
	b		23.1	0.19	0.034	0.40
CS2	а	48.5	35.5	0.33	0.093	1.13
	ь		40.7	0.26	0.054	0.27
CS3	a	49.5	35.7	0.28	0.045	0.79
	b	<u></u>	28.8	0.32	0.044	0.58
CS4	а	47.3	36.9	0.27	0.032	0.67
	b		35.2	0.24	0.035	0.59
CS5	a	46.7	38.3	0.33	0.028	0.56
	Þ		29.8	0.34	0.028	0.53

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<u>Table XXa</u>

	<u>solut</u>	ion (b) ICP	slurry atomiz	ation, % w/w	%E - Atomiza	tion
	effic	iency		·		
		510 ₂	A1203	MgO	T102	Fe ₂ 03
	а	46.5	38.5	0.19	0.030	0.49
SR Clay	ъ	36.3	27.8	0.14	0.026	0.35
	E\$	77.9	72.2	73.7	87.3	71.4
	a ·	47.5	37.9	0.19	0.030	0.58
BP kaolin	Ь	26.3	20.1	0.11	0.026	0.29
	E≸	54.8	53.0	57.9	86.7	50.0

Major and minor element data for reference clays by (a) ICP

Table XXb

Comparis	son of m	najor and	minor e	lement	(a)	ICP	solution	results
and (b)	slurry	atomizat	ion anal	vsis u	sing	nori	nalizatio	n based
and (b)	sturry	atomizat		<u>ysrs u</u>	. <u>5111</u>	1011		n babea
upon the	e ratio	of silic	on figur	'es (%	<u>w/w)</u>			

SR Clay	a b	46.5	38.5 35.5	0.19 0.18	0.030 0.034	0.49 0.49
BP kaolin	a b	47.5	37.9 36.5	0.19	0.030 0.047	0.58 0.52

Particle size was clearly the critical factor in determining the atomization efficiencies. For all the major and minor elements studied, atomization efficiency was biased in favour of slurries containing high concentration of finer particle sizes. Particles less than $3 \mu m$ produced the largest signals, for example, samples CS5 and 'SR' clay gave atomization efficiencies of around 70% and 'BP Kaolin' around 55%. However emission signal and hence atomization efficiency dropped with increase in particle size to give an atomization efficiency of approximately 1% for particles in the 25 μm size region. This is diagramatically shown in Figure 65. Particles greater than 5 μm contributed very little to the overall signal. This can be attributed directly to the rejection of large particles by the spray chamber.

Order sorting effects of the spray chamber results in this selective transport of very small particles to the plasma (as discussed briefly in Chapter 4).

The particle size distribution of a typical manufacturers clay determined by coulter counter is shown in Figure 66a. Particles size analysis of particles collected at the torch injector tube, i.e. sample actually delivered to the plasma, showed that there was in fact a cut-off of particles at approximately the 2 μ m size (Figure 66b) and this is strongly reflected in the slurry results obtained.

As previously, plots of the individual elements results ratioed to those obtained for silicon, have been used in order to correct for varying atomization efficiency arising from particle size effects (referred to in section 3). Results are shown in Tables XIXa and XXb for clay separates and bulk clays, respectively.

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Figure 65

Atomization efficiency as a function of particle size using double pass spray chamber and 2.2 mm i.d. injector tube as part of the sample introduction system





In addition, the Si/Al ratio was calculated for both ICP solution and ICP slurry (see Table XXI) as both ${\rm Si0}_2$ and ${\rm Al}_20_3$ are preferentially associated with a particular particle size it was hoped that the ratio may have promise as a simple, yet effective, on-line process-control indicator method of particle sizing. From Figure 67 it can be seen that the Si/Al results, plotted as a function of particle size, were reasonably encouraging, although further work is obviously needed.

It was hoped, by modifying the original sample introduction system (which comprised a Babington-type nebulizer with impact bead, doublepass spray chamber and a 2.2 mm i.d. torch injector tube), larger particles may enter the plasma and hence improve atomization efficiency. This would also facilitate an investigation to establish the slurry particle size able to be atomized in a plasma and at the same time assess the viability of slurry atomization as a simple and rapid technique for geochemical analysis. Obviously if the sample has to be ground to a very fine size, this could be time-consuming, with an additional risk of contamination introduced during the grinding process, then this technique would be less attractive for geological samples which do not naturally occur as finely-divided particles, <u>unless</u> a correction factor is used to adjust for varying particle size.

Various sample introduction systems were designed and characterised by particle sizing to establish the most suitable design to use for slurry atomization that would introduce larger particles to the plasma.

5.4 <u>Particle size characteristics of sample introduction systems</u> 5.4.1 <u>Introduction</u>

Sample introduction techniques for atomic spectroscopy have been

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Table XXI

Silicon to Aluminium ratio calculated for ICP solution and ICP

Sample	ICP solution			ICP slurry			
	\$10 ₂ (\$ v	A12 ⁰ 3	S1/Al Ratio	SiO ₂ Al ₂ O ₃ (X w/w)	S1/Al Ratio		
CS1	50.7	27.5	1.84	1.14 0.52	2.19		
CS2	48.	35.5	1.37	0.98 0.82	1.19		
CS3	49.5	35.7	1.39	2.34 1.36	1.72		
CS4	47.3	36.9	1.28	11.0 8.19	1.34		
CS5	46.7	38.3	1.22	33.4 21.3	1.57		
SR clay	46.5	38.4	1.22	36 . 3 27.8 [°]	1.31		
BP Kaolin	47.5	37.9	1.25	26.3 20.1	1.31		

slurry



recently reviewed by Browner and Boorn (215,216). The sample introduction system for solution analysis consists of three main components:

- a) nebulizer provides a mechanism to transform the sample solution into an aerosol;
- b) spray chamber principally a particle size order sorter and
- c) torch injector tube-introduces the sample aerosol into the ICP.

Aqueous aerosols produced from pneumatic nebulizers typically contain an extremely wide particle size range. From the nebulizer the aerosol is swept into a spray chamber and the presence of a spray chamber modifies these ranges considerably. The transport of aerosols in an atomic spectrometric system has been explained in terms of the interaction of a primary generation process, with various secondary and tertiary modifying steps, by Browner et al. (217). The aerosol modifying processes that convert the primary aerosol produced by the nebulizer to the tertiary aerosol arriving at the plasma are caused by devices such as spray chambers, and also impact beads and impaction surfaces placed in the aerosol path, which results in the production of secondary aerosols. Aerosol modifiers typically remove large droplets from the stream, in which aerosol loss usually results from impaction, turbulence, gravitional and centrifugal processes (218), and allows only drops less than a certain size to pass. Therefore the transition from primary to tertiary aerosol is accompanied by a large reduction in mean drop size of the aerosol. Spray chamber geometry directly influences the aerosol droplet size distribution that reaches the plasma and the importance of spray chamber geometry has been investigated by Schutyser and Janssen (219). The droplet size distribution reaching the plasma is important to spectrochemical analysis because it directly affects the apparent atomization efficiency. This has been very

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apparent with the slurry atomization work so far studied.

The droplet size distribution generated by nebulizer-spray chamber combinations, for aqueous samples, have been reported by a number of workers (175,220,221,222) and a significant contribution to this area has been made by Browner and co-workers (217,223,224) using cascade compactors to measure particles in range 0.4 - 11 μ m and an electrical aerosol analyser for droplets in the range 0.032 - 1 μ m in diameter. Comparison of methods for particles size measurements are reported later in this chapter.

This study entailed looking at the characteristics of sample introduction systems, by particle sizing of slurries, in order to find a suitable sample introduction system to allow larger particles to reach the plasma discharge. Obviously for large particles to enter the plasma, it was necessary to reform or remove existing aerosol modifying devices.

5.4.2 Experimental

Particle size distribution data was obtained for a clay sample containing a wide-range of particle sizes using 2 different nebulizer designs, several different spray chamber configurations and 4 different torch systems. Relative contributions to particle size modification during the sample introduction were deduced by trapping the particles in the aerosol at various stages in the sample introduction system and measurement of particle size distribution by coulter counter.

5.4.2.1 <u>Sample introduction systems</u>

i) <u>Nebulize</u>rs

a) Babington-type plastic/glass nebulizer with impact bead
(Figure 4) (see ref 146 for construction details).

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b) Babington type PTFE nebulizer without impact bead (Figure5). Details of construction are described in Chapter 3.

ii) Spray Chambers

- a) Double pass spray chamber, based on Scott's design (225) was constructed from two concentric glass cylinders (see Figure 68a), the outer (40 mm i.d.) being sealed at one end and fitted with an outlet and a drain, and the inner (25 mm i.d.) accepting the nebulizer-via a PTFE 'nebulizerspray chamber connector' shown in Figure 5a. The gap between the open end of the inner cylinder and the closed end of the outer was fixed at 20 mm, as it was previously used for aqueous solution work where only smaller particles were required to reach the plasma. This is probably the most popular spray chamber design and was used in the initial slurry work.
- b) Cyclone spray chamber or vortex type chamber is shown in Figure 68b. The diameter of the cyclone chamber at the top was 70 mm and the height of the chamber 115 mm. The drain exit was connected to a pump via a 'well' in which a tube for drainage was attached. Cyclone chambers have been described by Thelin (226) and Ebdon and Cave (146) for aqueous samples.
- c) 'Straight-through' spray chamber, shown in Figure 68c, was constructed, for this study, out of fibreglassas it was easy to handle and quick to construct for a 'test model'. The smooth shape of the chamber was designed to help minimize

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impaction surfaces and to allow some of the larger particles, which would otherwise have adhered to the sides of the impaction surfaces and drained away, to actually reach the plasma.

- d) 'Direct' spray chamber (vertical injection nebulizer), shown in Figure 68d, was designed to allow large particles produced by the nebulizer to directly enter the injector torch tube. The nebulizer was placed with its 'face' vertically below the torch and the direct spray chamber acted as a connector to the torch. The inner diameter outlet was the same diameter as the injector tube (3 mm i.d.) to minimize impaction which was found to occur at the chamber/torch interface and the length 70 mm, was minimized as far as it was practically possible to allow direct introduction. Sample waste was pumped away via a tube and pump attached to the base of the chamber and at the side of the nebulizer to avoid flooding of the nebulizer face which would impair analytical performance. Greenfield used a similar device in his initial ICP studies (25).
- iii) Torch injector tube (see Figure 31)

2.2 mm i.d. capillary injector tube (used in original instrumentation. 3 mm i.d. capillary injector tube.

4 mm i.d. capillary injector tube.

2 mm i.d. jet injector tube.





drain

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5.4.2.3 Results and discussion

a) <u>Nebulizer</u>

For both nebulizers with and without impact bead, no variation in particle size distribution was observed (see Figure 69a,b). This was surprising as an impact bead acts as a secondary impaction by shattering the larger droplets produced by the nebulizer itself and results in the production of additional small droplets. The impact bead also serves to remove the larger droplets from the aerosol and these effects have been reported for aqeuous samples (15⁴). However the slurry aerosol produced by the nebulizers had undergone little change, if any, in particle size distribution from the original clay aspirated (Figure 66a). This presumably can be attributed to the sample being a powder having already a pre-defined particle size. The PTFE nebulizer without impact bead, with its fixed capillary geometry and therefore considered more robust than the glass/plastic nebulizer, was combined with several different spray chambers.

b) <u>Nebulizer/Spray Chambers</u>

The effect of all the spary chambers studied was to drastically reduce the delivered droplet size by removing larger droplets via impaction, gravitational settling and centrifugation processes. Large droplets, on striking the impact surfaces, generally adhered and ran to waste. Similar particle size data was obtained for both the double pass (Figure 70a) and the 'straight through' (Figures 70c(i) and (ii)) chambers whilst the cyclone spray chamber exhibited a bias towards the finer particle sizes (Figure 70b). The spray chambers filtered out most of the large particles (>16 μ m) and therefore increased the relative percentage of smaller particles. This is shown in Figure 70cii for the 'straight-through' chamber. With the double-pass chamber,

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the aerosol is forced down an inner tube and back up an outer concentric tube before exit and the separation of particle sizes is affected by forcing the injector gas to change direction sharply. The smaller droplets follow the gas stream, but the larger droplets, because of their higher momentum, cannot turn so quickly and adhere to the walls of the chamber and drain to waste and consequently decreases the rate of analyte transport to the plasma discharge. Although evaporation may cause a slight downward shift in the size distribution. This 'cut-off' effect makes this type of spray chamber unsuitable for slurry work. A disadvantage of this type of chamber is the problem of memory effects due to dead spaces (<u>i.e.</u> not in the direct gas flow) and therefore a more compact design is desirable (157).

The cyclone spray chamber produced finer particle sizes and therefore was considered unsuitable for slurry work but has been considered promising by Gustavsson (218) for aqueous work. With the cyclone spray chamber the aerosol is shot tangentially into a cyclone chamber and the larger droplets fall to the drain at the base and the aerosol leaves from a tube at the top of the chamber.

The results from the straight-through chamber were surprisingly disappointing. As impaction surfaces were minimized it was hoped larger particles would reach the torch. However this spray chamber was used for the subsequent studies as the design was less prone to memory effect due to the addition of the drainage pump.

The direct vertical spray chamber results are discussed separately in section 5.3.3.2.

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c) <u>Nebulizer/Spray Chamber/Injector Torch Tube</u>

The particle size data obtained from collecting the slurry aerosol at the torch shows that the torch injector further conditions the aerosol (see Figure 71) reducing the cut-off to 2 - 2.5 μ m for the 2.2 mm i.d. injector tube normally used for this work (Figure 66b). The 3 mm i.d. (Figure 71a) and 4 mm i.d. (Figure 71b) injectors also reduce the droplet size which enters the plasma but not to the same extent. The 3 mm i.d. injector produced a cut-off 6 - 7 μ m and the jet (Figure 71c) and 4 mm, 8 - 10 μ m in particle size. The spray chamber and torch injector tubes produced the dominant influence over the characteristics of the aerosol actually entering the plasma.

Although both the 4 mm and the jet injector tubes produced particle size cut-off at approximately 8 - 10 μ m size, unfortunately they were found to be unsuitable for slurry atomization. With the jet injector as previously discussed in Chapter 3, the sample 'cones out' and enters the plasma fireball. When this occurs the conditions in the plasma change and this leads to considerable reduction in signal sensitivity.

Similar problems were observed using the 4 mm injector tube. This may be due to the emergent injector gas having insufficient velocity to punch a hole through the plasma, although, from the particle size distribution of clay collected at the torch, particles as great as 10 μ m are known to reach the plasma. This was confirmed by aspirating Sr (10,000 μ g cm⁻³) into the plasma, the sample was observed to pass around the sides of the plasma instead of passing through the centre. Clay deposits were also observed on the outside of the injector tube from the eddying effect, suggesting that this was the case.

The findings of this study suggest that the 3 mm i.d. injector was

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PARTICLE SIZE DISTRIBUTION



PARTICLE SIZE DISTRIBUTION

Figure 71c



the most suitable for slurry atomization and was used for subsequent studies, together with the PTFE nebulizer and the 'straight through' spray chamber.

5.4.2.4 Comment on particle size data measurements

In this work, particle size measurements were determined by coulter counter. The coulter principle or electrical sensing zones assumes voltage pulses are proportional to particle volume as they pass through an orifice on either side of which is an electrode. Samples are therefore required to be prepared in electolytic solutions before analysis. Clogging of orifices, correction for coincidence and a tendency to underestimate the lower particle size ranges for the particular orifice size tube used are disadvantages of the technique. However the coulter technique does have the advantage that it is a rapid technique and thus is widely used and consequently, was considered the best technique for measuring particle size ranges of slurries. As briefly mentioned in Chapter 3, the coulter counter is not directly comparable to other methods of particle sizing but does however give an indication of sample particles size distribution by the shape of the graph produced.

A variety of particle sizing techniques are available (205). Mechanical seiving is generally restricted to sizes greater than about 75 microns. The process can cause particle wear and depends on sieving time and loading although the sieving equipment is relatively inexpensive. Optical microscopy has the advantage of actually being able to see the particles. However, results depend somewhat on operator skill and are obviously quite tedious. Many hundreds of samples need to be counted if good statistical precision is required. Although especially

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useful for submicron sizes, electron microscopes are costly. Both of these techniques are very time-consuming and were not considered suitable for slurry particle size analysis. It is important to note that these methods, including the coulter technique, are for measuring solid particles and not for measuring droplet sizes. Therefore the characterizing of the sample introduction systems was based on measuring the solid part of the slurries and not the actual droplet size, which would obviously incorporate associated water.

Several mechanical and optical techniques for measuring droplet size distributions are available. Mechanical methods such as cascade impactors have been widely reported for measuring particle size distributions obtained by a variety of nebulizer/spray chamber designs (222,223). Cascade impactors consist of several horizontally stacked plates each with many holes, the hole sizes decreasing for plates downstream from the inlet. Decreasing hole sizes causes increasing velocity, and whenever the velocity of a droplet is large enough to overcome the aerodynamic drag of the airstream, it will impact on the plate. Gravimetric analysis of the plates yield mass fractions. The technique can be used for sub-micron sizes, although precision is low since the difference in weight between the plate with and without impacted droplets is very small. In addition, careful cleaning, drying and weighing increases the total time of measurement to 1 to 2 hours. However, a more reliable approach to the use of cascade impactor for droplet size measurements was reported by Browner et al. (224). A sodium chloride solution of known concentration was nebulized and the solution collected on each plate of the cascade impactor was washed off and diluted to a known volume with deionized water. This enabled the concentration of sodium to be readily determined by flame emission

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spectrometry, and hence the mass of droplets deposited could be calculated. Another such technique for measuring droplet size measurement, is using laser diffraction. An advantage is that the particles are not physically collected, as with most techniques, but a laser beam, which is a non-perturbing probe, is used making it possible to measure droplet size distributions without removing, collecting or disturbing the droplets in the system. The technique uses the diffraction pattern formed when particles are illuminated by a parallel beam of monochromatic, coherent light to determine the particle size distribution. A description of the theory and application of this technique is beyond the scope of this chapter, and the reader is directed to the review by Weiner (227). This technique was used to measure the particle size distributions of a clay sample, used in the particle size study in this chapter, which were collected at the 2.2 mm i.d. and 4 mm i.d. torch injector tubes (228). The instrument used was a Malvern 3300 laser particle size analyzer (Malvern Instruments Ltd, Malvern, Worcs, England). The results obtained from this preliminary investigation indicated that there was a cut-off of 8 μ m for the 2.2 mm i.d. tube and 9 μ m cut-off for the 4 mm i.d. injector. This disagreed with the results obtained for the 2.2 mm tube using the coulter counter technique. Cut-offs of 2 - 3 μ m and 8 - 10 μ m for the 2.2 and the 4 mm i.d. injector tubes respectively, were obtained. However, this can be explained by the fact that the laser technique measures droplet size, including both the solid and aqueous part of aerosol whilst the coulter counter measures the solid part only.

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5.4.3 <u>Effect of particle size on atomization efficiency using</u> the modified sample introduction system

5.4.3.1 Experimental

Different particle size clay fractions were analyzed by slurry atomization using the 3 mm i.d. injector together with the PTFE nebulizer and the 'straight through' spray chamber as the sample introduction system. The relationship between particle size and atomization efficiency was investigated.

Using the optimal plasma operating conditions obtained by the simplex optimization procedure for slurry atomization using the 3 mm injector tube (Table XXII below). Optimization was carried out on Mg II 280.270nm line using a 0.5% w/v slurry.

<u>Table XXII</u> Optimal solution conditions Mg(II)

280.270 nm for slurry atomization using modified sample introduction system

Parameter

Coolant gas/1 min ⁻¹	32.0
-1 Plasma gas/l min	4.2
Nebulizer gas/1 min ⁻¹	2.8
Forward Power*/kW	2.9
Height/mm	31.5
For Mg(II) 280.2 nm line	

*Forward power - reflected power

The optimum conditions identified by the simplex procedure for Mg in slurries showed an increase in gas flows and more r.f. power than the previously identified optimum conditions for the 2.2 mm i.d. injector tube (Chapter 3). This will produce a larger fireball and together with the decrease in lateral velocity obtained with this larger inner diameter tube, will increase the time the slurry aerosol can spend in the plasma for sufficient atomization and excitation to take place.

Particle clay fractions were those used in the previous study (Figure 62). The clay separate samples were made up to 0.2% w/v slurries with aqueous 0.35% m/v ammonia solution and major and minor elements were determined by slurry atomization.

5.4.3.2 Results and discussion

Atomization efficiency had markedly improved with the use of the 3 mm injector. This is shown in Table XXIII. Particles less than 4 - 5 μ m produced good atomization efficiency compared with only less than 2 μ m for the 2 mm injector. The fine clay fraction, sample CS5 (range 5 - <0.3 μ m) in fact gave nearly 100% atomization efficiency suggesting most of the sample actually entered the plasma. Atomization efficiency also improved markedly for samples CS4 (range 8-0.8 μ m) and CS3 (13 - 2.5 μ m) to give atomization efficiencies of approximately 72% and 40 - 50%, respectively, compared to 23% and 4% previously obtained with the 2 mm i.d. tube. This is diagrammatically shown in Figure 72. Again the atomization efficiency can be attributed directly to rejection of large particles, greater than 6 - 8 μ m, by the sample introduction system.

From the results it was noticed that low atomization efficiency results were obtained for aluminium, using both the 2.2 mm and 3 mm i.d. injector

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Table XXIII

Major and minor element (% w/w) data for clay separates by (a) ICP solution (b) ICP slurry atomization, using straight through spray chamber and 3 mm i.d. injector tube.

Sample		510 ₂	^{A1} 2 ^O 3	MgO	т10 ₂	Fe203
CS1 coarse sample	a b	50.7 1.67	27.5	0.5 0.0157	0.22 0.0122	1.95 0.0284
mean 2.5 µm %	E*	3.1	4.0	3.1	5.5	1.5
CS2	a	48.5	35.5	0.33	0.093	1.13
25 - 5 µm	b	6.15	2.0	0.029	0.0162	0.0965
mean 12.5 µm %	E	8.8	5.6	8.8	17.4	8.5
CS3	a	49.5	35.7	0.29	0.045	0.79
13 - 2.5 µm	ъ	20.55	10.3	0.118	0.0245	0.406
mean5µm %	E	42.1	28.9	47.1	54.4	57.4
CS4	a	47.3	36.9	0.27	0.032	0.67
8 - 0.8 µm	ь	35.35	24.46	0.20	0.0326	0.488
'mean 2.5 µm %	E	74.1	66.3	74.1	100	77.8
CS5	a	46.7	38.3	0.33	0.028	0.56
.5- 0.3 μm	ъ	44.8	26.35	0.325	0.0302	0.543
≃ mean 0.5 µm %	E	98.5	68.8	98.5% (100%)	107.8%	97%

* % E = % atomization efficiency slurry/aqueous

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Atomization efficiency as a function of particle size using straightthrough spray chamber and 3 mm i.d. injector tube as part of the sample introduction system 100 □ Fe₂0₃ • Al₂0₃ • Mg0 × TiO₂ + SiO₂ Atomization efficiency (%) 80 60 40 20 5 10 15 20 25 30

Mean particle size (um)

tubes as part of the sample introduction system, for the finest clay fraction (in which aluminium is found at its highest concentration - Table XVII). Alumina is a highly refractory metal and can withstand high temperatures without breaking or deforming and the results obtained can be explained by the phase diagram for a binary Al_20_3 - Si0₂ system (Figure 73) described by Aramaki and Roy (229). As the phase diagram shows, pure alumina is stable to 2050°C before it melts whereas pure silica can only withstand temperatures to approximately 1700°C. Material less than 72% Al_2O_3 (the alumina content in clay is typically 37%) form some liquid at temperatures above 1595°C. For temperatures above 1600°C, materials containing more than 72% Al_20_3 are more refractory as these form no liquid below 1840°C. At these compositions there is no free silica only alumina and mullite $(3Al_20_3 \cdot 2Si0_2)$. For even higher temperatures, above 1840°C pure alumina (95 - 100%) may have melting points up to 2050°C. All alumino-silicates form some mullite when fired at temperatures above 1200°C but the exact amount formed depends on many factors and not just the alumina to silica ratio. Therefore when clay is heated, as it would obviously do in the plasma, phase changes take place (also see Chapter 6) and at high temperatures alumina substitutes to a certain extent with the silica in the kaolinite structure and this refractory nature of alumina could account for the low atomization efficiency observed.

From studies using both the 2.2 mm i.d. and 3 mm i.d. injector tubes, the actual sample introduction systems were found to be directly responsible for the effect of particle size on atomization. Using the 3 mm i.d. injector together with a vertical injection nebulizer (i.e. with the direct spray chamber) it was hoped that larger particles might reach the plasma and hence improve atomization efficiency and

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% A12⁰3

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this would also facilitate an investigation to establish the slurry particle size able to be atomized in the plasma.

5.4.4 Effect of particle size on atomization efficiency using

3 mm i.d. injector with vertical injection nebulizer

5.4.4.1 Experimental

A vertical direct spray chamber was constructed out of glass and details are given in 5.3.2.2.1 (Figure 67d). Particle size distribution data obtained from a slurry sample collected at the 3 mm i.d. injector tube showed a cut-off of 16 μ m particle size, enabling larger particles than previously encountered to reach the plasma (Figure 74).

Using the vertical injection nebulizer, the plasma discharge was found to be very sensitive to change in operating conditions such as gas flow rates - in particular too high injecter gas flow rates or uptake rates tended to extinguish the plasma due to solvent overloading. As a result the simplex optimization procedure was not used to find the optimum operating conditions but compromise conditions were chosen where best plasma stability and signal reproducibility were achieved.

These operating conditions are noted below in Table XXIV.



Table XXIV

Compromise Plasma Operating Conditions for

Direct Injection Nebulizer

Parameter

Coolant gas/l min ⁻¹	27.6
Plasma gas/l min ⁻¹	3.7
Injector gas/l min ⁻¹	1.6
Forward power*/kW	2.7
Height/mm	2.8
Sample uptake rate/ml min ⁻¹	1.2

*Forward power - reflected power.

Major and minor elements were determined in the 0.2% w/v clay separates slurries previously used (section 5.3.3).

5.4.4.2 Results and discussion

Major and minor element results for the clay separates slurries are reported in Table XXV. Similar atomization efficiencies were obtained for the 3 mm i.d. injector using both the direct injection nebulizer and the 'straight through' spray chamber. For both systems the fine clay fraction with particle sizes less than $4 - 5 \mu m$ produced nearly 100% atomization efficiency. No marked improvement was obtained for the coarser size fractions, although particles as much as 12 - 16 μm in size were known to reach the plasma (Figure 74). This suggested that particles greater than 8 μm are only partially atomized or more likely pass through the plasma without being atomized. This is diagramatically shown in Figure 75.

5.5 <u>Conclusions</u>

Using the clay separate slurries, of varying particle size fractions,

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TABLE XXV

<u>Major and minor element (% w/w) data for clay separates by (a) ICP</u> solution (b) ICP slurry atomization, using 3 mm i.d. injector tube

Sample		Si0 ₂	A12 ⁰ 3	MgO	Ti0 ₂	Fe203
mwl	а	50.7	27.5	0.50	.0.22	1.95
coarse sample	e b	5-5	2.38	0.0266	0.00526	0.056
(mean size 25 μm)	%E	10.8	8.65	5.32	2.4	2.9
mw2	а	48.5	35.5	0.33	0.093	1.13
(mean size	ъ	8.6	3.12	0.0278	0.00424	0.0639
12.5 µm)	%E	17.7	8.9	8.4	4.6	5.7
 mw3	а	49.5	35.7	0.28	0.045	0.79
(mean size 5 µm)	Ъ	16.3	10.2	0.091	0.0124	0.268
	%E	32.8	28.6	32.5	27.6	33.9
mw4	a	47.3	36.9	0.27	0.032	0.67
(mean size 7.5 μm)	ъ	36.8	25.8	0.211	0.0231	0.531
	%E	77.8	69.9	78.1	72.2	79.3
mw5	a	46.7	38.3	0.33	0.028	0.56
fine sample	b	46.5	33.0	0.329	0.030	0.543
(mean size 10.5 µm)	%Е	99.6	86.0	(100)	107	97.0
1				99.7		

and direct injection nebulizer

% = % atomization efficiency slurry/aqueous

Direct injection nebulizer 3 mm i.d. injector (12 - 16 $\mu\text{m})$

. Figure 75

Atomization efficiency as a function of particle size using

3 mm i.d. injector tube and vertical injection nebulizer



particle size was found to have a critical effect on transport efficiency. For the initial sample introduction system, this was found to be directly attributed to the cut-off of the spray chamber and injector tube. By characterizing the different spray chambers and injectors tubes by particle sizing, the 'straight through' chamber and 3 mm i.d. injector tube were found to be most promising for slurry atomization as larger particles were allowed to reach the plasma. Using the new sample introduction system results showed that atomization efficiency was again directly related to the cut-off of the sample introduction system itself. However marked improvements in atomization efficiency was increased for the fine clay fraction where nearly 100% was obtained. Using the direct injection nebulizer together with the 3 mm i.d. injector, particles as much as 16 μ m reached the plasma, although atomization efficiencies were similar to those obtained with the 'straight through' chamber which suggested that particles greater than 8 μ m were not atomized in the plasma. This type of design was found to produce an unstable plasma and from these findings the 3 mm i.d. injector and 'straight through' spray chamber together with the fixed geometry PTFE Babington type nebulizer, are considered a suitable sample introduction system for slurry atomization and adopted for rest of the work.

5.6 <u>Major, minor and trace analysis using the modified sample introduction</u> system

5.6.1 Major and minor element analysis

Major and minor elements were determined in the bulk 'SR' clay, by slurry atomization. The results were compared with the fusion results obtained by ICP-OES reported in Table XVIII in this chapter.

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5.6.1.1 Experimental

'SR' clay was made up to a 0.2% w/v slurry with 0.35% m/v aqueous ammonia. The plasma operating conditions were those identified by the simplex optimization procedure and are shown in Table XXII. Wavelengths were those chosen for the clay separates study (section 5.2.1.1).

5.6.2 <u>Trace element analysis</u>

Trace elements were determined in the bulk 'SR' clay, by slurry atomization and the results compared with those obtained using hydrofluoric/perchloric digestion procedure (this digestion procedure was more appropriate for trace element analysis as it included a lesser dilution factor than the lithium metaborate fusion technique previously used for the major element analysis).

5.6.2.1 Experimental

5.6.2.1.1 <u>Digestion procedure</u>

Into a platinum dish kaolin powder (2g) was weighed accurately and a small amount of distilled water (1 ml) was added to disperse the sample. To this, perchloric acid (5 ml) and hyaropivoric. acid (10 ml) was added, and placed on a hot place to evaporate until fumes of perchloric acid was observed. This was to ensure complete removal of hydrofluoric acid. Hydrofluoric acid preferentially evaporates off first as its boiling point (120°C) is lower than that of perchloric acid (203°C). The H∋removes the silica as the volatile silicon tetrafluoride. A further 10 ml hydrofluoric was added to completely remove the silica and placed on a hot plate to evaporate, this time to dryness. The residue was then digested with perchloric acid (5 ml). Hot perchloric acid is a powerful oxidizing agent and ensured decomposition of the fluorites formed. After evaporation to dryness, the residual

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was extracted with hydrochloric acid (5 ml) and placed on a hot plate to dissolve the salts. This was then made up to 50 ml with distilled water. The plasma operating conditions used were those optimal for solution analysis (Table IX).

5.6.2.1.2 Slurry procedure

'SR' clay was made up to a 20% w/v slurry with 0.35% aqueous ammonia. Plasma operating conditions are shown in Table XXII and wavelengths chosen were those used in the preliminary study (Table X). Lanthanum was used as an internal standard to correct for viscosity effects (see Chapter 4).

5.6.3 Results and Discussion

Table XXVI compares the major and minor element results obtained using slurry atomization technique with those obtained by the conventional fusion technique. Almost 100% atomization efficiency was obtained for all elements. Slurry trace element results were adjusted by use of internal standard, to correct for the viscosity effects arising from the increased slurry concentration used for the analysis. These are reported in Table XXVII together with the digestion results. Good agreement was shown for Cu and Ni and reasonable results for Mn and Zn. Discrepancy in results was observed however for chromium. This may be attributed to chromium, in the form of Cr_2O_3 , being of similar nature to alumina and as with the previously noted problems of alumina, is not fully atomized in the plasma.

5.7 <u>Influence of 3 mm injector on emission signal and stability</u> The following aspects were considered in this investigation.

(i) detection limit

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Table XXVI

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Major, minor element data for 'SR' clay (% w/w)

Element	XRF/ICP soln	ICP_slurry	<u>%</u> E
Si0 ₂	. 46.5	46.7	100
A12 ⁰ 3	38.5	36.4	95
MgO	0.19	0.17	90
Ti0 ₂	0.03	0.03	100
^{Fe} 2 ⁰ 3	0.49	0.44	90

Table XXVII

Trace element data for 'SR clay (µgg⁻¹)

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Element	ICP Soln	ICP slurry*
Zn	18.8	24.3
Ni	4.18	4.1
Mn	17.2	20.5
Cr .	11.2	4.9
Cu	20.0	20.0

%E Atomization efficiency

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* Corrected for viscosity effects by use of internal standard

 (ii) the stability of the analyte signal for both slurries and standards <u>i.e.</u> reproducibility

(iii) sample reproducibility

5.7.1 Detection limits

The detection limits (dl) were calculated by the formula below:-

 $dl = 3 \times sbg \times c/(s - bg)$

where

sbg = standard deviation of background intensity

c = 1st standard concentration ($\mu g g^{-1}$)

bg = background signal intensity (cs^{-1})

s = net signal intensity of first standard (cs^{-1})

Detection limits for magnesium in slurry and magnesium in solution were determined at the 280.270 nm line and compared to those obtained using the 1.8, 2.2 and 4 mm i.d. injector tubes as part of the sample introduction system. Table XXVIII shows that the best detection limits were obtained with the 1.8 and 2.2 mm i.d. tubes. However, they are only slightly better, by a factor of 2, than those obtained for the 3 mm injector. Detection limits for the 4 mm i.d. injector tube are drastically poorer. This was expected as the velocity emergent of injector gas was insufficient to punch a hole in the plasma for the sample to enter and hence poor signals together with poor signal to noise ratio (SNR) were observed.

No significant difference in detection limits for magnesium in slurry and magnesium in solution was observed, although from previous analysis it was noticed that detection limits for trace elements in slurries tended to be poorer than those obtained in solution due to increased background caused by ion recombination (see Chapter 1) particularly for element wavelengths in the 200 - 300 nm region of the spectrum.

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Injector tube	Gas F	lows	1 min ⁻¹	Maximum	Height/mm	Power/kW	Detection	Detection	Comments
	Coolant	Plasma	Injector	lateral velocity 	velocity ms ⁻¹		for slurry/ ppb	for aqueous/ ppb	
(a) 1.8 mm ID	30.6	3.7	2.4	15.7	28.4	3.2	9	8	prone to partial blocking
(b) 2.2 mm ID	16.0	3.6	2.6	11.4	23.3	1.8	9	7	conventional injector tube
(c) 3 mm ID	32.0	4.2	2.8	6.6	31.5	2.9	22	15	suggested tube for slurry work
(с) 4 mm ID	20,5	4,1	3.0	4.0	31.1	2.7	11,000	6,000	unstable plasma

Table XXVIII Detection Limits for Magnesium using Simplex Optimised Plasma Conditions Mg II 280.270 nm

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5.7.2 Stability

The stability measurements were preformed at the optimum operating conditions for that particular torch/spray chamber, nebulizer system. The ICP was allowed to stabilize for $\frac{1}{2}$ hour before any measurement was taken.

A 10 μ g g⁻¹ solution of magnesium was nebulized continuously, during which time 18 - 20 x 10 sec integrations were recorded. A 0.5% slurry was nebulized in the same way as the solution.

The emission signal for both the slurry and solution, were relatively stable, giving acceptable RSDs of 1.6 and 1% respectively (Figure 76). Sample reproducibility, by preparing six slurries from one powder sample, were also determined and gave a similar RSD of 1%.

5.7.3 Reoptimization

The simplex optimization procedure had so far failed to find the best conditions for slurry atomization. Similar optimal operating conditions were obtained for both slurries and solutions. It was thought that the initial simplex procedure failed to find the best conditions as both the slurry and solution background signals were similar and therefore cancelled each other out, leaving the criterion of merit without a background term. Another approach to the simplex procedure was investigated, changing the criterion of merit to incorporate a background term and to weight the slurry signal, by squaring the SBR of the slurry, as follows:-

(SBR)² slurry

SBR solution

The optimal operating conditions obtained using this criterion of

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merit were not dissimilar to those obtained previously for slurry atomization. However a slight improvement in the slurry atomization efficiency was observed when looking very high in the plasma where emission signal was poor for both slurries and aqueous solutions. This could be seen when SBR slurry/SBR solution was plotted against the height profile, as in the univariate search (Figure 77), suggesting that perhaps atom lines (as they are more sensitive than ion lines at that height in the plasma) might be more suitable for slurry atomization. This was investigated by aspirating a 5% w/v clay into the plasma together with an aqueous standard of equivalent concentration. The emission signals were measured for iron, as the test element, using the 371.994 nm atom line and 239.562 nm ion line. The results were disappointing with no difference in atomizaton efficiency observed, suggesting that the simplex optimization procedure had already found the best operating conditions for slurry atomization.

5.8 <u>Conclusions</u>

Using the modified sample introduction system clay slurries containing particles less than 5 μ m, such as the 'SR' clay, can be fully atomized in the plasma, and hence 100% atomization efficiencies can be achieved. For clay samples containing particle sizes greater than 5 μ m, the Si correction factor (see Chapter 3 Tables XXb and XIV) can be successfully applied to the results obtained to correct for varying atomization efficiencies due to variation in particle size. Acceptable RSDs for both signal stability and sample reproducibility can be obtained using this modified sample introduction system for slurry atomization.

As a suitable analytical method has been established for the analysis of kaolin, using slurry atomization, this approach was applied to

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a range of sample types and are discussed in the following chapter.

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height above load coil (mm)

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6. INVESTIGATION OF SLURRY ATOMIZATION CHARACTERISTICS BY POST-PLASMA TRAPPING OF MATERIAL

6.1 Introduction

A water-cooled quartz 'cold-finger' was used for the trapping of postplasma material by placing it approximately 50 mm above the load coil for a couple of hours until sufficient sample was collected. Initially a kaolin slurry, consisting of a wide particle size distribution, was introduced to the plasma using the initial sample introduction system.

From obtaining the post-plasma sample it was hoped that by using several different analytical techniques it might be possible to identify the transition process of a kaolin sample through the plasma and hopefully giving some indication of the slurry atomization characteristics.

X-ray diffraction is a method wich has been extensively used in understanding the crystallographic mineralogy of kaolin. It serves as the major method of identification of kaolin and interpretation of its crystal structure. Comprehensive literature has been assembled by Brindley (230) and Brown (231).

In addition to X-ray analysis, another useful tool for the characterization of clays is thermal analysis. Weight changes, such as water loss, may be followed by thermal gravimetric analysis (TGA) and phase changes by differential thermal analysis (DTA). The temperatures at which such changes occur are typical for various types of clays. The literature on DTA has been authoritatively and comprehensively discussed by Mackenzie (232).

Infrared spectroscopy (IR) is also a useful tool in identifying mineral

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species and in deriving information concerning the structure and composition of minerals and mineral products. Infrared radiation is absorbed and converted by a covalent-bonded molecule into energy of molecular vibrations. Since infrared absorption is related to covalent bonds, the spectra can provide much detailed information about the structure of molecular compounds. Literature on the applicability of IR spectroscopy to ceramics and thermal transformations of minerals has been assembled by Freund (233).

Finally electron microscopy, although primarily a qualitative technique, allows the study of individual particles and is helpful in identification of the mineral.

6.2 X-ray diffraction analysis of clays

6.2.1 <u>Experimental</u>

The instrumentation used was a Philips Diffractometer with a PW 1770 diffractometer control (Philips, York Street, Cambridge). X-ray diffraction was carried out on two samples, (a) original 'BP Kaolin' sample and (b) the post-plasma 'BP Kaolin' sample. The specimens were mounted as flat powders and presented to the X-ray beam. The diffracted beams were received at a receiving slit and passed through a plate collimator and finally entered the counter through a scatter slit. The counter was electronically set to give maximum response to the CuKg radiation used and the equipment was allowed to scan through the 2 σ range of interest, 50 to 80°. The pulses from the counter were fed into a chart recorder, recording the peaks (high count-rates of radiation) in relation to the varying 2 σ angles.

6.2.2 Results and discussion

X-ray diffraction traces for (a) original kaolin sample and (b) postplasma material are given in Figures 78a and b. XRD data is also given for (a) in Table XXIX. In the table a reference spectrum of the principal kaolin mineral is included with calculated d-values. These were taken from Brown (231).

From Figure 78a it can be seen that the original 'BP Kaolin' was well crystallized. Good agreement was found with literature X-ray diffraction data for kaolin. However, no 'd' spacings were observed in the postplasma 'BP Kaolin' sample spectrum suggesting that the crystalline structure had broken down on heating through the plasma and the resulting post-plasma material was amorphous.

6.3 Differential thermal analysis of clays (DTA)

6.3.1 Experimental

The instrumentation used was a Stanton Redcroft STA simultaneous thermal analysis system (Stanton Redcroft 671B, Copper Mill Lane, London). Simultaneous TGA (measures change in weight) and DTA was performed on two single samples (a) original 'BP Kaolin' sample and (b) the post-plasma material from aspirating 'BP Kaolin' sample. In the DTA apparatus, a small portion of each of the powdered samples was placed individually in a platinum crucible. The furnace was heated at a constant rate of 20° min⁻¹ to about 1500°C. The actual temperature of the samples at any one time was measured by determining the temperature difference between the sample and an inert material (aluminium oxide, which does not change in the temperature range studied) by means of a thermocouple. With constant heating, any transition or thermal induced reaction in the samples was accompanied

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Figure 78

a. X-ray diffraction pattern for original clay

5°

80° (RFS 5000c/s)

b. X-ray diffraction pattern for post-plasma material



. (221)-		
Lit Ref (231)	$\frac{d(A)}{d(A)}$	
	9.91	m
	9.04	m
7.16	7.12	
4.46	4.45	m
4.36	4.35	
4.18	4.17	
3,84	3.83	m
3.74	3.71	m
3.57	3.56	
3, 37	3.34	m, Q
3.14		
· · · · 3.10		
2.56	2.56	m
2.53		
2.49	2.49	
2.38	2.38	
2.34	2.34	
2.29	2.29	
2.25		
2.19		
2.13	· ·	
2.06		
1.99	1.99	m
1.94		
1.90)	
1.87	,	
1.84	· ·	•
1.81		
1.78		
1.71	L	
1.69)	
1.66		
. 1.62	1.62	
1.58	}	
1.54		
1.49	1.49	
1.45	5	
Q = Quartz)		
)	impurities	
<pre>m = muscovite mica)</pre>		

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X-ray diffraction data for (a) original kaolin sample

by the absorption (endothermic) or the liberation (exothermic) of heat, recorded as negative and positive peaks respectively, in an otherwise straight line.

6.3.2 <u>Results and discussion</u>

Figures 79a and b show the DTA/TGA curves for the original kaolin sample and the post-plasma material respectively.

The original 'BP Kaolin' clay exhibited a typical kaolin DTA curve. An endothermic peak was observed at about 570°C. This peak corresponds to the dehydration of the kaolin when all water molecules and (OH) ions are driven off. This was confirmed by the TGA curve where a weight loss was observed at this temperature. The mineral produced at this stage is called meta-kaolinite. These are generally highly disordered but some workers (234,235) have shown by the use of X-ray and electron diffraction that some order remains. The nature of the metaphases is not known in detail, but they are found to yield a fairly well ordered kaolinite on rehydration (236).

When kaolinite minerals are heated beyond 800°C their layered structures are further disrupted and cannot be reconstituted by rehydration.

At still higher temperatures, phase changes of crystal lattice take place, which is indicated by an exothermic peak around 990°C and many different conclusions have been reached. The interpretation of Brindley and Nakahira (237) is considered to be the most satisfactory, this is represented by the reaction sequence as follows

 $A1_20_3$. $2Si0_2$. $2H_20$ \longrightarrow $A1_20_3$. $2Si0_2$ + $2H_20$ Kaolinite 400 - 600°C Meta-Kaolinite

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Figure 79 a Differential thermal analysis (DTA) and thermal gravimetric



analysis (TGA) of the original kaolin

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Figure 79b Differential thermal analysis (DTA) and thermal gravimetric analysis (TCA)

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$2(A1_{2}0_{3} \cdot 2Si0_{2})$	>	$2A1_{2}0_{3}$. $3Si0_{2} + Si0_{2}$
	900 - 1000°C	silicon spinel amorphous silicon
^{2A1} 2 ⁰ 3 · 3Si0 ₂		$2(A1_{2}0_{3} \cdot Si0_{2}) + Si0_{2}$
	1100°C	1:1 mullite-type cristobalite phone
3(A1 ₂ 0 ₃ . Si0 ₂)	>	3A1 ₂ 0 ₃ . 2Si0 ₂ + Si0 ₂
	above 1400°C	3:2 mullite cristobalite

In Figure 79b, the post-plasma 'BP Kaolin' DTA/TGA curves showed no corresponding endothermic or exothermic peaks or water loss, suggesting that the post-plasma sample had already exceeded the temperature of 1400°C and that no kaolinite or meta-kaolinite remained in the sample.

6.4 Infrared spectroscopy of clays

6.4.1 Experimental

The instrumentation used was a grating infrared spectrophotometer (Perkin Elmer 357,Perkin Elmer Ltd.,Beaconsfield, Buckinghamshire). Infrared spectroscopy was performed on two samples, (a) original 'BP Kaolin' sample and (b) the post-plasma 'BP Kaolin' sample.

Samples were prepared for analysis by incorporating them into a pressed disc of potassium bromide (KBr). A weighted portion (2mg) of each of the powdered samples were thoroughly mixed with a weighed quantity (200 mg) AnalaR salt powder. Then the mixture was submitted to a pressure of several tons in an evacuated die, producing a highly transparent disc which was inserted into a special holder for the spectrophotometer. A KBr disc without the kaolin powder was used as a blank, in the reference beam. Radiation was passed through the sample and the intensity of infrared radiation absorbed was recorded.

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The calibration of the spectrophotometer with respect to wavenumber scale was performed by scanning the infrared spectrum of a polystyrene film.

6.4.2 Results and discussion

The IR spectra for (a) the original kaolin sample and (b) the postplasma material are shown in Figures 80a and 80b respectively.

From Figure 80a it can be seen that the original kaolin sample exhibits a typical spectrum of a well crystallized kaolinite. The general features of the OH stretching absorption are well established for kaolinites. A study by Jacobs (238) indicated that the 3669, 3652 and 3620 cm⁻¹ bands of kaolinite are indistinguishable in their behaviour. Kaolinite minerals, as can be seen in Figure 80a have distinctive perpendicular vibrations near 755 and 701 cm⁻¹ that probably involve the surface hydroxyl layer. The strong absorption in the 400 - 550 cm⁻¹ region can be associated with Si-0 bending vibrations.

From Figure 80b it is noticed that the dehydration introduces a number of important changes in the spectrum. All modes involving vibrations of OH groups disappear. The broad absorption band between 1000 -1100 cm⁻¹, assigned to (Si-O) - and (Al-O)- stretching modes, shift to higher wavenumbers. Workers (239,240) have shown that the strong 990°C exothermal reaction observed by DTA introduces little change in the IR spectrum. The single broad band at 450 cm⁻¹, which builds up after the exothermal reaction, (<u>i.e.</u> above 990°C) can be assigned to (Al-O)- and (Si-O)- bending modes in a random arrangement of (AlO₄)and (SiO₄)- tetrahedra.

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Figure 80a The infrared spectrum of the original kaolin sample

Wavenumber (cm^{-1})



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% Transmittance

Figure 80c The infrared spectrum of the post-plasma material obtained using modified sample introduction system



In the phase changes which take place when kaolin is heated, Al-Si spinel is formed from kaolin and this in turn begins to change into mullite. As the formation of mullite proceeds, silica would be expelled and Al/Si ordering causes the band to split into two separate bands. These bands shift apart and gain sharpness. Eventually for wellcrystallized mullite formed from the melt at 1700°C, these bands would be located at 550 and 430 cm⁻¹ (233). However these bands are not detected for the post-plasma material which suggested that wellcrystallized mullite had not been formed. This is confirmed by the XRD results which indicated the post-plasma material collected was amorphous.

6.5 Electron microscopy

6.5.1 Experimental

The instrumentation used was a Transmission Electron Microscope (Philips EM 300,Philips, Cambridge, England). Electron microscopy was performed on two samples, (a) original 'BP Kaolin' sample and (b) the post-plasma material. Samples were prepared for analysis by suspension in distilled water. A portion of the suspension was dropped onto a copper grid, dried and placed in the electron microscope (operated at 80 KV current).

6.5.2 Results and discussion

The micrographs for (a) the original kaolin sample and (b) the postplasma material are shown in Figures 81a, b, c and d.

From Figures 81a and b it can be seen that the major part of the original 'BP Kaolin' sample consists of pseudohexagonal particles which are thin and of variable dimensions. Numerous dislocations and deformations can be discerned and each particle is monocrystalline.

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magnification 130 x 10^3



magnification 28 x 10^3





81a

magnification 130 x 10^3



magnification 5 x 10^3

81d



using modified sample introduction system magnification 30 x 10³



magnification 8 x 10^3



81e

81f
However the post-plasma material exhibits no specific particle shape or structure (Figures 81c and d) again suggesting that the crystalline structure had broken down on heating through the plasma and the resultant post-plasma material is amorphous.

6.6 General discussion

Preliminary results suggested that the collected material was more representative of a metamorphosed fraction than of atomization although the electron microscopy results seemed more suggestive of recombination. Also of these techniques used for identifying mineral types, IR spectroscopy looked the most promising. It was thought, however, that the large particles from the clay slurry may have passed straight through the plasma and impacted on the water-cooled tube, hence the results observed may be attributed to a 'baking' effect from the heat and not of atomization. To alleviate such problems the post-plasma trapping of material was repeated but this time using the modified sample introduction system (i.e. 'straight through' spray chamber and the 3 mm i.d. injector tube) and the fine particle-sized 'SR' clay as it has been shown, in the previous chapter, that all the particles reaching the plasma appeared to be atomized. The water-cooled tube was also placed nearer the plasma fireball (20 mm) to enable a closer contact with the aerosol stream in the central channel.

The post-plasma sample was then analysed using the IR spectroscopic and electron microscopic techniques. The results obtained are shown in Figures 80c and 81e and f for IR and electron microscopy, respectively. The post-plasma materials collected, showed similar results to the previous material (see Figures 80b and 81cd). The IR traces suggested that either the temperature experienced by the slurry particles in

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the plasma was less than 1700°C, as no peaks were observed at 430 and 550 cm⁻¹ which are indicative of well crystalline mullite (forms at \approx 1700°C) or more likely that the post-plasma sample was non-crystalline. The DTA indicated temperatures higher than 1400°C had been experienced. However the electron micrographs did suggest that the post-plasma material was representative of atomization and recombination, as the particle structures were completely broken down into small amorphous particles, loosely packed together and of a 'feathery' edged appearance.

7. APPLICATIONS OF SLURRY ATOMIZATION

7.1 Introduction

Slurry atomization has been applied to the analysis of various samples. Slurry atomization was applied to elemental monitoring of abrasive materials in kaolin. Particular emphasis was placed on finding anomalies, rather than on absolute accuracy, in an attempt to find an elemental indicator of abrasivity.

Previous studies on the determination of trace metals in coal slurries (148) seemed more promising than preliminary results for refractory geological samples such as silicates. For coal a two stage atomization process was suggested. Firstly the relatively large particles are pyrolysed in the plasma fireball, leaving behind smaller particles of ash, which are subsequently atomized. Consequently 'soft' rocks such as the carbonate material of dolomite and 'hard' rocks such as basalts were also considered for slurry atomization.

7.2 <u>Elemental monitoring of abrasive samples by slurry atomization</u>

7.2.1 Introduction

The clays used in the present work came from the primary deposits in Cornwall. Here the clay is extracted by the pit face being bombarded with jets of water at high pressure (which reduces the kaolinised rock to a fluid slurry). The slurry flows to the bottom of the pit and from there to a trough. There, the coarse non-kaolinite minerals settle out rapidly and are raked from the trough and discharged to waste. A second separation of the finer 'impurities' which are still coaser than the kaolinite, follows by hydrocyclone process. The raw kaolinite slurry, purified from most of the non-kaolin minerals, is then passed on for further processing.(220) This may consist of a further particle

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size separation of the clay sedimentation into 'coarse' and'fine'particle sized minerals. English China Clay is normally refined by a cut at 20 µm (214).

Fortunately, the kaolin produced consists essentially of much smaller particles than most of the associated minerals and the commercial production of china clay is based on this fact. However; impurities such as quartz and feldspars have been found in particles as little . as 2 μm in size (241). The china clays, which seldom consist of the single mineral kaolinite (see Figure 64) may contain various amounts of other constituents, notably mica, quartz, feldspar, tourmaline, rutile, anatase and montmorillonite. The amounts of these constituents vary with location and there is evidence that it is these non-kaolinite constituent minerals that contribute to the increase of abrasive properties in clay (241). The removal of abrasives from the kaolin bulk is of great importance to the china clay industry with particular regard to the final commercial use of the clay. Some clays, with low abrasion values, are used for 'Juling' in the paper industry and any significant level of abrasives in the clay could lead to expensive mechanical wear to the machinery and especially decrease the use of paper machine wires. The abrasivity/particle size relationship contributes to the appropriate grading of the clay product. The relative abrasion levels in clays are commonly determined by ECLP using the 'valley abrasion' technique, based on the relative hardness of the minerals. The hardness of the minerals using the Moh scales are: kaolinite 2.0 - 2.5, muscovite 2.76 - 3.00, anatase 5.5 - 6.0, potassium feldspar and rutile 6.0 - 6.5, quartz and tourmaline 7.0 - 7.5 (241). Thus it might be expected that the non-kaolinite minerals would increase the abrasion of a china clay in the order mica < anatase < feldspar

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and rutile < quartz <tourmaline. The valley abrasion technique, however, is tedious and time consuming, with reproducibility of abrasion measurements $\pm 10\%$ RSD and large volumes of slurry (approx 1 litre) are needed.

In this study it was hoped to identify elements characteristic of abrasive minerals and thus provide a quicker and less tedious means of monitoring the relative abrasivity via elemental composition for on-line processing. From a literature survey, six trace elements were found to be strongly associated with the abrasives, B,Ba,V,Rb, Cs and Li. Boron is a major constituent in tourmaline, typically <u>eg</u> $NaFe_{3}B_{3}Al_{3}$ (OH)₄(Al_{3}Si_{6}O_{27}), whilst the rest are more associated with the micas at trace level. The general formula which describes the chemical composition of micas is

X₂Y₄₋₆Z₈O₂₀(OH,F)₄ X is mainly K,Na, or Ca but also Ba,Rb,Cs etc Y is mainly Al,Mg or Fe but also Mn,Cr,Ti,Li etc Z is mainly Si or Al but perhaps also Fe³⁺ and Ti Barium is also strongly associated with the alkali feldspars.

Selected elements were determined in samples supplied by ECLP, of the product, feed and residue from a froth-flotation plant in Cornwall.

7.2.2 <u>Preliminary Studies</u>

7.2.2.1 Experimental

Initially, feed, product and residue samples were spectrally scanned for the trace elements referred to above. Further elemental monitoring of abrasives by slurry atomization was confined to only three elements (B,Ba and V) as Li, Rb and Cs could not be detected in the samples

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as the most sensitive spectral lines needed for this work, were outside the wavelength range of the spectrometer. Boron, barium and vanadium were determined. The slurries were spray as received and the percentage solids together with particle size distribution data measured.

7.2.2.2 Operating conditions and wavelength selection

Plasma operating conditions were those identified as optimal for slurry atomization, referred to in Table XXII in Chapter 5.

Table XXX	Wavelength selection for	r element monito	oring of abrasives
Element	Wavelength/nm	Atom/Ion	Sensitivity Ranking (Ref 193)
Boron	249.678	I	2
Vanadium	292.403	II	3
Barium	455.403	II	1

7.2.2.3 Results and discussion

A qualitative spectral scan of the abrasive samples yielded little information. The product and residue samples appeared to be contaminated by the flotation process. Discussions with ECLP Research Department on this matter suggested the contamination may be via the water source used to spray the froth down.

However the quantitative results were more encouraging as can be seen in Table XXXI.

Table XXXI	Element	determinations	in Abrasive	Samples
Sample	Boron	Vana % w/	ıdium 'w	Barium
Feed	0.0094	1.06	$x 10^{-4}$	0.00228
Product	0.0044	7.89	10^{-5}	0.00124
Residue	0.0164	2.88	10^{-4}	0.00532

The highest concentration for all three elements was found in the residue sample, as would be expected if these elements are indicative of the abrasive material. The figures obtained by slurry atomization were calculated with respect to the original percentage slurry (shown in Table XXXII).

Table XXXII	Percentage weight per	volume of	slurries	used	in	this	study
	Product	30.4%					
	Feed	21.1%					
	Residue	4.55%					

The mass balance of the flotation plant process (assuming the feed is equivalent to 100%) was reported as typically 60 - 65% product and 35 - 40% residue. When this mass balance is applied to the figures in Table XXXI, the balance was encouraging (see Table XXXIII). The slight discrepancy may be due to differences in the time of sampling for all three samples.

Table XXXIII	<u>Mass bala</u>	nce assuming 60/40 ratio	2
Sample	Boron	Vanadium % w/w	Barium
Product	0.00265	4.73 x 10 ⁻⁵	2.87×10^{-3}
Residue	0.00656	1.15×10^{-4}	7.44×10^{-4}
= Feed	0.00921	1.63×10^{-4}	2.13×10^{-3}

The particle size distribution data of the product, residue and feed samples are shown in Figure 82a,b and c respectively. These would seem to be all essentially similar.

From the preliminary studies, boron, vanadium and barium looked promising as elements characteristic of abrasive minerals, which might provide a means of monitoring abrasives via elemental composition. A more detailed study of the relationship between abrasion levels and B,V and Ba was preformed.

7.2.3 <u>Study of relationship between abrasion levels and elemental</u> compositon

For this study four batches (termed batch(s) 1 - 4) of product, feed and residue samples, of varying abrasion levels, were supplied by ECLP. A further batch of 3 samples (termed batch 5) each exhibiting similar particle size range, were later supplied to investigate if the apparent correlations between the concentrations of B,Ba and V with the abrasivity was not an artefact of particle size correlations.

7.2.3.1 Experimental

7.2.3.1a Batch 1

The first batch of samples were washed to ensure freedom from previous reagent contamination introduced during the froth-flotation process and then dried in an oven at 110°C overnight. Two sub samples were taken from each sample type to enable the determination of B,Ba and V by both the conventional ICP analysis, in solutions following a standard sodium hydroxide fusion, and by slurry atomization. Sodium hydroxide fusion was used for this particular study, instead of the previous

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lithium metaborate fusion, to enable the determination of boron.

7.2.3.1.1 Sodium hydroxide fusion procedure

Into a nickel crucible AnalaR sodium hydroxide pellets (7g) were placed and gently fused until the water was expelled and a clear melt was obtained. After this was allowed to cool, the weighed sample (0.5g)was introduced evenly on the solidified melt, moistened with a little ethanol, which was then gently heated over a Bunsen burner, with occasional rotation of the crucible, until the sodium hydroxide was just molten, after which the temperature was raised to a dull red heat for 2 - 5 minutes; the sample was then completely dissolved. The crucible was carefully cooled by partial immersion in a beaker of cold water. When the melt had just solidified the crucible was removed from the beaker with clean tongs, a jet of hot water was introduced into the crucible which sufficed to dissolve the fused mass. When the vigorous reaction had subsided, and having carefully rinsed the crucible inside and out with hot water, the dissolved sample together with the rinsings were transferred to a volumetric flask into which concentrated HCl (20 ml) had been placed. This was cooled to room temperature and diluted to 100 ml in the volumetric flask.

7.2.3.1.2 Direct slurry atomization

The solid clay samples were made up to 6% w/v slurries with distilled water and placed in an ultrasonic bath for $\frac{1}{2}$ hr before aspiration into the ICP.

7.2.3.1b Batches 2 - 4

The slurries were sprayed as received and the percentage solids together with particle size distribution data measured.

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7.2.3.1c Batch 5

Samples, received as solids, were made up 20% w/v slurries with distilled water.

Plasma operating conditions were those identified as optimal for slurry atomization as given in Table XXII. Aqueous standards were used for the slurry analysis.

7.2.3.2 <u>Results and discussion</u>

Element determinations in Batch 1 abrasive samples are shown in Table XXXIV. The highest concentrations for the elements determined by both the fusion and slurry atomization procedures were found in the residue sample, confirming previous findings that suggested these elements are indicators. However the atomization efficiencies (approx 13%) were relatively low compared to previous work on clay slurries, which reflected the coarse nature of the abrasive samples analysed.

No vanadium results were obtained for this batch of samples as both the vanadium concentration in the fusion and the slurry were below the instrumental detection limits (see Table XXXV). From Table XXXV it can be seen that poor detection limits were obtained for boron, but this was mainly due to bad memory effects often found to be a problem with boron determinations.

Batches 2,3 and 4 showed similar results, as can be seen in Table XXXVI, with an increase in concentration for Ba, V and B with increase in abrasion levels. A direct correlation between the figures obtained by direct slurry atomization and the abrasion figures supplied by ECLP are shown in Figures 83,84 and 85 for barium, boron and vanadium.

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Elemental analysis of 1st Batch of Abrasive Samples - Batch 1

		sio ₂	Ba	В
Duradurat 1	a	58.5	0.00701	0.0234
Product 1	ъ	7.9	0.00122	0.0034
Abrasion e. 54	с	13.5% E	17.5% E	14.5%
	a	-	0.00906	0.0250
	a	61.5	0.0141	0.0341
Feed l	ъ	9.2	0.00188	0.0042
Abrasion 148	с	15.0%	13.3% E	12.3%
	d		0.0127	0.0281
	a	63	0.0234	0.0456
Residue l	ъ	8	0.00272	0.0043
Abrasion 200	с	12.7% E	11.6% E	9.3% E
	đ	-	0.0212	0.0339
1		1	1	1

(% w/w)

- (a) Fusion (NaOH fusion. 0.5 g sample \rightarrow 100 mls)
- (b) Slurry atomization (sample 6 g → 100 mls)
- (c) % E Atomization efficiency
- (d) Si corrected figures
- (e) Valley abrasion as reported by ECLP

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Detection limits/ng ml -1

	aqueous standards	slurry	fusion
Barium	2.9	2.7	2.7
Vanadium	29	43	38
Boron	47	64	-

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Table XXXVI

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Element determinations in Abrasives samples by

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<u>slurry atomization for Batches 2 - 4</u> ‰/v

	Sample	Valley	Barium	Vanadium	Boron
		Abrasion	<u>(x10³)</u>	$(x10^{3})$	<u>(x10³)</u>
		Figure			
	2F	107	2.62	6.88	3.8
Feed	3F	250	2.58	8.15	4.22
	4F	120	2.23	8.41	2.53
	2R	273	4.87	7.77	6.99
Residue	3R	340	6.57	0.14	5.66
	4R	255	5.04	9.97	5.82
	2P	74	1.87	-	2.74
Product	3P	82	1.79	5.06	2.47
	4P	50	1.50	6.03	1.93





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Figure 85



The lines drawn on the graphs were calculated from linear regression analysis and the correlation co-efficients are given. The graphs for barium and boron were particularly encouraging, with a good spread of points and correlation co-efficients of 0.89 and 0.87 respectively. The results for vanadium (Figure 85) showed slightly poorer correlation, as expected, as the levels of this element were close to the instrumental detection limit. The figures obtained by slurry atomization were calculated with respect to the original percentage slurry (see Table XXXVII). The particle size distribution data for the product, residue and feed samples are shown in Figures 86,87 and 88. A slight increase in particle size was observed in the sample order residue > feed > product.

Elemental determinations for Batch 5 abrasive samples are shown in Table XXXVIII. For all elements similar results were obtained for the four samples, reflecting no substantial difference in their abrasion levels. The concentrations for Ba,B and V were slightly higher than in previous abrasive studies, which could be attributed to the finer particle size range exhibited by this particular batch of samples.

7.2.4 <u>Viability of elemental monitoring to determine relative</u> <u>abrasivity as an on-line process</u>

7.2.4.1 Introduction

As the results were promising, a further batch of 27 samples (<u>i.e.</u> 9 residue, 9 feed and 9 product samples) from various flotation sources, a,b and c were evaluated using this technique to assess the viability of this method for on-line monitoring. But this time the Si levels were monitored simultaneously to allow for correction of varying slurry concentrations and hence atomization efficiencies, as would be necessary in an on-line application.

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Results on Froth-Flotation plant samples

for Batches 2 - 4

	Valley Abrasion Figure (⁺ 20%)	v /v of slurry
2 F	107	21.7
2 P	74	10.1
2 R	273	7.9
. 3 F	250	21.8
3 р	82	12.0
3 r	340	6.0
4 F	120	. 21.5
4 P	50	10.9
4 R	225	7.4

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PARTICLE SIZE DISTRIBUTION









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Table XXXVIII

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Sample	Valley Abrasion Figure (± 5%)	Barium (x 10 ³)	Boron (x 10 ³)	Vanadium (x 10 ⁺)
i	51 ± 2.6	6.75	3.97	1.74
ii	83 ± 4.2	2.52	4.88	1.69
iii	103 ± 5.2	2.50	5.11	1.64
iv	86 ± 4.3	2.56	5.85	1.80

Element determination in Abrasive samples - Batch 5 % w/w

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7.2.4.2 Experimental

Selected elements and wavelengths were those previously chosen for the initial work on abrasives, with the addition of silicon measured at the 505. 610 nm atom line. Samples were analysed as received. A subsample of each slurry was dried in an oven at 110°C overnight and used to determine the percentage water content. This was to check the use of Si levels as a correction factor for varying solids content. Abrasive figures were determined using the valley abrasion technique by ECLP.

7.2.4.3 Results and discussion

As previously mentioned, silicon was determined in order to correct for varying water content of the slurries. In Table XXXIX, good agreement between SiO_2 levels and the percentage (w/v) slurries was observed indicating that this would be a suitable correction factor for online monitoring. This is diagramatically shown in Figure 89.

Tables XXXX- XXXXII show the abrasion figures with the corresponding element levels ratioed to the silicon, for Ba,V and B respectively and are diagramatically shown in Figures 90(i),91(i) and 92(i). The results obtained were less encouraging than those from the previous studies. Of the three elements, Ba seemed to be the most promising with a correlation coefficient of 0.60. The boron results were particularly dissapointing with a correlation coefficient of 0.27. As previously mentioned, B is strongly associated with tourmaline which is considered to be a significant contributor to abrasivity. These results suggested that perhaps micas and feldspars to which Ba is associated, play an important role. It was thought that the correlation of element concentration and abrasion might be source

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Table XXXIX

from varying sources						
Sample	Source	Valley abrasion	% w∕v slurry	SiO ₂ (µg g ⁻¹)		
Products		Figure				
		(<u>+</u> 8%)				
1 2 3 4 5 6 7 8 9	a b c	162 77 70 67 71 73 73 64 71	24.79 18.97 21.98 24.60 11.78 10.11 11.52 12.48 10.77	9,590 8,860 9,350 12,400 3,140 2,950 2,780 2,440 2,240		
Feeds						
1 2 3 4 5 6 7 8 9	} a } b } c	190 185 167 171 129 126 123 179 182	22.55 18.67 17.26 20.08 22.34 24.01 7.51 21.12 21.30	7,460 7,510 5,920 4,480 6,440 7,460 5,520 4,530 4,720		
Residues						
1 2 3 4 5 6 7 8 9	a b c	251 280 264 248 180 194 248 410 213	13.43 8.94 14.54 11.32 11.11 6.97 7.17 4.36 4.41	3,140 2,690 3,760 3,680 2,860 1,890 1,640 650 832		

Slurry concentration and silicon figures for samples 1 - 9

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		Valley Abrasion Figures	Barium %w/w (x10 ³)	Barium SiO ₂ Ratio (x103) ²
<u>Sc</u>	ource a			
3	Feed	167	3.62	1.06
	Product	70	2.71	0.637
	Residue	264	5.09	1.97
1	Feed	190	3.58	1.08
	Product	162	2.30	0.594
	Residue	251	3.90	1.67
4	Feed	171	4.87	2.18
	Product	67	3.96	0.785
	Residue	248	6.28	1.93
2	Feed	185	3.38	0.840
	Product	77	2.97	0.635
	Residue	280	6.04	2.01
So	urce b			
5	Feed	129	3.97	1.38
	Product	71	2.41	0.904
	Residue	180	6.84	2.66
6	Feed	126	3.17	1.02
	Product	73	3.45	1.18
	Residue	194	11.74	4.33
7	Feed	123	7.50	1.02
	Product	73	2.71	1.12
	Residue	248	8.31	3.63
So	urce c			
8	Feed	179	2.40	1.12
	Product	64	1.47	0.754
	Residue	410	6.03	4.05
9	Feed	182	5.21	2.35
	Product	71	3.36	1.62
	Residue	213	. 10.89	5.73

feed and residue samples

Barium results ratioed to silicon for product

Table XXXXI

Vanadium results ratioed to silicon

For Feed, Product and Residue samples

		Abrasion ·	Vanadium/SiO_Ratio (x10 ⁵)	
Sourc	e a			
3	Feed Product Residue	167 70 264	1.31 1.09 2.85	
1	Feed Product Residue	190 162 251	0.676 1.12 0.503	
4	Feed Product Residue	171 67 248	1.82 0.903 4.49	
2	Feed Product Residue	185 77 280	0.283 0.551 ND	
Source	<u>e b</u>			
5	Feed Product Residue	129 71 180	0.627 1.03 1.47	
6	Feed Product Residue	126 73 194	1.07 2.35 2.21	
7	Feed Product Residue	123 73 248	0.861 1.35 4.49	
Source	<u>e c</u>			
8	Feed Product Residue	179 64 410	1.15 1.58 2.85	
9	Feed Product Residue	182 71 213	2.18 2.26 0.731	

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Boron results ratioed to silicon,

for feed, product and residue samples

		Abrasion	Boron/Si0 ₂ Ratio
			$(x \ 10^{\overline{4}})$
Source a 3	Feed Product Residue	167 70 264	5.07 3.90 6.89
1	Feed	190	3.73
	Product	162	4.13
	Residue	251	4.36
4	Feed	171	1.09
	Product	67	3.23
	Residue	248	3.89
2	Feed	185	1.96
	Product	77	3.39
	Residue	280	3.00
Source b 5	Feed Product Residue	129 71 180	3.2 6.05 4.20
6	Feed	126	2.06
	Product	73	5.08
	Residue	194	6.98
7	Feed	123	2.3
	Product	73	4.68
	Residue	248	6.83
Source c 8	Feed Product Residue	179 64 410	2.47 4.71 6.74
9	Feed	182	3.33
	Product	71	5.27
	Residue	213	9.69

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Figure 90(i) Correlation of barium results ratioed to silicon, with abrasion

figures for product, feed and residue samples obtained from all sites





product, feed and residue samples obtained from source a





for product, feed and residue samples obtained from source b



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for product, feed and residue samples obtained from source c










for product, feed and residue samples obtained from source a





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for product, feed and residue samples obtained from source b



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figures for product, feed and residue samples obtained from source c





Figure 92(ii)a Correlation of Boron results ratioed to silicon, with abrasion figures



for product, feed and residue samples obtained from source a

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Correlation of Boron results ratioed to silicon, with abrasion figures for



product, feed and residue samples obtained from source b



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dependent and a better correlation might be achieved if these were plotted with regard to a particular source from which the samples were obtained. These are shown in Figures 90(ii),91(ii) and 92(ii) for Ba,V and B respectively where graphs a,b and c refer to that particular source. Improvement was observed for all elements, particularly for barium, for which correlation coefficients of 0.78 and 0.86 were obtained for sources a and b respectively (see Figure 90(ii)). This suggested that abrasivity may be source dependent.

From these initial studies, barium looked the most promising element indicative of abrasivity. Together with the use of silicon to adjust for varying water content of the slurries could be used as a potential means of elemental monitoring of abrasion levels for on-line monitoring in the flotation process. This method could prove to be more rapid and less tedious than the commonly used valley abrasion technique and as already mentioned, also has the potential for on-line monitoring for which, as yet, there is no such available method.

7.3 Analysis of dolomite using slurry atomization

7.3.1 Introduction

Dolomite is a highly-ordered mineral consisting of calcium and magnesium ions in separate layers, alternating with carbonate ions. It is a sedimentary rock with composition CaMg $(CO_3)_2$. Most dolomites result from the alteration of calcium carbonate sediments which are derived from biological materials.

A standard reference sample (BCS No 368) was initially analysed using the slurry method established for the kaolin samples and then was repeated using a partial dissolution technique.

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7.3.2 Preliminary studies

7.3.2.1 Experimental

The dolomite sample was wet-ground with water using a McCrone micronising mill (McCrone Research Associates Ltd, London) for approximately $1\frac{1}{2}hr$ until the majority of the particles were reduced to less than $5 \mu m$ in size (Figures 93a and b show the particle size distribution of dolomite before and after grinding). The grinding elements used in the micronising mill were corundum and therefore the determination of aluminium was omitted from the dolomite analysis due to the potential for contamination.

Dolomite was made up to a 0.2% w/v slurry using 0.35 m/v aqueous ammonia and calibrated using aqueous standards. This was then repeated but this time with an equivalent amount of ammonia added to the standards (see Chapter 4). Major and minor elements were determined in the dolomite using the plasma operating conditions identified as optimal for slurries using the 3 mm i.d. injector tube as part of the sample introduction system and are shown in Table XXII. The following wavelengths, Table XXXXIII were selected as giving best signal to background ratio, consistent with linearity of calibration over the concentration of interest and freedom from spectral line interferences by the components in the sample.

Table XXXXIII Wavelength selection for major and minor

Element	Wavelength/nm	Atom I/Ion II	Sensitivity(193)
Si	212.412	I	2
Fe	259.940	II	1
Mn	260.569	II	3
Mg	280.270	II	2
Ti	334.941	II	1
Ca	393.366	TI	1
Al	396.152	I	3

analysis of dolomite



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7.3.2.2 <u>Results and discussion</u>

Major and minor element results for dolomite using aqueous standards with and without ammonia for calibration is given in Table XXXXIVa and b. The results were surprisingly disappointing when compared to the certificate values supplied with the certified reference material. Atomization efficiencies were in the range 28 - 33%. As Figure 93b showed, the dolomite slurry contained a particle size thought to be ideal for slurry atomization. The results were even more surprising as dolomite is less refractory than silicates, and in comparable analysis of coal slurries (148) were found to be less dependent on particle size. This preliminary investigation had shown that aqueous ammonia was not a suitable dispersant for dolomite slurries and the results obtained were a reflection of the partial agglomeration of particles which were therefore unlikely to reach the plasma, hence the low atomization efficiencies. As with the Si correction factor used for kaolin analysis, to correct for varying atomization efficiencies arising from the effect of particle size, a similar factor was used for dolomite. If the results for individual elements are ratioed to those obtained this time for calcium (as calcium is one of the major constituents of dolomite and the concentration is relatively constant within dolomite types) the situation is greatly improved. Good results were obtained for all elements studied and therefore this appears a promising technique for the analysis of dolomites with varying particle sizes.

The results obtained for dolomite using aqueous ammonia in the standards, for calibration, showed a slight increase in atomization efficiencies for iron only. This was due to the suppression of the standard arising from the colloidal effect of the hydroxide species formed (discussed

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Table XXXXIVa

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	<u>Major and</u>	l minor elemer	nt data for	r dolomi	<u>te</u> (% w/w)	
Sample	Si0 ₂	MgO	Ti0 ₂	Mn0	Fe 2 ⁰ 3	Ca0
a	0.92	20.9	<0.01	0.06	0.23	30.8
Dolomite b	0.26	5.79	0.00384	0.02	0.07	8.86
%Е	28.3%	27.7%	-	33.3%	28.7%	28.8%
с	0.90	20.1	0.0086	0.07	0.23	
			<0.01			

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Table XXXXIVb

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Sample	SiO ₂	MgO	Ti0 ₂	MnO	^{Fe} 2 ⁰ 3	Ca0
a Dolomite	0.92	20.9	<0.01	0.06	0.23	30.8
b	0.26	5.79	0.007	0.02	0.08	8.86
%E	28.3	27.7	-	33.3	34.8	28.8

- a certified values
- b slurry atomization
- %E Atomization efficiency

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c Ca corrected

in Chapter 4). For further reduction, an increased concentration of ammonia could have been added to adjust the pH to form further element hydroxide species. However as this is element dependent the Ca correction factor could obviously only be applied to correct for elements unaffected by the addition of aqueous ammonia or otherwise overcorrection would result.

As the addition of an alkali 'dispersant' such as aqueous ammonia, was found to be unsuitable for the slurry analysis of dolomite, an alternative approach was to try an acid dispersant which in effect acted as a partial dissolution technique. This involved the simple addition of an acid to the powdered sample which enabled the analysis of samples without preliminary grinding and therefore decreased the sample preparation time. A similar approach has ben reported for the determination of metal particles in wear oils (242).

7.3.3 <u>Analysis of dolomite for major, minor and trace elements</u> by the partial dissolution technique

7.3.3.1 Experimental

a) Major and minor elemental analysis

Dolomite (0.2g) was initially made up to 100 ml with 1% v/v concentrated HNO_3 acid. This was then repeated using 1% v/v concentrated HCl to see if any improvement in atomization efficiency could be achieved. Equivalent concentration of acid was added to the aqueous standards to eliminate possible sample operating conditions and wavelength selection were those used in the previous study (Section 7.3.2).

b) Trace elemental analysis

To find the optimum addition of HNO_3 for a 5% w/v slurry used for

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the trace element analysis, a range of acid concentrations 0 - 30% v/v were added to both the slurry and an equivalent concentration standard. The emission signal was measured for manganese using the 260 . 569 nm ion line. The addition of 20% v/v HNO₃ was found to be optimal for the partial dissolution of a 5% w/v dolomite slurry (Figure 94) and consequently was used for this study. Element wavelengths chosen for the analysis of trace elements in dolomite are shown in the Table below:-

Table XXXXV

Selected wavelengths for trace element

analysis of dolomites

Element	Wavelength/nm	Atom I/Ion II	Sensitivity (193)
Cr ·	205.552	II	1
Cu	324.754	I	1
Zn	213.856	I .	4
Pb	220.353	II	1
Sr	407.771	II	1

7.3.3.2 Results and discussion

Results obtained using the slurry partial dissolution technique were compared to the certificate values (see Table XXXXVIa for major and minor elements and Table XXXXVII for trace elements). Encouraging results were obtained for all major, minor and trace elements with atomization efficiencies ranging from 79 - 100% except for silicon and aluminium which, as expected, gave lower atomization efficiencies of 59 and 31% respectively, due to their refractory nature and poor solubility in nitric acid. No significant improvement in atomization efficiency was observed for the major and minor elements using HCl except for aluminium (Table XXXXVIb) for which only a slight improvement

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Figure 94 Effect of nitric acid concentration on Mn (II 260.569 nm) emission signal

 HNO_3 concentration (%)

Table XXXXVI(a)Major and minor element data for dolomite
using the partial dissolution procedure (% w/w)SampleSi02Al203Mg0Ti02Mn0Fe203Ca0

							5	
	a	0.92	0.17	20.9	<0.01	0.06	0.23	30.8
0.2% slurry	Ъ	0.55	0.053	20.5	0.0048	0.06	0.203	30.8
+ 1% HnO ₃ 5	%E	59.8	31.3	98.1		100	88.3	100

Table XXXXVI(b)

Sample		Si0 ₂	^{A1} 2 ⁰ 3	MgO	^{TiO} 2	MnO	^{Fe} 2 ⁰ 3	Ca0
	а	0.92	0.17	20.9	<0.01	0.06	0.23	30.8
0.2% slurı	ry b	0.52	0.064	20.5	0.0050	0.06	0.204	30.3
1% HC1	%E	56.5	37.6	98.1	· - 1	.00	88.7	98.4

- a certificate values
- b slurry atomization
- %E Atomization efficiency

Table XXXXVII

	Trace	element	data for	<u>dolomite</u>	using the	partial
		dis	solution	procedure	(Aig g ⁻¹)	
Sample		Cr	Cu	Zn	РЪ	Sr
	а	40 <u>+</u> 4	3 <u>+</u> 1	82 <u>+</u> 6	61 <u>+</u> ľ	• 67 <u>+</u> 15
5% slurry	b	39.4 [,]	3.94	62.8	52.2	2 66.2
+ 20% HAO ₃	%E	98.5	131%	78.5	85.6	5 98.8

a = Certificate values

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b = Slurry atomization

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%E = Atomization Efficiency

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was observed due to its increased solubility in the acid.

This method could prove to be a viable alternative to the conventional technique, requiring minimal sample pretreatment. However this is dependent on whether knowledge of aluminium and silicon concentrations are important for the conmercial use of the dolomite product. Alternatively the slurry atomization technique using the calcium correction factor could be used.

7.4 Analysis of basalts using slurry atomization

7.4.1 Introduction

The basalt samples used in this study were derived from Mt Etna and are composed of mixed mineral types with no defined composition. They are an igneous microcystalline volcanic rock composed of pyroxene and plagioclase. The chemical composition of such rocks are frequently determined to gain information on magma processes produced from volcanic eruptions.

As with the dolomite sample, the basalts were initially analysed using the established slurry technique for kaolin.

7.4.2 Preliminary studies

7.4.2.1 Experimental

The basalt samples were wet-ground with water using the McCrone micronising mill for approximately $1\frac{1}{2}$ hr until the majority of the particles were reduced to less than 5 µm. This is shown in Figure 95. The samples were dried in an oven and then were made up to 0.2% w/v slurries with 0.35% w/v aqueous ammonia and placed in an ultrasonic bath for $\frac{1}{2}$ hr before determination of major and minor elements. Wavelengths were those used for the dolomite work and are shown in Table XXXXIII. The results were then compared with XRF results (243).

7.4.2.2 Results and discussion

Results for major and minor elements are given in Table XXXXVIII. The results were disappointing when compared with the corresponding results, with atomization efficiencies in the range 14 - 32%. Although

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the particle size was optimal for slurry atomization (i.e. < 5 µm), the poor atomization efficiencies could be assigned to the mixed mineral nature of the basalts and the separation of the lighter type minerals may have occurred during agitation process, using the magnetic stirrer, before aspiration. However large agglomerates were clearly visible by optical microscopy and therefore were unlikely to reach the plasma. It was felt that the drying process of the sample, after grinding, mayhave contributed to the aggregation of the particles by packing them into a well ordered form and therefore the removal of this process for future work, may help to overcome the agglomeration problem. The results did however indicate that aqueous ammonia was not a suitable dispersant for basalt slurry atomization. As with the kaolin samples, if the individual elements are ratioed to silicon i.e. using the Si correction factor to correct for varying atomization efficiencies arising from particle size effect, reasonable results can be obtained (Table XXXXVIII).

Several dispersants, for slurry atomization of basalts, were investigated including Triton X-100, Microclean, sodium hexametaphosphate, and tetra-sodium pyrophosphate. Unfortunately none of the reagents used showed any significant improvement in the dispersion of basalts.

A feasibility study, using an equal density medium (<u>i.e.</u> equal density to basalt, ρ 2.8 - 2.9) to help remove the agglomeration problem previously encountered, was performed. The dispersion problem may possibly be overcome by the use of equal density medium but the effect of solvent on the analytical performance of the ICP was unknown.

· bade name

Figure 95



Table XXXXVIII

	Major and minor element data for Basalts									
	using slurry atomization* (% w/w)									
Samp	ole	SiO ₂	MgO	Ti0 ₂	Mn0	^{Fe} 2 ⁰ 3	Ca0			
1	а	38.2	13.15	2.61	0.2	12.84	13.87			
Basa	b 1t	6.5	2.49	0.527	0.03	1.99	2.79			
5454	%E	17.0%	18.9%	20.2%	15.0%	15.5%	20.1%			
· .	с	-	14.63	3.10	0.18	11.70	16.4			
2	a	48.78	4.77	1.67	0.19	10.14	10.36			
Basa	b	10.0	1.32	0.514	0.037	2.35	3.3			
5404	%E	20.5%	27.7%	30.8%	13.2%	21.4%	31.9%			
	с	-	6.44	2.51	·0.18	11.46	16.10			
3	а	48.36	4.69	1.68	0.18	10.52	10.27			
Basa	b lt	7.05	1.08	0.47	0.03	2.07	2.11			
	%E	14.6%	23.0%	28.0%	16.7%	18.2%	20.5%			
	с	-	7.41	3.22	0.21	14.2	14.48			

* using initial sample introduction system <u>i.e.</u> 2 mm i.d. injector tube and double pass spray chamber.

a = XRF results

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- b = Slurry atomization
- %E = Atomization Efficiency
- c = Si Corrected

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7.4.3 <u>Feasibility study on the slurry atomization of basalts using</u> an equal density medium

1,1,2,2 tetrabromoethane was chosen as the organic medium for the basalt slurry, with a density 2.9 g/cm³ at 20°C. It is commonly employed in geochemistry to separate samples into their constituents, by use of their different densities (244).

The introduction of organic solvents to the ICP has been widely reported, including the use of solvent extraction in sample preparation to remove the analyte of interest from a complex matrix and may also be used to produce a preconcentration of the analyte, before aspirating into the ICP (81). Introduction of organic matrices to ICP have also been reported for determination of wear metals in used lubricating oils (242) and when the ICP is used as an element selective detector for high-performance liquid chromatography (245). The use and effects of organic solvents for ICP analyses have recently been reported by Boorn and Browner (246) and Barrett and Pruszkowska (247).

7.4.3.1 Experimental

Basalt sample 2 was analysed for Si, Fe and Cu only, as organo metallic standards for these elements were readily available in the form of dimethyldichlorosilane, ferrocene and copper 4 cyclohexylbytrate respectively. The basalt sample was made up to a 3% w/v slurry with tetrabromoethane and then analysed using the organo metallic standards also prepared in tetrabromoethane.

Plasma operating conditions were those previously used in both the dolomite. Wavelength selections were also those previously used and are shown below:-

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Element	Wavelength/nm	• <u>Atom I/Ion II</u>
Si '	212.412	I
Fe	259.940	II
Cu	324.754	I

7.4.3.2 <u>Results and discussion</u>

Results using the equal density medium for slurry atomization of basalts are given in Table XXXXIX.

Table XXXXIX

	<u>Element</u>	data for b	asalt obtained b	y slurry atomization
		using	an equal densit;	y medium
	Fe2 ⁰ 3	(% w/w)	Si0 ₂	Cu (mg g ⁻¹)
а	10.14		48.2	131
Ъ	2.79		1.06	23
% Е	27.5		2.2	17.6

a Results obtained by XRF

b Slurry atomization using equal density medium

%E Percentage atomization efficiency

Only a slight increase in atomization efficiency was observed for iron compared to the result obtained using aqueous ammonia as the medium. Iron and copper gave atomization efficiencies of 27.5 and 17.6% respectively and these low atomization efficiencies could still be explained by the effect the dispersion problem. With the aid of an optical microscope, flocculation of particles were still observed although disaggregation of the larger particles was apparent. The silicon results were very disappointing, with atomization of only

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2.2% compared to 20% previously obtained. This may be attributed to the influence of the low boiling point of the dimethyldichlorosilane on the evaporation rate of the tetrabromoethane medium, resulting in an enhancement of the standard emission signal. This evaporation effect appears to dominate the transport efficiency and the difference in solvent loading in the plasma would also be expected to affect the plasma excitation mechanism.

A detailed investigation of the nebulization of organic solvents in atomic spectrometry has been reported (248). The relative rates of solvent evaporation from aerosol droplets, were shown to be critical in determining the transport efficiencies of organic solvents more volatile than water. On comparison solvents of low volatility, such as nitrobenzene, the difference in surface tension was considered to be the main effect of transport efficiency.

A major problem encountered in the use of an organic media for slurries, was finding suitable and easily available organic standards which were miscible or soluble in the organic solvent used. It is essential to matrix match standards with that of the slurry to eliminate possible transportation or plasma mechanisms effects, as highlighted in the silicon results.

The use of an equal density medium such as tetrabromoethane for slurry work appeared to have little or no effect on the dispersion of basalts. However the use of organic solvents should not totally be dismissed. Improvements in atomization efficiency may be achieved by optimizing the plasma operating conditions for the particular solvent used. Boorn and Browner (246) found that an increase in forward RF power

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and nebulizer gas flow produced a corresponding increase in the ICP tolerance to organic solvents. This was interpreted in terms of solvent evaporation from the aerosol droplets. Performance was also found to vary with viewing height and analyte line selection due to changes in the plasma excitation mechanisms. This was attributed to large vapour loadings by highly volatile solvents which caused a temperature decrease in the plasma and low emission signals for ion lines were observed.

From these preliminary studies slurry atomization appears to have a useful application in the analysis of geochemical samples, providing a simple, rapid technique with minimal sample preparation. The partial dissolution technique proved to be a successful alternative for the analysis of dolomites, with the exception of the silicon and aluminium determinations, whilst the use of an equal density medium to help overcome the agglomeration problem, for analysis of basalts,would obviously need further work.

8. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The atomization of kaolin slurries using the high temperature atom cell available with the inductively coupled plasma has been, investigated. The method has been found to show considerable promise for the determination of major, minor and trace elements in kaolin. Clearly the use of slurries would markedly reduce analysis times by combining matrix destruction, analyte atomization and excitation into one step, thus avoiding dissolution techniques which have been found to be tedious, risk contamination and sometimes the need of potentially hazardous chemicals.

While preparation of kaolin slurries was simple and rapid, analytical problems of a more fundamental nature were encountered. Atomization efficiency in nebulizer based systems was shown to be dependent on particle size. Traditionally problems of nebulizer blockages are encountered when samples containing suspended solids are nebulized, due to the small orifice (0.35 mm i.d.) through which the sample emerges. A significant contribution to the avoidance of such problems has been made by the modified 'Babington' type nebulizer, used through this work, in which the sample is not required to pass through a narrow orifice but instead, through a relatively broad capillary (1 mm) enabling high solid content slurries (up to 35%) to pass through without blockage. The construction and performance of the 'high solids' PTFE nebulizer based on the Babington design shows great promise for the ICP-OES analysis of slurries. The one-piece, fixed-geometry, nebulizer additionally offers the advantages of being robust, chemically inert and just as important, the design is reproducible.

Despite obvious advantages, the preliminary kaolin studies showed

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the plasma atomization efficiency in the slurry nebulization technique to be low, typically 50% or less of those of aqueous solutions of equivalent concentration. However a marked improvement in atomization efficiency (50-70% for Mg) was achieved by the addition of aqueous ammonia (0.35% m/v) as a dispersant. Although preliminary studies on the application of the slurry atomization procedure to the analysis of both dolomite and basalt samples found aqueous ammonia was unsuitable as a dispersant. Dispersion is one of the major problems of using slurry atomization for a variety of sample types. There are however a number of surfactants/dispersants commercially available and an investigation into finding a suitable dispersant for a particular sample type is obviously a great need.

The effect of viscosity on the nebulization process was also found to impair the atomization efficiency, especially when using high concentration slurries (>8% w/v) as in the trace element analysis of kaolin. This was successfully corrected by the use of an internal standard. Precision and accuracy could further be improved by the use of two internal standards (which do not give rise to complex spectra), determined at both atom and ion lines of varying difficulties of excitation.

The failure to achieve equal atomization efficiency for aqueous and slurry nebulization was found to be related to particle size. By analysing slurries with different defined particle sizes and relating the results to the particle size distribution of the sample actually reaching the plasma, the relationship between particle size and atomization efficiency and the influence of sample introduction design parameters on the emission signal intensity was determined. Particle

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size was clearly the critical factor in determining atomization efficiency for slurries. Using the original sample introduction system (consisting of a Babington type nebulizer with impact bead, doublepass spray chamber and a 2 mm i.d. injector tube) for all major and minor elements studied, atomization efficiency was biased in favour of slurries containing a high concentration of finer particle sizes. Particles less than 3 µ.m produced the largest signal, with atomization efficiencies around 70%. Particles less than 5 µm were shown to contribute very little to the observed signal. This was attributed directly to the rejection of the larger particles (greater than 3 -5 μ m) by the sample introduction system. To allow larger particles to enter the plasma, the sample introduction system was modified by reforming or removing the original aerosol modifying devices such as impact beads and impaction surfaces were minimized. From investigating a variety of nebulizers, spray chambers and injector tube configurations, a 3 mm i.d. straight capillary injector tube and 'straight through' spray chamber were found to be the most suitable for slurry atomization, allowing larger particles, $6 - 8 \mu m$, into the plasma. Results from the clay separate slurries showed that atomization efficiency had markedly improved. The fine clay slurry (particles less than 5 µm) in fact gave nearly 100% atomization efficiency suggesting that most of the sample actually entering the plasma was atomized. Atomization efficiency also improved markedly for the coarser particle size slurries. But again the atomization was influenced by the larger particles, greater than $6 - 8 \mu m$ being excluded, by the sample introduction system. However, the construction of a vertical injection nebulizer together with the 3 mm i.d. injector tube enabled particles as much as 16 μm in size to reach the plasma and similar results were obtained for the clay separate slurries. This suggests that particles greater

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than 6 - 8 μ m in size are not atomized in the plasma. For slurries containing particles greater than 6 μ m, reasonable results can be achieved by use of the silicon ratio (Chapter 3) as a correction factor for varying atomization efficiencies arising from variation in particle size. As kaolin particles are strongly associated with water, an increase in the percentage of sample actually reaching the plasma might be achieved by the evaporation of the slurry droplets before entering the plasma, by means of a heated spray chamber.

Another area of work could use slurry nebulization to elucidate details of the atomization mechanism in the plasma. The theory of nebulization and atomization in an ICP is at present embryonic with evidence for four different atomization/excitation theories (66) and that water plays an important role in connection with atomization of aqueous samples (67). As previously mentioned, it has been suggested that introducing water into the plasma brings the ICP closer to local thermal-equilibrium. The ability of slurry samples with varying water contents to thermalise the plasma could be investigated. For aqueous solution samples good signal to backgrounds are favoured by a high excitation temperature and low kinetic temperature, but for slurry samples it is presumed the kinetic temperature plays an important role in atomization. Effects of signal and background, at analyte wavelengths of different difficulties of excitation, of varying aqueous solution and slurry content may enable the effects of water, nonmaxwellian behaviour and influence of analyte form to be studied, hence providing a useful tool for probing ICP mechanisms.

In conclusion to this study, slurry atomization, with the aid of simple aqueous calibration, can be successfully used to determine major,

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minor and trace elements in powdered geological samples such as kaolin. Using the modified sample introduction system, clay slurries containing particles less than 5 µm, can be fully atomized in the plasma and hence 100% atomization efficiency can be achieved. For clay slurries containing particles sizes greater than 5 µm, a correction factor (such as the silicon ratio for kaolin), can be successfully applied to correct for varying atomization efficiency arising from variation in particle size. Also, as acceptable RSDs for both signal stability and sample reproducibility can be achieved using this modified sample introduction system, ICP-OES slurry atomization seems an attractive technique for both geological prospecting and quality control, providing adequate grinding and a suitable dispersant is sought. Success of the application of slurry atomization to different geochemical type samples would depend on the particle size distribution produced by grinding, and hence would be influenced by the grinding characteristics of the geological samples of interest.

Slurry atomization would have the advantage over traditional solid analysis techniques, such as XRF, by the ease of calibration using simple aqueous standards. This method also has the potential to analyse varying slurry concentrations up to 25 - 30% w/v and therefore minimises dilution factors, a problem associated with the conventional dissolution techniques needed for ICP analysis, thus enabling the direct determination of major, minor and trace elements. The method, however, may be limiting for the determination of certain elements such as the refractory alumina in clay, but this may not necessarily be a problem as it is minor and particularly the trace elemental data that is usually of major concern to the geochemist.

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