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OPTIMISATION OF THE INDUCTIVELY-COUPLED PLASMA FOR THE ANALYSIS OF SOLUTIONS AND SLURRIES

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ABSTRACT

The application of inductively-coupled plasma (ICP) spectrometry for the analysis of solutions and slurries is reviewed. The critical parameters which affect analytical performance are identified and methods for the optimisation of the ICP for such applications demonstrated.

Particle size of the suspended sample is shown to be the most important factor in the analysis of slurry samples. It is demonstrated that only particles less than 8 um in diameter reach the plasma even when the maximal diameter injector tube (3 mm i.d.) is used. Accordingly various methods for the reduction of particle size have been investigated and milling shown to be the preferable approach. A low cost method using blown zirconia spheres in a screw-cap plastic bottle agitated on a flask shaker was developed. Using this method it proved possible to analyse a wide variety of solid samples using slurry atomisation using both ICP- atomic emission spectrometry (ICP-AES) and ICP-mass spectrometry (ICP-MS) with aqueous calibration.

Results are presented for the elemental analysis of certified reference material (CRM) soils, catalyst samples, a zeolite, titanium dioxide, P.T.F.E. powder, and unfiltered natural waters by slurry atomisation ICP-AES.

Comparison by other techniques showed excellent accuracy for major, minor and trace elements and equivalent precision to solution analysis. The CRM soils, catalysts and the zeolite were also analysed by ICP-MS using slurry atomisation with similar success and enhanced accuracy at the trace level. Aluminium proved to be an exception and generally low recoveries (80-90%) were observed for this element using slurry atomisation.

Finally the uses of the simplex optimisation algorithm to improve analytical performance, particularly in ICP-AES, is discussed. A computer program to facilitate the use of simplex optimisation for a variety of instrumentation was written and its use in three different analytical techniques demonstrated.

The necessary hardware and software modifications to a commercially available ICP spectrometer to enable automated simplex optimisation are described. The prospects for such intelligent self-optimising instrumentation are discussed as is the potential extension of the application of slurry analysis by ICP-AES and ICP-MS.

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CHAPTER 1

1.1

Introduction

The analytical chemist of today is called upon to perform an increasingly large number of varied tests on the raw materials and products of industry. To this end he has developed a set of techniques which cover every aspect of characterising unknown materials. These include not only the structure and composition of the bulk material but also properties of the surface, the homogeniety of the materials, partical size, viscosity and a large number of other important characteristics. Perhaps one of the most common pieces of information required is that of elemental composition. This need not be solely for the determination of the major constituents of a material and is frequently required as a measure of the purity of a material where the bulk composition is already known. It is in this area of analysis where the analyte is at minor, trace or ultra-trace levels that the chemist relies most heavily upon the techniques of atomic spectrometry. Since the 1950's these techniques have gained acceptance and have become the methods of choice for elemental determinations. With the ever increasing demands of industry for speed, accuracy and lower limits of detection, atomic spectrometry has grown and developed into a whole series of powerful techniques and become a distinct area of analytical chemistry with its own conference meetings, journals and specialist terminology. Due to the many advantages gained by calibration and analysis using simple solutions, such as reduction of matrix effects and guaranteed homogeniety, most of these techniques have developed requiring the sample to be in the form of a solution. This has left the analytical chemist in the somewhat absurd position of spending as much as twenty times as long preparing his sample for analysis as actually making the measurement. With the current trend of reduced manpower within the analytical laboratory there has been a great deal of pressure placed upon the chemist to reduce the time spent preparing samples for analysis since this is by far the most time consuming activity. This is being tackled in two ways, one of which is laboratory automation which is arousing a great deal of interest possibly due to its impressive and emotive terminology. The second and perhaps most practical approach is that of the development of new analytical methods and techniques which require far less sample preparation. This in itself would have many benefits not only due to time saving but also in terms of reduced risk of contamination (and increased matrix in the case of fusion based methods) and the possibilities of higher sample concentration and hence analyte concentration in the atom cell leading to lower levels of determination. A discussion of the direct analysis of solid samples by various techniques is given as the introduction of Chapter 2.

The remainder of this thesis deals with the refinement of one already established analytical technique for the analysis of solutions, inductively-coupled plasma optical emission spectrometry, and the extension of its capabilities to include the analysis of solids by a slurry sample introduction technique. A slurry being a homogeneous dispersion of solid particles within an aqueous medium.

1.2

Introduction to the Inductively-Coupled Plasma

The past decade has seen the maturing and popularisation of Inductively-Coupled Plasmas (ICP) as powerful tools for simultaneous or sequential multi-element analysis of solutions by atomic emission spectrometry. This is due to the outstanding properties that this atom cell has as an atomic emission source. In brief the atom cell is hot enough to produce atomic emission from virtually all elements, the detection limit for most being in the 0.1-100 ngml-1 region with sample introduction by conventional nebulisation. This high temperature also gives the technique virtual freedom from the classic molecular interferences seen in flame atom cells but there are still interferences from easily ionisable elements (1) and from the general sample matrix cooling the plasma (2). Geometrically the emission source removes the self absorption problems encountered in flame emission spectrometry and other atomic emission techniques since the analyte is excited in the cooler central channel of the plasma and any lateral migration of analyte atoms is into a hotter region, hence the atom cell is not surrounded by cool atoms capable of absorbing emitted radiation. Thus the ICP is capable of linear response to analyte concentration over 4 or 5 orders of magnitude. It is thus obvious why the inductively coupled plasma is now firmly established as one of the most powerful instrumental techniques available to the analytical chemist.

1.3

The Plasma Emission Source

A conventional inductively-coupled plasma consists of a volume of partially ionised argon gas sustained within a quartz tube by a powerful radio frequency field. A diagramatic representation of the two types of ICP torch is shown in Figure 1.1. The torch consists of three concentric quartz tubes surrounded at its upper end by a 3-turn water-cooled copper induction coil. The argon gas is introduced as three separate flows, the outer flow is conventionally introduced tangentially between the two outer tubes and is termed the coolant in this thesis. This flow cools the outer tube and prevents the fireball from coming into contact with this tube. The flow-rate is dependent on the size and geometry of the torch as well as the radio-frequency power applied to the induction coil but is typically 10 to 20 litres per minute. The flow introduced between the inner two tubes is termed the plasma or auxillary flow and is also conventionally introduced tangentially. The value of this flow has been the subject of some disagreement but essentially it adds gas to the body of the fireball, pushing it slightly higher in the load coil and keeping it away from the injector tube. Depending on the torch geometry the auxillary flow is not essential but typical flow-rates are between 0-3 litres per minute although flow-rates as high as 19 litres per minute have been used (3).

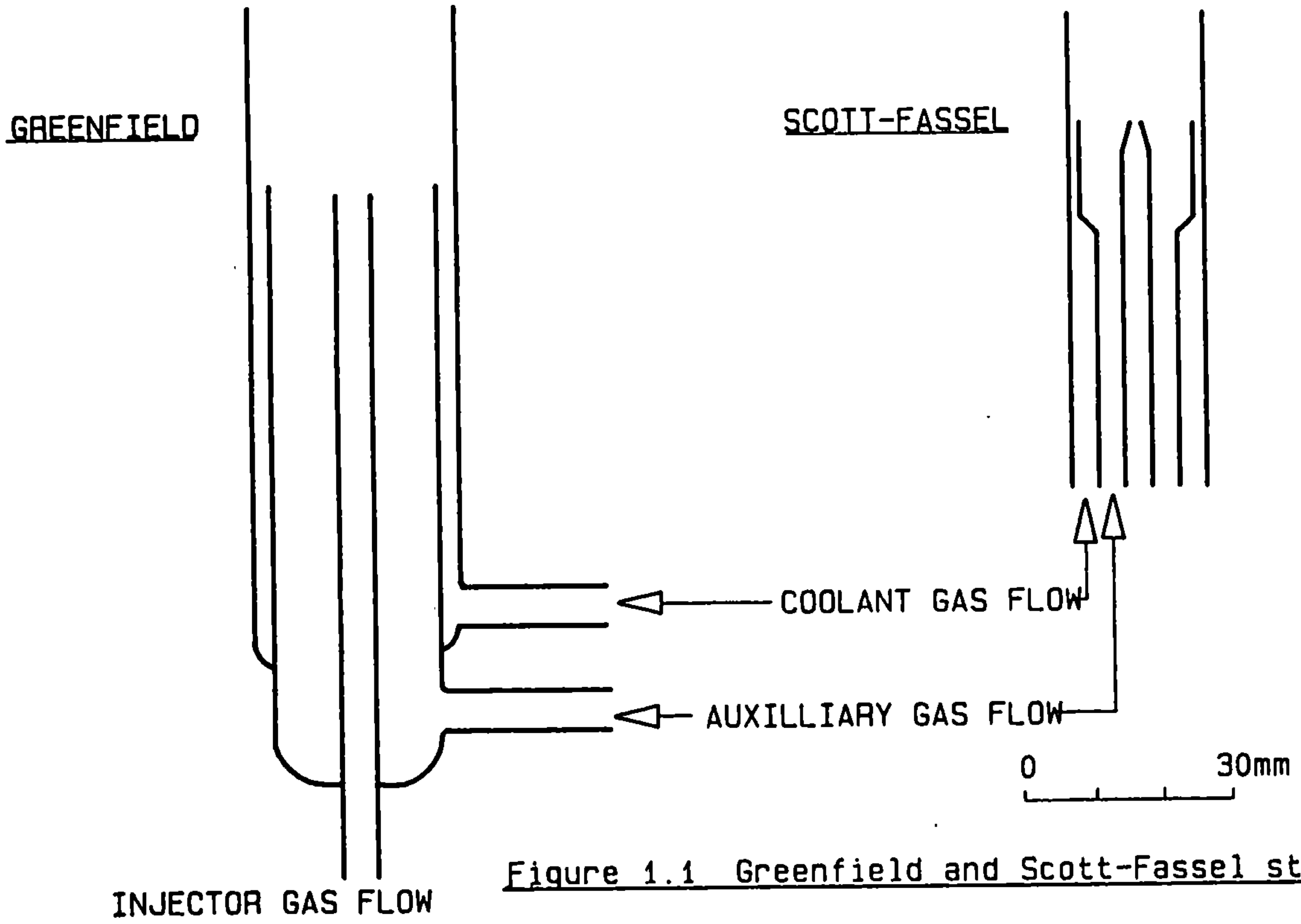


Figure 1.1 Greenfield and Scott-Fassel style Torches

The third gas flow is, in terms of the analytical performance of the ICP, the most important. Termed the injector or carrier flow it performs two important tasks. Firstly it is used, in the vast majority of instruments, to generate a fine aerosol from the analyte solution, this process of nebulisation will be discussed in detail later. Secondly it then carries this aerosol into the atom cell by punching it through the centre of the fireball. This second task is achieved by using a narrow bore injector tube, typically 0.5-3 mm i.d. such that the flow has a high enough velocity to penetrate the fireball's natural resistance to rupturing. This resistance is due to the 'skin-effect' whereby the largest current flow occurs in the outer surface of the plasma rather than in the bulk of the fireball. This arises due to the increased free electron concentration in the outer region of the discharge due to the influence of the strong magnetic field on the plasma. (The so-called magneto hydrodynamic effect.) Typical nebuliser flow-rates are between 0.5-3 litres per minute.

The plasma is heated through the inductive coupling of free charged species to the magnetic field generated within the load coil by the high frequency alternating current, typically 1-3 kW at 27 MHz. Thus the plasma can be considered analogous to the secondary windings of a transformer with the load coil acting as the primary windings. Initiation of the fireball is achieved by generating a few 'seed' ions using a spark from a Tesla coil to ionise a small number of argon atoms. As these ions and electrons enter the load coil they are accelerated by the magnetic field, which has lines of force running axially within the load coil, in closed circular horizontal paths.

Collisions between ions and neutral atoms result in a rapidly increasing number of ions and free electrons from which the fireball forms within a few milli-seconds. Eddy current within the plasma heat the fireball to the region of 7000-10000k with neutral atoms entering the load coil being rapidly ionised and thus a self-sustaining plasma has been formed.

The plasma is initially 'pear-shaped' with ions and electrons recombining rapidly once they have left the influence of the induction coil. When the injector gas is turned on it punches a cooler channel through the centre of the fireball to form an annular shaped plasma with an extended flame-like tail. Hence the sample passes through the cooler central channel and experiences temperatures in the region of 5000-8000k. The analyte emission is not measured in the hottest part of the fireball due to the high intensity background continuum produced by radiative recombination and Bremsstrahlung radiation. Better signal to background ratios can be achieved by making measurements in the tail-flame where the background continuum is considerably lower (see Figure 1.2).

1.4

The Development of the Inductively-Coupled Plasma

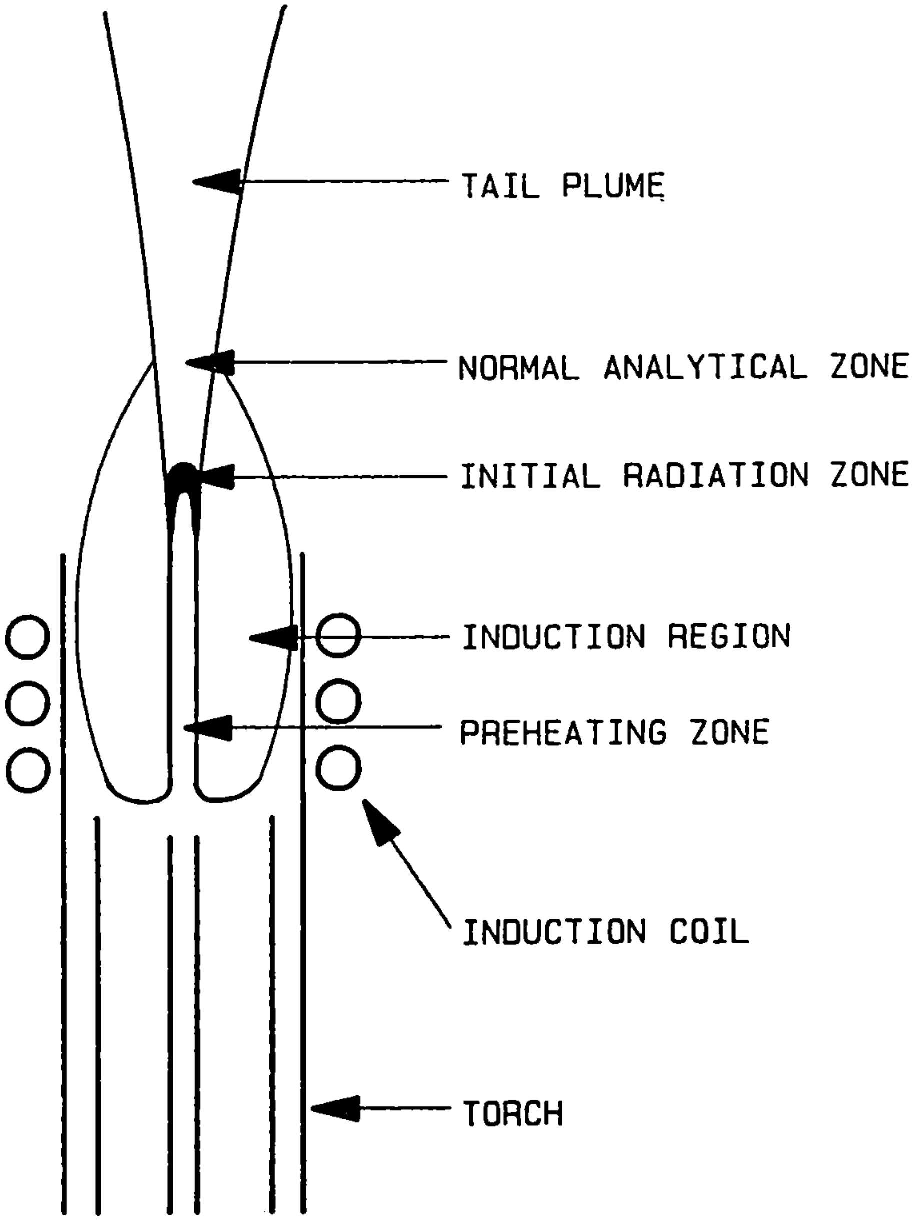
Capacitively and inductively-coupled discharges were described in detail as early as the 1940's (4). These were however static systems and it was 20 years before Reed (5) described the first inductively coupled discharge in a flowing system and at atmospheric pressure. Reed originally described this discharge or plasma for growing crystals but later (6) suggested that it could be used as a spectral emission source.

Interest in the Inductively-Coupled Plasma (ICP) grew rapidly in the early 1960's as its analytical potential was recognised. Greenfield et al. (7) reported the first practical use of an ICP as an emission source in 1964. They described a torch consisting of 3 concentric quartz tubes with nitrogen supplied tangentially between the outer tubes and argon supplied between the two inner tubes and through the central tube to produce a nitrogen cooled, argon fireball. The power was supplied to the fireball by a water cooled induction coil connected to a high power radio frequency generator. The sample aerosol punched a hole through the centre of the plasma and the spectral emission was viewed in the flame-like tail of the fireball. This plasma geometry forms the basis of all modern plasma instrumentation with the sample aerosol passing through the centre to form an annular shaped plasma (see Figure 1.2). In 1965 Wendt and Fassel (8) described a laminar flow torch design in which the sample aerosol flowed around a solid plasma fireball but this design was considerably more problematical and not as useful since the analyte does not experience such high temperatures.

Almost 10 years later the first commercial instrument was released. These years of research produced very few modifications to the original design published by Greenfield et al. (7) but were important in establishing ICP-Optical Emission Spectrometry (OES) as a very powerful analytical technique. Dickinson and Fassel (9) published an important paper detailing detection limits clearly showing the considerable improvement over flame atomic absorption or flame atomic emission techniques. Boumans and de Boer (10) described the physical, theoretical and practical considerations of ICP-OES.

Figure 1.2

Regions of the inductively coupled plasma



Research workers have investigated almost every aspect of the basic ICP design. The plasma torch evolved into two designs; the larger diameter 'Greenfield' design which consists of three straight concentric quartz tubes the larger of which has a diameter of 28 mm and the smaller Scott-Fassel design which has an outer tube of 18 mm diameter and a 'tulip' shaped auxillary tube (see Figure 1.1). Even these two basic designs have many slightly different variants and the only criterion which is used to distinguish one from the other is the overall size of the torch. Current research into torch design mainly involves the development of low power, low gas consumption designs (11, 12, 13), some of these low power designs have capabilities normally associated with higher power plasmas in that they are suitable for the analysis of organic solvents (14). Further description of these torches is beyond the scope of this report and the reader is directed to the review by Hieftje (15). An important development which is worthy of mention is that of the laminar flow torch (16, 17). The coolant and auxillary are both laminar flows with the sample aerosol punching through the plasma in the usual way. This design removes the optical noise component which is present in the normal tangential flow torches due to rotation of the central injector channel.

The radio frequency (r.f.) power supplied to the plasma has also come under close investigation, the frequency and level of power supplied having been the main points of interest after the stability of power supplied which is of paramount importance since it directly influences the noise in the plasma. Much of the early work on ICPs was carried out using very large r.f. generators capable of supplying 10-20 kW.

This was thought to be essential in producing a very powerful plasma with a great deal of stability and freedom from matrix interferences. Today most commercial plasma spectrometers have r.f. generators in the region of 1-3 kW which is now known to be the best power range to obtain low detection limits and reasonable operating costs. Modulation of the r.f. power supplied to the plasma has been used (18) as a method of elucidating more information about the plasma discharge.

The frequency of the r.f. power has been an area of interest (19) with results showing that as the supplied frequency is increased from 5 to 56 MHz both excitation temperature and electron number density decrease in a linear manner. Initially this appears to be detrimental since the signal also decreases linearly with frequency but the signal to background ratio (SBR) is the important factor and this is enhanced since the background intensity decreases by a square function with respect to frequency. The most common plasma generator frequency of 27.12 MHz has been questionned (20) as perhaps not being the optimum frequency of ICP-OES, but the gains made by going to higher frequency generators have not yet persuaded all the major plasma spectrometer manufacturers to move to higher frequencies. In addition to sample introduction and inductively-coupled plasma-mass spectrometry which will be covered in detail later, many other variations and ideas have been investigated in the development of the inductively-coupled plasma. Most of these are beyond the scope of this report and the reader is directed to the literature especially Annual Reports on Analytical Atomic Spectroscopy (ARAAS) which runs from Volume 1 (reviewing 1971) to 14 (1984) and is now incorporated in the bi-monthly publication of the Journal of Analytical Atomic Spectrometry (38) and renamed Atomic Spectrometry Updates (ASU). This is an essential source of material reviewing all areas of atomic spectrometry. As a starting point the following areas and references may be useful:- mixed gas ICPs and ICP discharges in gases other than argon (21, 22, 23, 24); ICPs run at pressures other than atmospheric (25, 26, 27); viewing the ICP axially rather than 'side-on' (28, 29); atomic fluorescence using the ICP as the atom cell (30, 31, 32, 33); general reviews (34, 35, 36).

For the reader requiring a review not only of the literature but also of the general principles of plasma emission spectroscopy they are directed to the R.S.C. review by Sharp (37).

1.5

Evaluation of Novel Instrumentation

Obtaining the best results from analytical techniques requires not only an understanding of the fundamental principles, but also a careful and rigorous testing in a systematic mathematical way. Far too many novel methods and techniques which are developed are compared with existing systems without either of the two systems working at the maximum of their capabilities. Many workers consider that after they have performed a 'trial-and-error' experiment to improve the performance of their novel system, the system is 'optimised'. This could not be farther from the truth since this method is neither systematic or rigorous and relies heavily on previous experience which may or may not be relevant to the novel system which they have developed.

In recent years this lack of a systematic approach for comparing ICP systems has been recognised by several workers. Various methods for the optimisation of ICP systems exist including response-surface mapping (39) which is slow, cumbersome and impractical for more than two variables; the factorial-design method (49) has some attractive features but is also regarded as being generally unsatisfactory due to time taken to find the optimum of an unknown system. The univariate search method (41) yields a considerable amount of information but is slow and may not truly find the optimum of a system if false optima are encountered. Perhaps by far the most encouraging method is that based on the simplex algorithm proposed by Spendley et al. (42). The attractive features of the method are the simple arithmetical calculations involved, the lack of assumptions concerning the shape of the response surface, and the speed with which optimum conditions can be established. The most common used version of this original algorithm is that described by Nelder and Mead (43) with additional material on starting methodology by Yarbro and Deming (44). Termed the modified simplex algorithm this method of optimisation has been used successfully to optimise ICPs by many workers (e.g. 45, 46, 47). The performance of this algorithm and several variants has been fairly extensively tested and reviewed (48, 49, 50, 51) and generally has shown the modified simplex algorithm to be a successful method of optimisation in most situations.

With the advent of the microcomputer into the laboratory there is an increasing routine usage of high powered mathematical techniques applied to the 'tune-up' and running of analytical instrumentation. At least one software distributor (52) is offering a commercial program to perform all of the mathematical and logical functions required by the simplex optimisation algorithm and several workers have written their own programs (46, 49, 53). These packages remove the time consuming and error introducing manual calculations which have suppressed the enthusiasm of many workers for complex optimisation experiments in the past. They are unfortunately still labour intensive since the scientist is required to actually perform the experimental changes and input the data to the microcomputer.

Within the area of High Performance Liquid Chromatography automation of instrumentation and computer control has perhaps been more advanced than in the area of atomic spectroscopy. Thus instruments capable of self-optimisation experiments have been available for some years and some commercial instruments have simplex optimisation routines available (54) as standard features. This trend of optimisation experiments under automatic computer control has involved the work of Betteridge (55) who has also critically assessed various simplex algorithms (49, 50).

The routine use of optimisation has been recognised within the area of ICP-OES and the first commercial 'self-optimising' instrument has become available (56). The optimisation algorithm employed is based on the univariate search approach and as such may not find the true optimum of the system (49), but the experiment is truly automated requiring no input by the operator.

1.6

The Aims of This Investigation

The overall aim of this investigation is the application of simplex optimisation techniques for the refinement of inductively-coupled plasma optical emission spectrometry for the analysis of solutions and slurries.

The ICP is well established for the analysis of solutions and has been optimised many times in the laboratories at Plymouth (57, 58). Each of these experiments has been performed with manual calculation of the simplex iterations. Thus initially the development of a microcomputer based program to perform the computations was considered to be essential. The further extension of this to bring an ICP spectrometer fully under computer control for automatic optimisation experiments was considered to be a major step forward in the evaluation of novel sample introduction systems and torch designs.

Several workers have reported the analysis of solids by slurry introduction into the ICP (59, 60, 3) and reported poor atomisation efficiencies when compared to aqueous solutions. This can be overcome by either use of internal standards (60) or calibration using matched solid standards (3). Recently workers have reported far better atomisation efficiencies (57, 60, 61) even as high as 100%.

These superior results are due to improved transport efficiency of the slurry. It was thought that the application of simplex optimisation studies to existing sample introduction systems, novel design and methodology could bring about the development of reliable and consistent methods of slurry analysis for a much wider variety of sample types. Slurry introduction of industrially important materials and minerals, including zeolite catalysts was chosen as an important application of this technique.

Inductively-coupled plasma - mass spectrometry has made a significant impact in the field of trace element analysis with the first commercial instrument being released in 1982. An investigation of the capabilities of this technique in the analysis of slurries could well produce new information relating to the stability of particulates within the plasma. Hence this was considered to be an important area of novel work to be included in this study.

CHAPTER 2

PRELIMINARY INVESTIGATION INTO SOLID SAMPLE ANALYSIS BY ICP-OES

2.1

Introduction

Solid Sample Analysis

Techniques for the analysis of solid samples directly without sample dissolution forms a very important part of the analytical chemists' armoury of techniques. The direct analysis of solids has many benefits over dissolution methods. Principally the sample is not diluted, most solution methods only achieving at most a few percent of sample in the final solution for analysis, thus the analyte concentration is also drastically reduced. Dissolution methods are also frequently dependent on a fusion with a suitable flux which introduces a large increase in matrix and the risk of contamination.

Several analytical techniques for the analysis of solid samples exist, some finding extremely widespread and important use. X-ray fluorescence (62) is perhaps the most important being suitable for virtually all solid matrices. Its main disadvantage is the lack of sensitivity with detection limits being in the $\mu g\ g^{-1}$ region rather than the $ng\ g^{-1}$ region. The technique also requires closely matched solid standards to obtain accurate results at lower concentrations.

Neutron activation analysis (63) has high sensitivity, multi-element capability, solid samples usually require no chemical pretreatment and is free from reagent contamination. Unfortunately it is slow, elements with long half-lives requiring activation for 100 hours or longer to achieve ng g^{-1} sensitivity, and is very expensive requiring specialised equipment for handling radioactive material.

Spark source mass spectrometry (64) is another very sensitive technique offering ng g^{-1} levels of detection but it is expensive, requires very homogeneous samples which are conducting or samples have to be pelletised into an electrode with a conducting material such as graphite.

Arc and spark atomic emission techniques have been used for many years by the metallurgical industry and are best suitable to samples of good conductivity. Although this approach has been applied to non-conducting samples by the formation of conducting pellets with graphite or copper this approach is plagued with matrix interferences. Thus there is a need for very carefully matched standards if trace element work is undertaken.

There are a wide range of techniques which are essentially surface techniques which can only provide semi-quantitative information if the sample is not truly homogeneous. These include Glow discharge lamps (65), Hollow-cathode discharges (66) and Laser ablation - ICP-MS (67).

Several methods for introducing solids into flames for atomic absorption measurements have been described in the literature. In general the flame, which already suffers from molecular interferences with simple solutions is not hot enough to atomise solid material other than organics or highly volatile inorganics. Langmyhr (68) has given a reasonably comprehensive review of the analysis of solid samples using flames and a variety of other atomisers.

Interest in graphite furnace AAS as a method for analysing solids has had a slow rate of growth since the early work of L'vov (69, 70). Recently sample introduction of slurries has caused increasing interest and the number of conference reports and publications (71, 72) are growing slowly but continuously. It is an attractive approach with very good sensitivity although problems may arise from matrix interferences and careful temperature programming is required.

The technique which is possibly attracting the most attention as a new technique for rapid, accurate, multi-element analysis of solid samples is that of slurry introduction into the inductively coupled plasma.

2.2 SOLID SAMPLE INTRODUCTION INTO THE INDUCTIVELY COUPLED PLASMA

The now almost exhausted quote from Browner and Boorn's paper (73) describing sample introduction as "the Achilles' heel of atomic spectroscopy" applies perhaps more pertinently to ICP-OES than to any other atomic spectrometric technique. The conventional method of sample introduction is that of the nebuliser/spray chamber combination for the analysis of solutions. This simple and robust system suffers from nebuliser noise, drift due to temperature changes in the spray chamber and perhaps worst of all poor efficiency of analyte transport to the atom cell (ca 1-2%). These problems are made worse by the limited gas flow available for the nebulisation process, typically 1-3 litres per minute. It is hardly surprising, bearing these facts in mind, that the literature is full of reports of attempts at improving existing nebuliser/spray chamber systems and the development of new systems. There are so many that the reader is directed to the reviews by Browner and Boorn (73, 74, 75), Smythe (76), Gustavsson (77) and Barnes (78).

The introduction of solid samples into the ICP has been approached in a variety of ways. Several workers have used laser ablation, from conducting and non-conducting solids, as a method for generating a fine aerosol of dry particles which can then be blown into the fireball by a stream of argon. Horlick and Carr (79) have used a ruby laser in both q-switched and free running modes, finding the latter to be more suitable for the analysis of aluminium-based alloys and brass. Thompson and Hale (80) have used laser ablation to analyse stream sediments, Ishizuko and Uwamino have analysed various metals (81) while Dittrich and Wennrich (82) have reviewed the use of laser vaporisation in atomic spectroscopy. This method of generating dry aerosols from solids suffers from two major problems, sample homogeneity which is crucial in obtaining a representative aerosol since so little material is vaporised. Secondly and probably worse, is the difficulty in calibration of the system since closely matrix matched standards are required for quantitative work. This approach does have advantages over spark sampling in that the sample does not have to be conducting.

Arc (83) and spark (84) generation of sample aerosols for ICP-OES have been more widely used than laser ablation but in addition to suffering from the same two problems previously mentioned for laser ablation it has the added problem of requiring samples to either be conducting or to be pelletised with a conducting solid, usually graphite. At least two manufacturers have reported analytical applications of spark erosion (85, 86) as aerosol generation for ICP-OES. Aziz et al. (87) have studied optimal spark conditions and found that 1 kv sparks at a 400 Hz repetition rate produced the best detection limits. Higher voltage sparks increased the particle size distribution of the aerosol. Arcs have been used less probably because the larger sample erosion rates and heat generated are less compatible with the ICP. Despite these problems direct current arcs have been used for solid sampling (88, 89). As well as these fairly conventional arc and spark stands for dry aerosol generation, two other novel approaches have appeared in the literature. The first is the use of a microarc operating at 1500V and 20mA (90) which has only been used for desolvated solution deposits rather than solids. The second is unusual in that it draws power from the plasma by grounding a conducting sample beneath the fireball (91) and an r.f. arc is struck between the sample and the fireball drawing approximately 400W from the plasma. Sample particles formed by this arc are carried into the plasma by an argon flow as usual. The problems of calibration and the need for closely matched standards are the main drawbacks with these arc and spark sample introduction techniques making them only suitable for the analysis of metal samples where closely matched standards are available.

The direct insertion of samples into the fireball with the aid of a graphite probe has been extensively investigated (92, 93, 94, 95).

This technique on first consideration seems to have a reasonable number of advantages, including the possibility of simple aqueous calibration for the analysis of solids, freedom from homogeneity problems provided a large enough sample can be placed on the probe, and to be able to analyse non-conducting as well as conducting and aqueous samples. Unfortunately there are problems which are caused mainly by the inability of the probe to reach temperatures greater than 1800-1900°C (93) due to its thermal mass. This low temperature leads to incomplete vaporisation of high boiling point solid samples with certain elements being released from the molten matrix while others are retained (96). Despite these problems the graphite probe has been used for a variety of solid samples (92, 96, 97) with some degree of success.

Electrothermal vaporisation (ETV) of both liquid and solid samples also has the potential benefits of simple aqueous standardisation and has been closely investigated. The types of vaporisers considered include modified, conventional graphite tube AAS atomisers (98), graphite rods (99), tantalum boats (100), platinum filaments (101) and tungsten boats (102) although these have mainly been used for the introduction of aqueous samples they are all potentially viable for solid samples, although considerable refinement of the technique is still required. For more details on thermal vaporisation techniques for sample introduction into the ICP including ETV, arc/spark nebulisation, laser ablation and graphite probe, the reader is directed to the review by Matusiewicz (105).

These thermal vaporisation techniques all suffer from problems which to a certain extent cancel out the benefits gained from a solid sample analysis approach or are very limited in the type of samples they can handle. There are a variety of other solid sample introduction systems for ICP-OES but in the main these are of less use than those mentioned. Readers interested in pursuing these are directed to the review by Zil'bershtein (106).

The final technique to be mentioned is that of the introduction of solid samples by the nebulisation of a finely powdered solid dispersed in either aqueous or organic solvent to produce a slurry. This technique lacks some of the advantages that other solid sample introduction techniques have, such as very high sample transport efficiency into the atom cell, (approaching 100% for some thermal vaporisation methods) and the benefits gained by not introducing a solvent loading into the plasma (water thermalises the plasma, cooling and bringing it closer to local thermal equilibrium). But in return it keeps some of the important advantages of continuous nebulisation, such as the simplicity and robust nature of the sample introduction system, rapid sample throughput and better precision due to having a continuous rather than discrete sample input to the atom cell. Slurry introduction improves upon solution techniques in that it can remove lengthy dissolution procedures, reduce risk of contamination due to sample pretreatment and avoid the use of hazardous acids such as hydrofluoric and perchloric. It also gives the possibility of much higher sample loading than with solutions since solubility no longer limits the analyte concentration. Finally it offers the possibility of detection limits for analytes in insoluble matrices which were previously unachievable for ICP-OES using solution introduction and the possibility of analysing matrices which previously were almost impossible to consider using conventional dissolution techniques, such as P.T.F.E.

2.3

Slurry Sample Introduction Into The ICP

The concept of introducing slurries into the ICP was mentioned by Greenfield et al. in the first applications paper (7). Few workers took up these early ideas of using slurries although a large number of early papers were concerned with the introduction of dry powder samples into the ICP (106, 107, 108).

The introduction of dry powders has a great many problems due to segregation of the larger and smaller particles and also of variable sample input to the atom cell. The number of papers describing slurry analysis is still very small although there are growing numbers of conference presentations detailing applications (109, 110, 111, 112) and methodology (113). This lack of publications may be considered unusual when one remembers the only changes to an existing ICP spectrometer required for the introduction of slurries are the use of a Babington-type nebuliser and the use of a straight capillary injector.

Fuller et al. (59) published results showing how the particle size distribution of a slurry affected the quality of the analytical results when compared to simple aqueous standards. Preliminary work in these laboratories (58) showed that possibly it was the internal diameter of the injector tube which was the main component involved in cutting out larger slurry particles and so causing the lowering of analytical results. Hence an in-depth investigation of the whole sample introduction system is clearly timely and was an objective of this work.

2.4
Use of Laser Diffraction Particle Size Analysis in the Characterisation of an ICP Sample Introduction System

The aim of this study was to measure the actual airborne particle size distributions of the aerosol at all the significant points within the sample introduction system and hence determine the importance of each of the components of the sample introduction system. As well as this main objective there was also interest in determining any significant differences in the distributions of aerosols generated from simple aqueous solutions, benzyl alcohol, aqueous slurries and benzyl alcohol slurries.

2.4.1
Instrumentation and Procedure

A Malvern 3300 laser particle size analyser (Malvern Instruments Limited, Malvern, Worcs, England) was used for all particle size distribution measurements (readers are directed to the review by Weiner (114) for the theory and application of this technique).

The sample introduction system comprised of a Babington-type high solids nebuliser (P.S. Analytical, Orpington, Kent, England, Figure 2.1) with an in-house constructed double pass Scott-type spray chamber (Figure 2.2) and a Kontron (Eching, West Germany) all P.T.F.E., fully demountable Greenfield diameter torch (Figure 2.3) with a range of straight capillary injectors of 2.2 mm, 3.0 mm and 4.0 mm internal diameters. The configuration of the apparatus is shown as Figure 2.4.

In the instrumental arrangement the aerosol to be measured passed through the He-Ne laser beam and the droplets within the aerosol cause diffraction of the parallel coherent laser light proportional to their particle size. The diffracted light falls on the outer segments of the diode array detector and the Commodore microcomputer fits a Rosin-Rammler distribution to the data. The particle size range is governed by the focal length of the focusing lens and these can be changed easily to re-run data collection if the size distribution falls out of the scope of that range. Because of the finite number of elements within the diode array detector (30 elements) the resolution of the particle size distribution is limited to a set of bands.

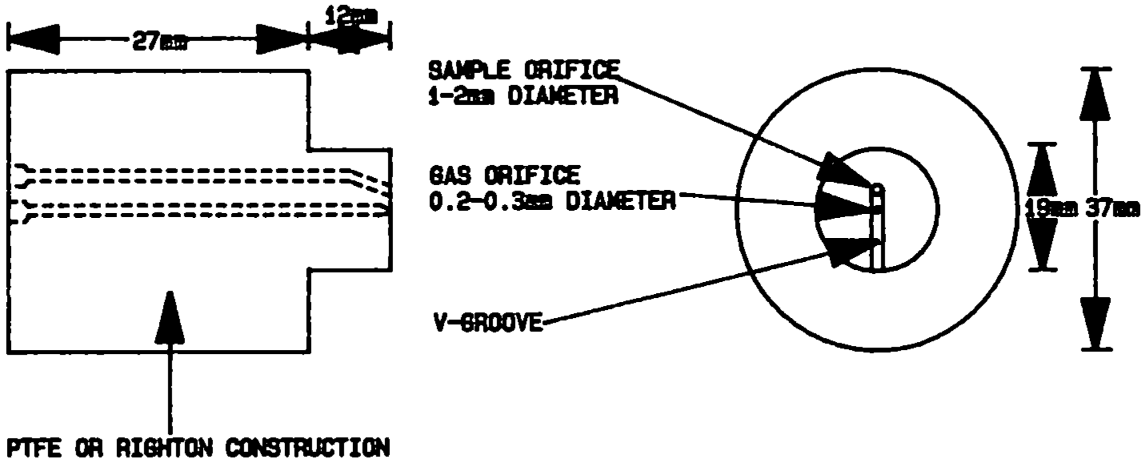


Figure 2.1 PS Analytical Babington-type high solids nebuliser

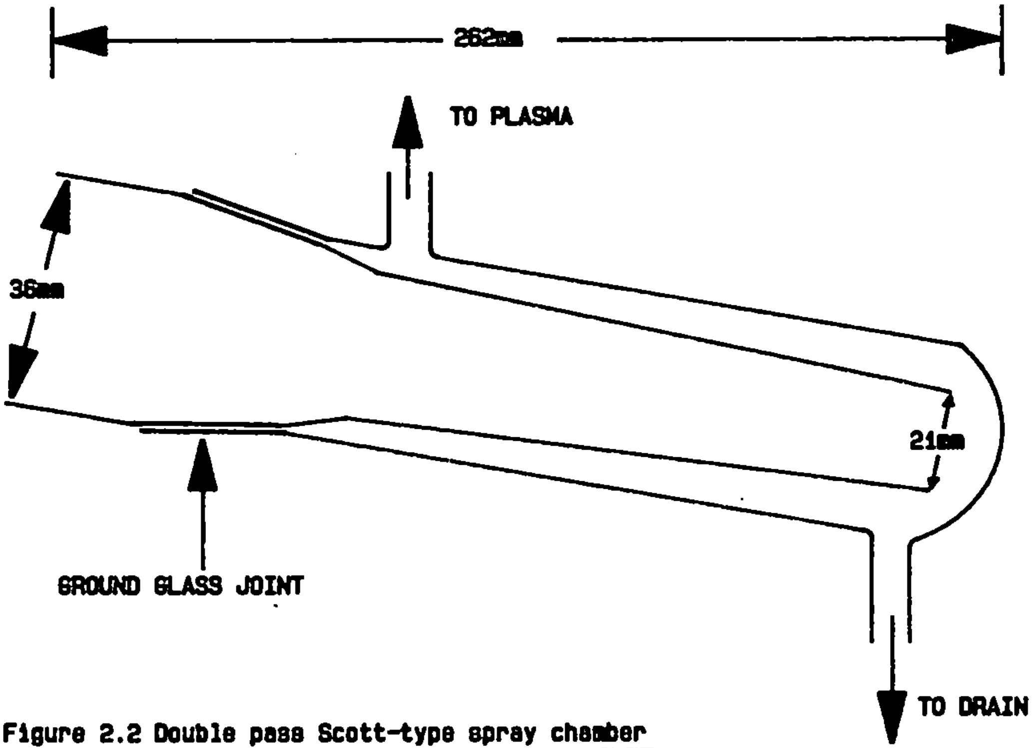


Figure 2.2 Double pass Scott-type spray chamber

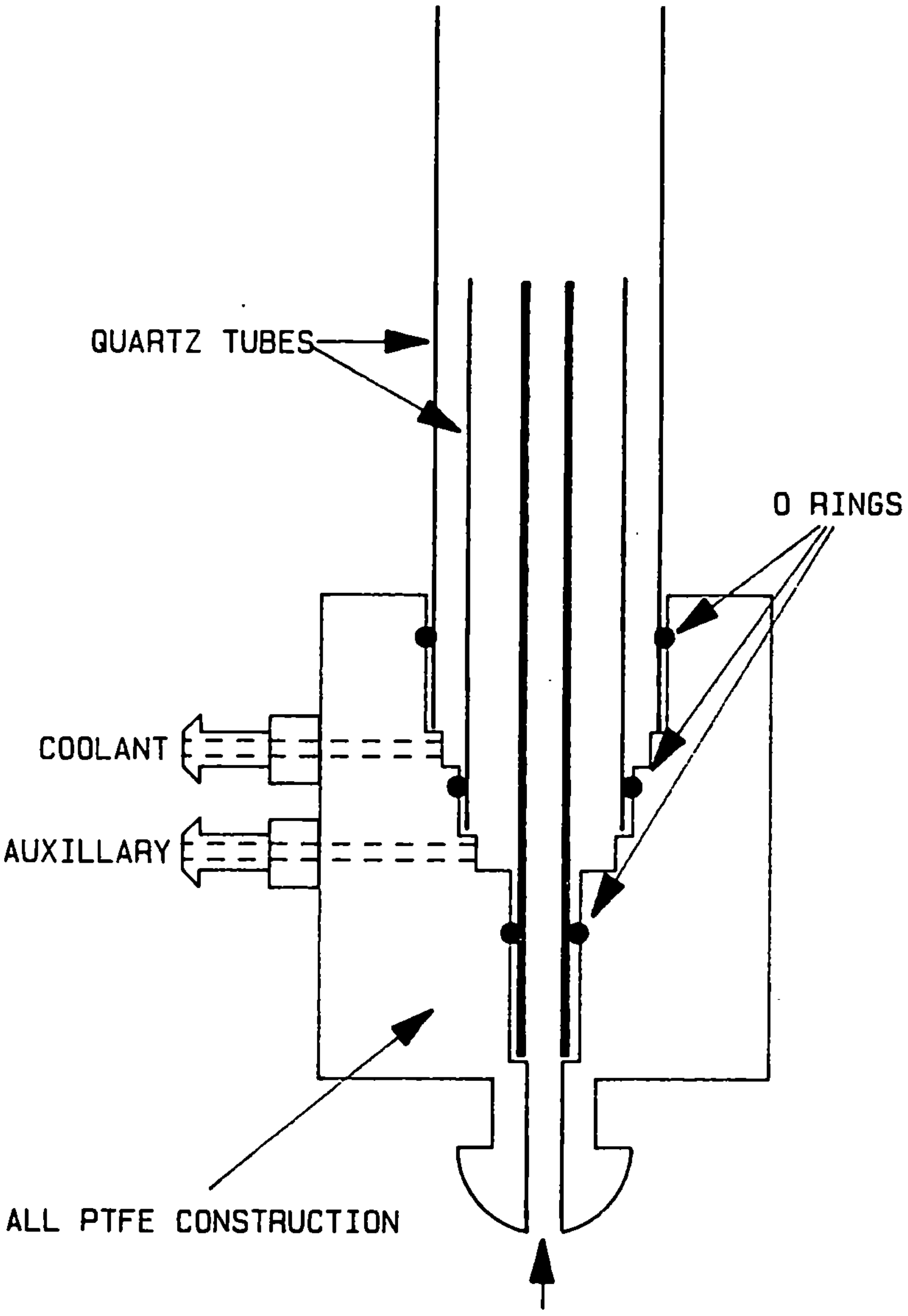


Figure 2.3 Fully demountable Kontron plasma torch

2.4.2

Effect of Sample Uptake on Aerosol Distribution

Unfortunately the nebuliser could only be operated using compressed air at a fixed pressure (28 psi) due to the limited resources available and the immobility of the Malvern system. There was slight adjustment of the nebuliser pressure available but it was not quantitative. Hence an initial study of the effect of sample flow rate on aerosol distribution was carried out to obtain the best nebuliser performance. The nebuliser was clamped so that the aerosol density passing through the laser beam was within the linear working range of the system but was as high as possible to overcome any background effects.

A blank consisting of the nebuliser running without any sample solution was subtracted from all runs to correct for airborne particulates.

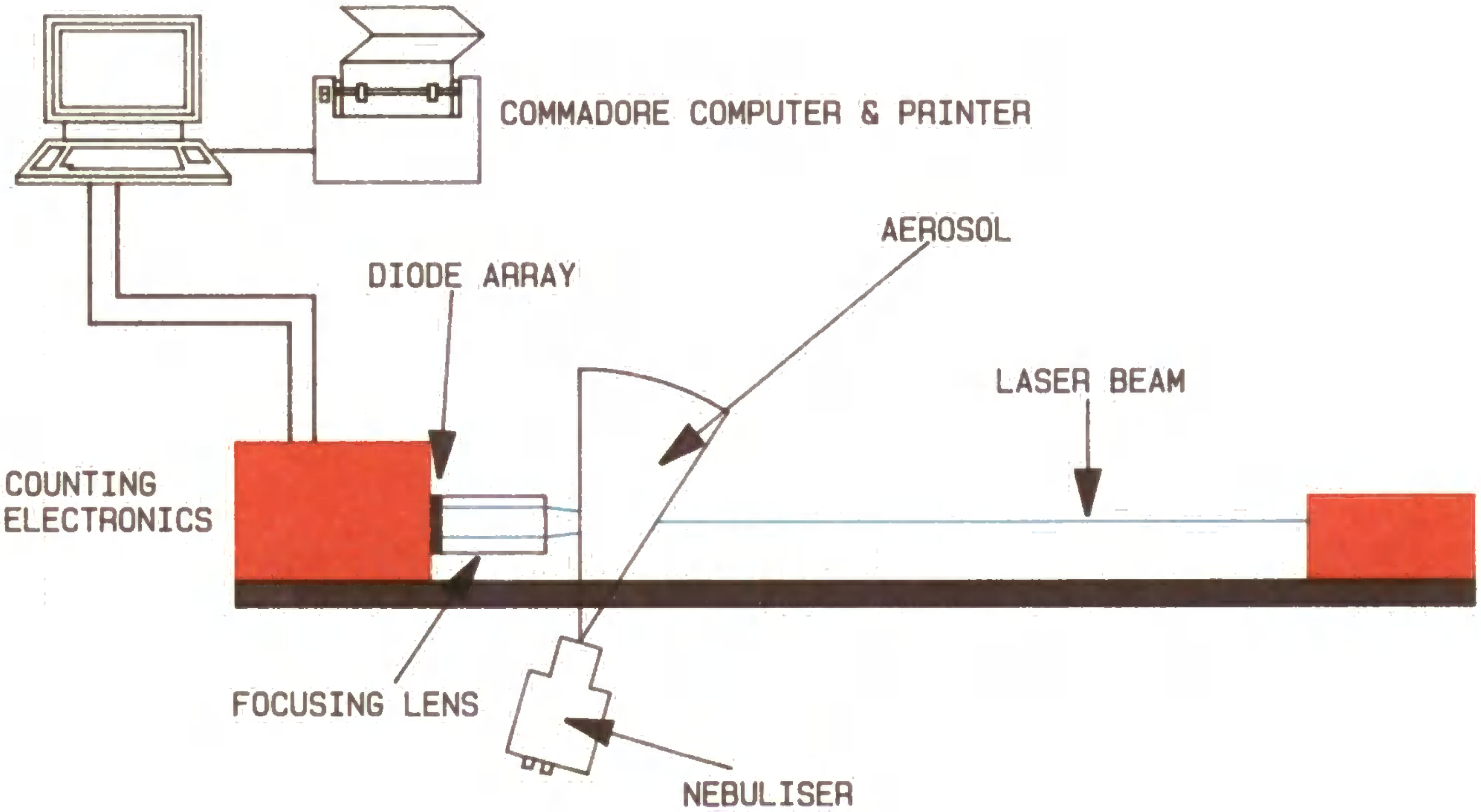


Figure 2.4 Instrument configuration for aerosol droplet size measurements using a Malvern 3300 system

2.4.3

Results and Discussion

Sample flow rates were dependent on the diameter of the pump tubing as the peristatic pump was of the constant speed type. Five different flow rates of distilled water were used, 0.5, 0.55, 1, 2, and 5 ml min-1 and the aerosol distributions obtained shown in Figure 2.5.

These results must be considered to be of comparative use only for a number of reasons. Firstly the distributions generated are simple percentages and as such no true comparison of absolute intensity can be made between the distributions. Secondly as shown by Cresser and Browner (113) evaporation of droplets is highly significant for droplets of 5 µm diameter in a time state of 10 seconds and for 1 µm droplets in approximately 0.1 seconds. Thus the distribution obtained for the systems described appear somewhat larger than those actually produced by the nebuliser. These effects are probably almost negligible for droplets >5 µm for all the measurements described but the small sizes <5 µm must be considered to be unreliable in most cases.

Thus, considering the effect of sample flow rate on nebuliser performance it is interesting to note that for all but the 5 ml min $^{-1}$ flow there is a definite maximum droplet production in the 13-20 µm range and similar distributions up to that maximum. This corresponds with results obtained on the analytical performance of the nebuliser (58) which show a plateau in response only falling off slightly as the nebuliser is flooded with excess sample above 3 ml min $^{-1}$.

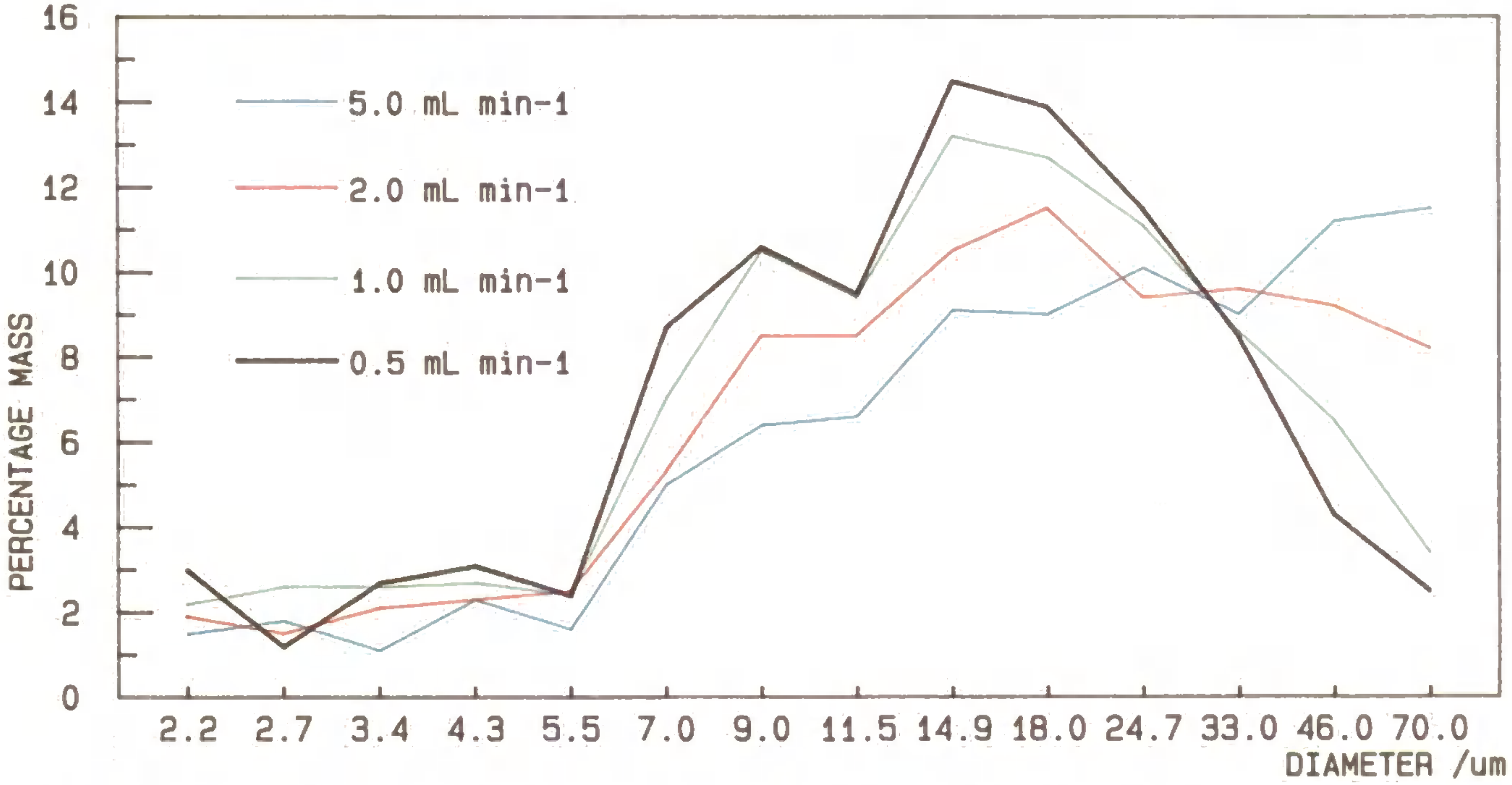


Figure 2.5 Effect of nebuliser uptake rate on aerosol droplet size distribution

The 2 ml min $^{-1}$ flow rate was chosen for further experiments since it has a higher proportion of large droplets which will make characterisation of the spray chamber and torch system easier.

2.4.4
Effect of Sample Introduction System on Aqueous Aerosol Droplet Size Distribution.

Distributions were determined at the following positions:

a) Immediately after the nebuliser (see Figure 2.5).

b) The end of the insert in the double pass spray chamber.

c) At the outlet of the spray chamber.

d) After the torch assembly with 2.2 mm, 3 mm and 4 mm bore injector tubes.

2.4.5

Results and Discussion

The results of the experiment are shown in Figure 2.6. Unfortunately the particle size categories are not linear and so the differences between the systems are not very clear on the graph but Table 2.1 shows a numerical summary which is perhaps easier to interpret.

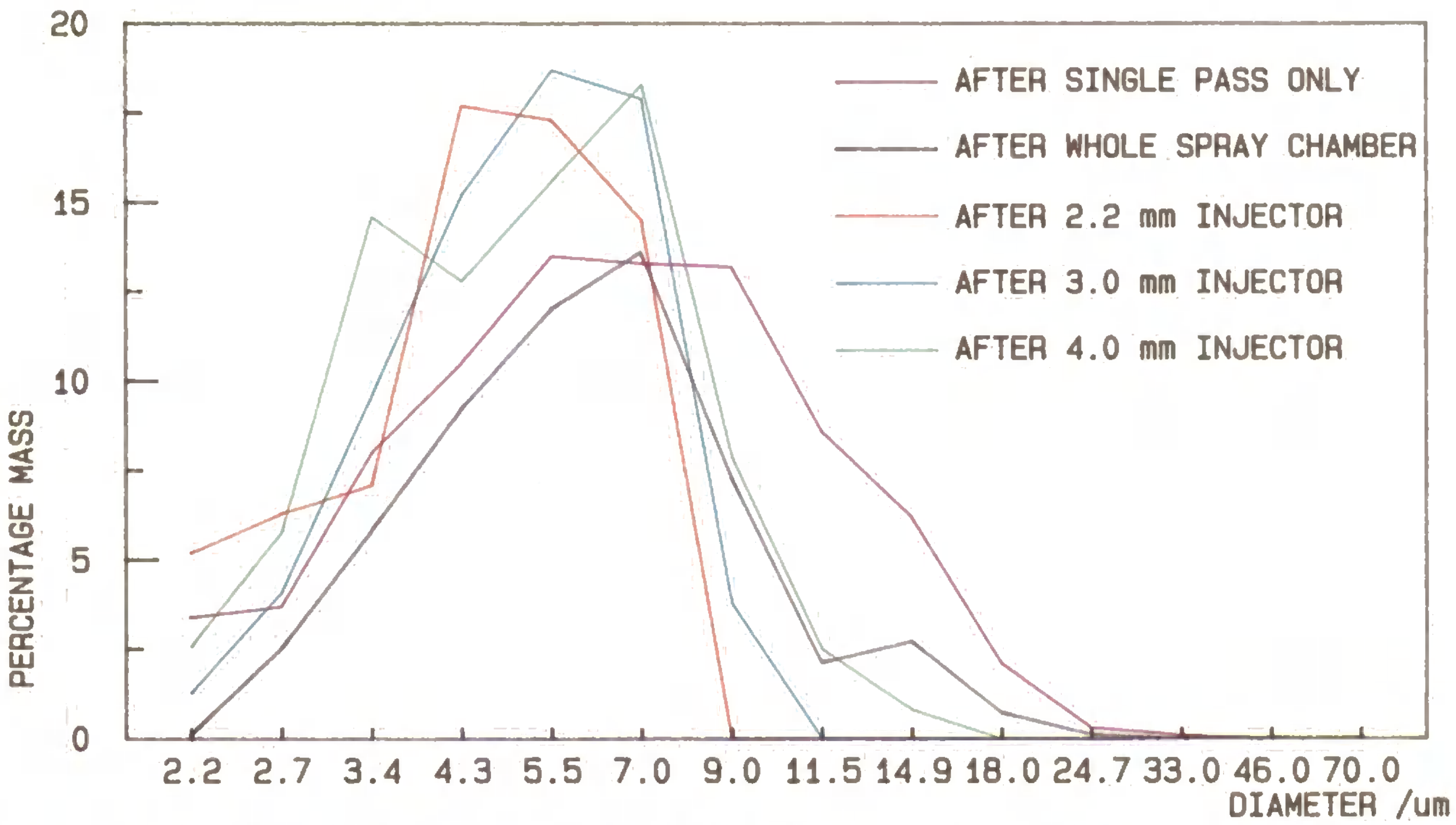


Figure 2.6 Aerosol distribution at various points withinthe sample introduction system.

Table 2.1

Results of Sample Introduction Investigation

Measurement Point of System	Maximum Size Droplet Detected	Peak of Distribution µm
(a)	70 µm	14.9 - 24.7
(b)	24.7 - 33 µm	5.5 - 9.0
(c)	18 - 24.7 µm	5.5 - 9.0
(d) 2.2 mm	7.0 - 9.0 µm	4.3 - 5.5
3.0 mm	9.0 - 11.5 µm	5.5 - 7.0
4.0 mm	14.9 - 18 µm	7.0 - 9.0

The results for the spray chamber seem to agree with the paper by Browner et al. (115) whereby in dual concentric spray chambers aerosol loss occurs predominantly in the inner concentric tube and can be explained by either a turbulent or gravitational loss model. Even if these results are too large or small the comparison of the figures is still valid and as such clearly shows that the injector tube internal diameter is a very important factor in this sample introduction system and is responsible for preventing larger droplets from reaching the plasma. Previous experiments (58) have shown that the largest solid clay particles which reach the plasma are around 2 µm for the 2.2 mm injector and 6-7 µm, 8-10 µm for the 3 mm and 4 mm injectors respectively. There is a significant difference between these solid particle sizes and those for aqueous droplets which can probably be explained by the clay particles having a large associated water droplet. The dipole moment of these clay particles (58) may cause them to attract small water droplets to them when in the aerosol and so grow in size, eventually becoming too large to get through.

2.4.6

Slurry Aerosols in Benzyl Alcohol and Distilled Water

Zeolites had previously been analysed by a slurry atomisation technique (60) using xylene as solvent due to its superior dispersion of zeolites compared to water. A brief investigation (discussed in Section 2.5.5) showed that benzyl alcohol was possibly a better solvent for the dispersion of Zeolite A (BHD Ltd, Dorset, UK) and as such was included in this study to see if any differences could be noted between simple solvent aerosols and slurry aerosols.

Aerosols of distilled water and of 5% m/v SPS clay (ECLP, Cornwall, UK) aqueous slurries were compared as well as benzyl alcohol and 5% m/v Zeolite A slurries in benzyl alcohol. In an attempt to allow potential droplet coallessing to occur, these aerosols were all determined after passing through the inner tube of the spray chamber.

2.4.7

Results and Discussion

Considering the simple solvent aerosols first, very large differences can be seen between the aerosol distributions. The organic solvent (Figure 2.7) aerosol droplet distribution is obviously much smaller than that of the aqueous aerosol (Figure 2.6) having more than 50% of its mass below 4.3 µm compared with only 25% for the aqueous aerosol. This is not unexpected considering the differences in surface tension viscosity and volatility of the two solvents (see Table 2.2). However, no significant differences can be seen between the aqueous and the aqueous clay slurry aerosols (Figure 2.8) or the organic and the organic Zeolite A slurry aerosols (Figure 2.9) when the variation in replicate determination is considered.

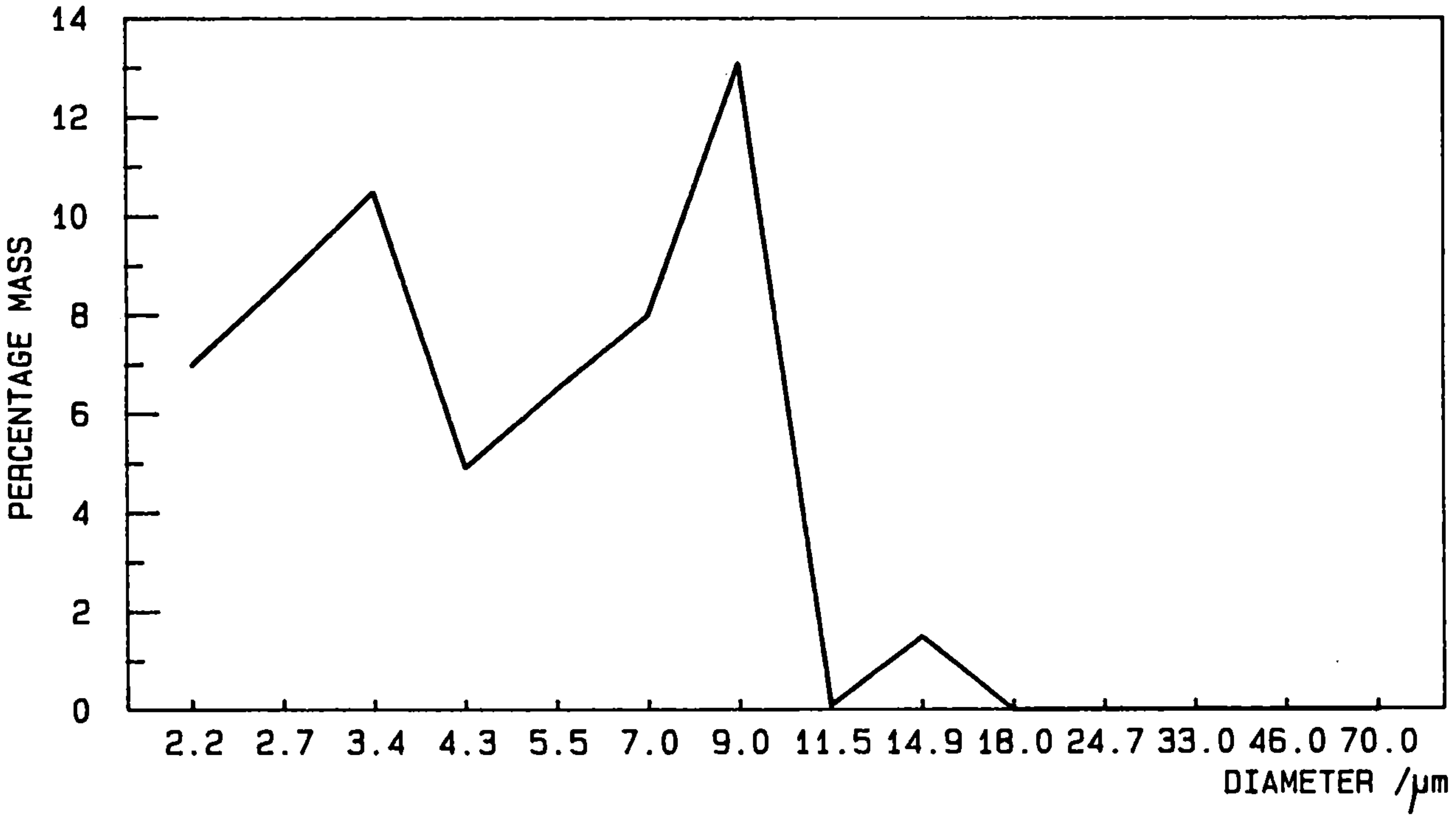


Figure 2.7 Benzyl alcohol aerosol droplet size distribution after inner pass of spray chamber.

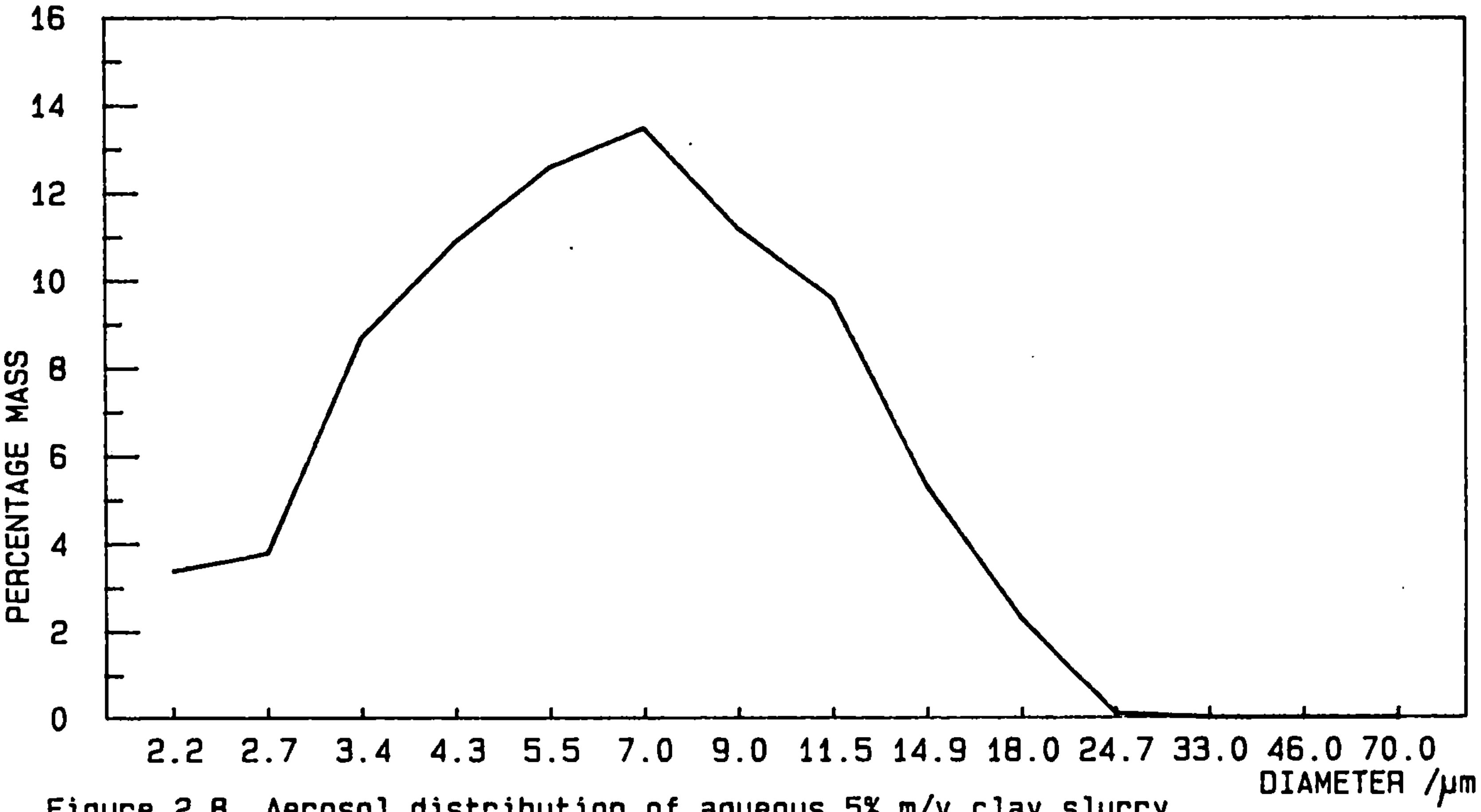


Figure 2.8 Aerosol distribution of aqueous 5% m/v clay slurry.

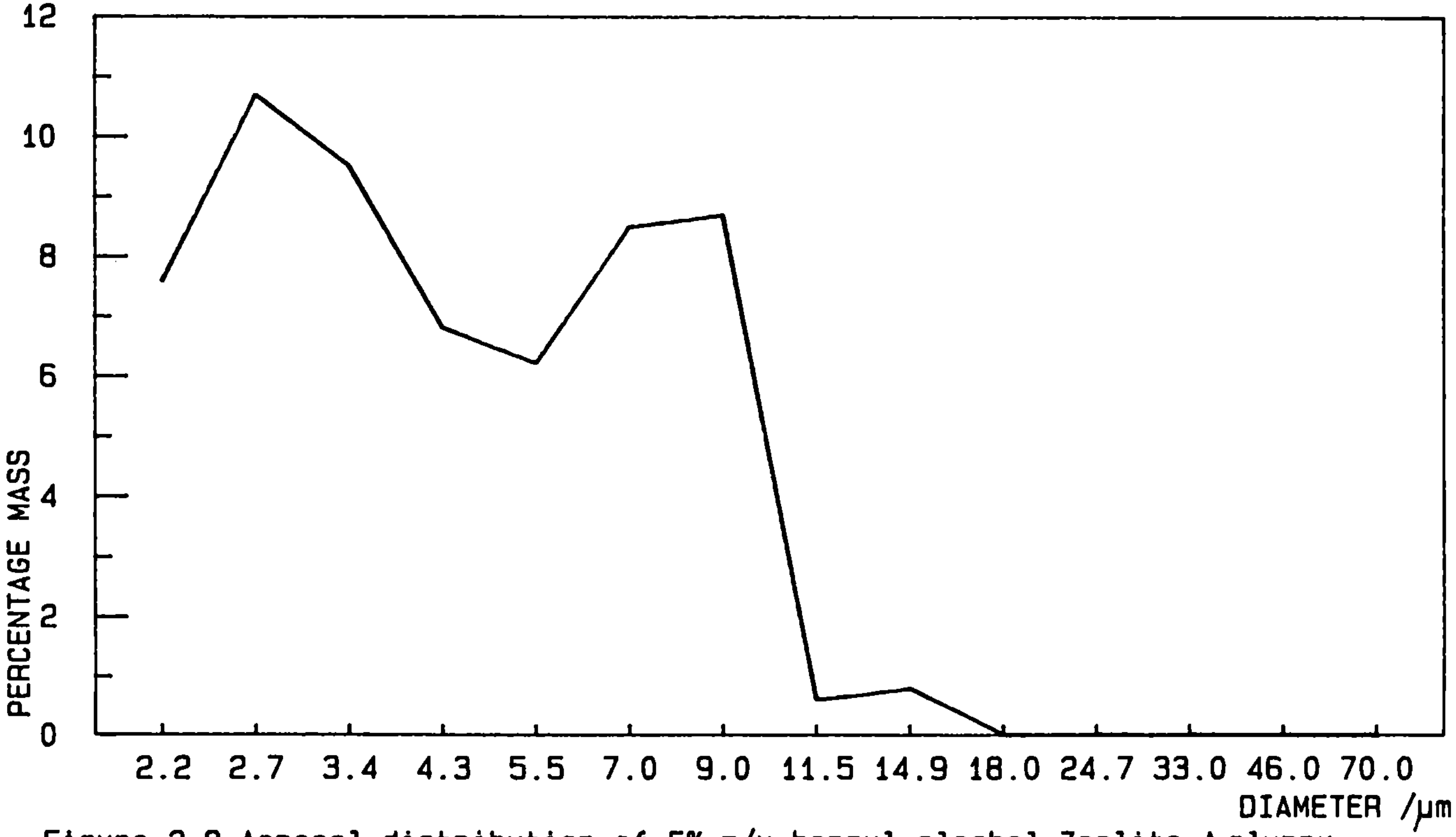


Figure 2.9 Aerosol distribution of 5% m/v benzyl alcohol Zeolite A slurry

Table 2.2

Physical properties of Benzyl alcohol and water.

	Surface Tension Grams/cm	Viscosity CP	B.P. °C	Vapour Pressure at 20°C
H_2O	7.45×10^{-2}	1.0	100	1
Benzyl Alcohol	3.98×10^{-2}	5.8	205.4	18

All data obtained from 'Handbook of Chemistry and Physics' 49th Edition, published by the Chemical Rubber Co, Ohio, U.S.A.

2.4.8

Conclusion of Sample Introduction Investigation

The laser diffraction measurements confirmed the earlier results (58) on particle collection proving that the injector tube is very important in controlling the aerosol droplet size which reaches the plasma fireball. It also showed that hydrophilic solids such as clays have a large associated water droplet when nebulised from aqueous slurries, although there is no evidence that changes do not occur within the aerosol to increase or decrease this associated droplet size. This may not be the case for strongly hydrophobic, difficult to wet solids, such as P.T.F.E.

The implications for slurry analysis using this sample introduction system are that the solid particles must be at the most 18 μm in diameter, even if they are completely desolvated, in order for them to negotiate a 4 mm i.d. injector and 11.5 μm for a 3 mm i.d. injector. Obviously under normal operation particles are likely to have an associated water shell and as such the particle size limits of 10 μm for a 4 mm i.d. injector and 8 μm for a 3 mm i.d. injector previously determined (58) for clays, are probably a reasonable guideline for future slurry analysis.

2.5
Slurry Analysis of Zeolite A
Preliminary Experiments

2.5.1

Introduction

Zeolite A (B.D.H. Ltd., Poole, Dorset) was chosen as the sample to be used in all preliminary experiments because of its availability and because it is supplied as a powder with a very fine particle size, 0.5-5 μm, which was considered to be ideal for analysis by slurry introduction into the ICP.

2.5.2

Instrumentation

All early experiments were carried out using a Kontron S35 Plasmakon Spectrometer (Kontron Spectroanalytic, Eching, West Germany). The system is shown schematically in Figure 2.10 and consists of four basic areas for:

a) Radio frequency power generation;

b) Plasma torch and sample introduction;

c) Wavelength selection and optical detection;

d) Data collection and processing.

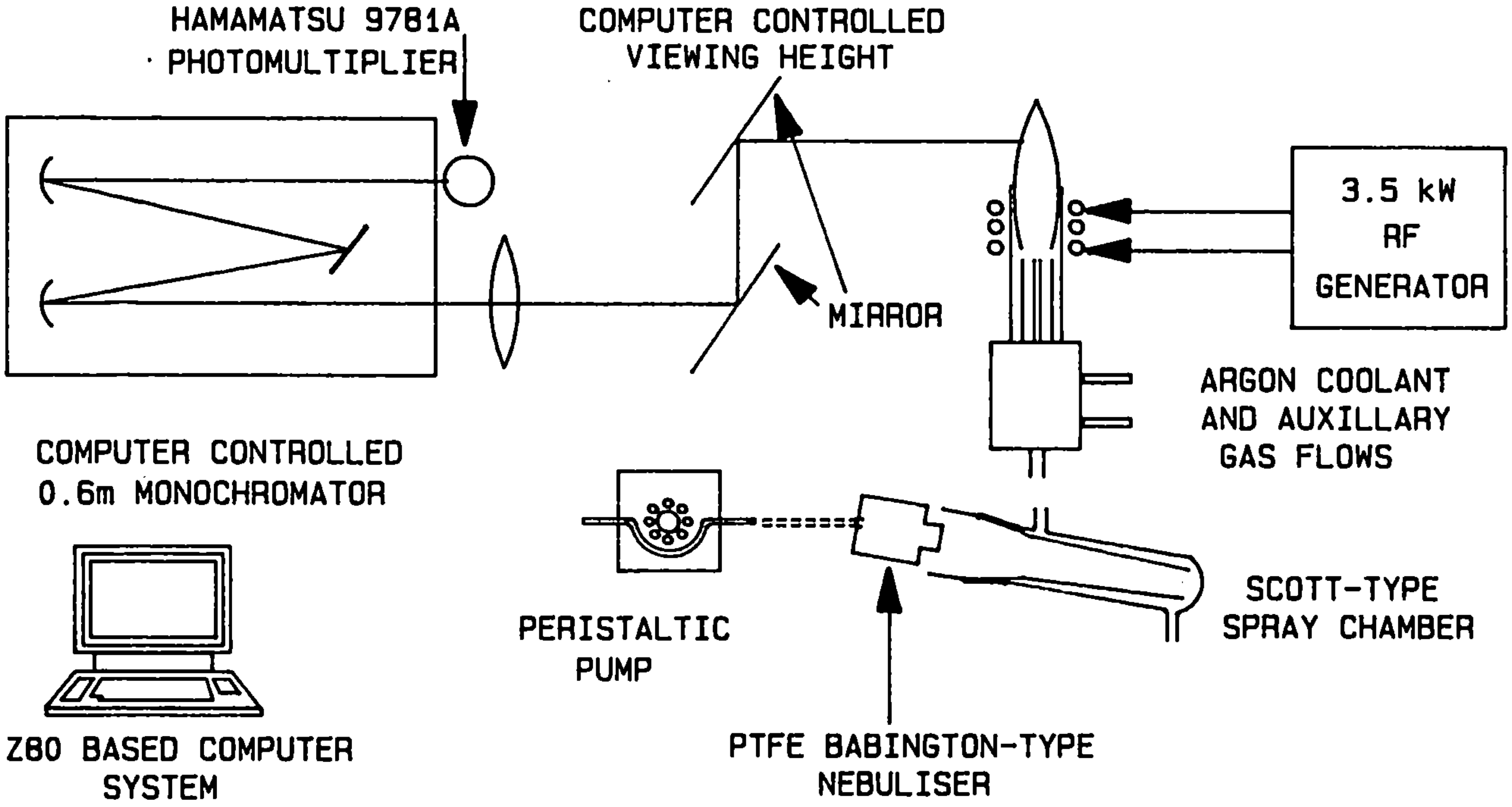


Figure 2.10 Schematic diagram of a Kontron S35 Plasmakon.

2.5.2.1

R.F. Power Generation

The radio frequency power was generated by a crystal controlled 27.12 MHz generator with a maximum output of 3.5 kw. This was supplied to a three turn, water-cooled load coil via an automatic tuning circuit.

2.5.2.2

Plasma Torch and Sample Introduction

The torch was of the larger Greenfield type, having three concentric quartz tubes held firmly in an all P.T.F.E. base by a series of O-rings; hence the torch was fully demountable. The dimensions of the torch were an outer tube of 28 mm diameter, 24 mm bore, an auxillary tube of 22 mm diameter 19 mm bore and a variety of injector tubes each of 6 mm diameter but bores of between 2.2 and 4 mm. This torch was held concentric within the load coil and an all argon plasma ignited by a high voltage spark from a Tesla coil.

Sample aerosols were generated by an all P.T.F.E. Babington type nebuliser (P.S. Analytical, Orpington, Kent). The aerosol then passed through an in-house constructed, all glass, double pass spray chamber and into the plasma via the injector tube.

2.5.2.3

Wavelength Selection and Optical Detection

Radiation from the plasma passes through to a 0.6 m (Czerny-Turner) type monochromator via a computer controlled periscope arrangement which allows accurate adjustment of the viewing zone within the plasma. This zone extends from the top of the load coil to a position 60 mm higher. The monochromator has a computer controlled wavelength adjustment system capable of reproducing selected wavelengths to within 0.0015 nm by the use of an angle encoder. The intensity of the selected wavelength was increased using a Thorne EMI 9781A photomultiplier tube operated at one of four voltage settings (500, 600, 700, 800 volts).

2.5.2.4

Data Collection and Processing

Signals from the photomultiplier were collected and processed by the onboard microcomputer. The computer, based on a Z80A microprocessor, controlled the wavelength selection, the periscopic viewing position and the photomultiplier voltage as well as performing the mathematical and statistical calculations required for line calibration etc.

2.5.3

Experimental

After the previous work on the sample introduction system (Section 2.4) it was considered that Zeolite A could be analysed directly by a slurry introduction technique provided that a 3 mm i.d. injector was used. Unfortunately the 4 mm i.d. injector could not be used for any analysis since it had been shown (58) to cause unacceptable instability due to insufficient penetration of the fireball.

Thus it was anticipated to analyse the zeolite sample using simple aqueous standards and the 3 mm i.d. injector since the zeolite was stated to be 0.5 to 5.0 µm diameter particles.

2.5.3.1

Dispersion of Zeolite A in Aqueous Media

A 1% m/v slurry of Zeolite A was made up using distilled water and this slurry was analysed for particle size distribution using a Coulter counter, TAII multichannel particle counter (Coulter Electronics, Luton, Beds). The resulting distribution (Figure 2.11) was considerably different from the 0.5-5 µm range quoted by the supplier. Observation under an optical microscope showed the particles to be highly agglomerated confirming the particle size results. Use of an ultrasonic bath (Orme Scientific, Manchester) and changing the pH of the slurry in unit intervals from pH 1.0 to pH 10.0 using analytical grade nitric acid (BDH Chemicals Ltd, Poole) gave no improvement in dispersion.

2.5.3.2

Comparison of Effect of Dispersive Agents

The particle size distribution of the simple aqueous slurry (Figure 2.11) was so much larger than that desired that a significant improvement in dispersion was required before the zeolite slurry could be considered for analysis.

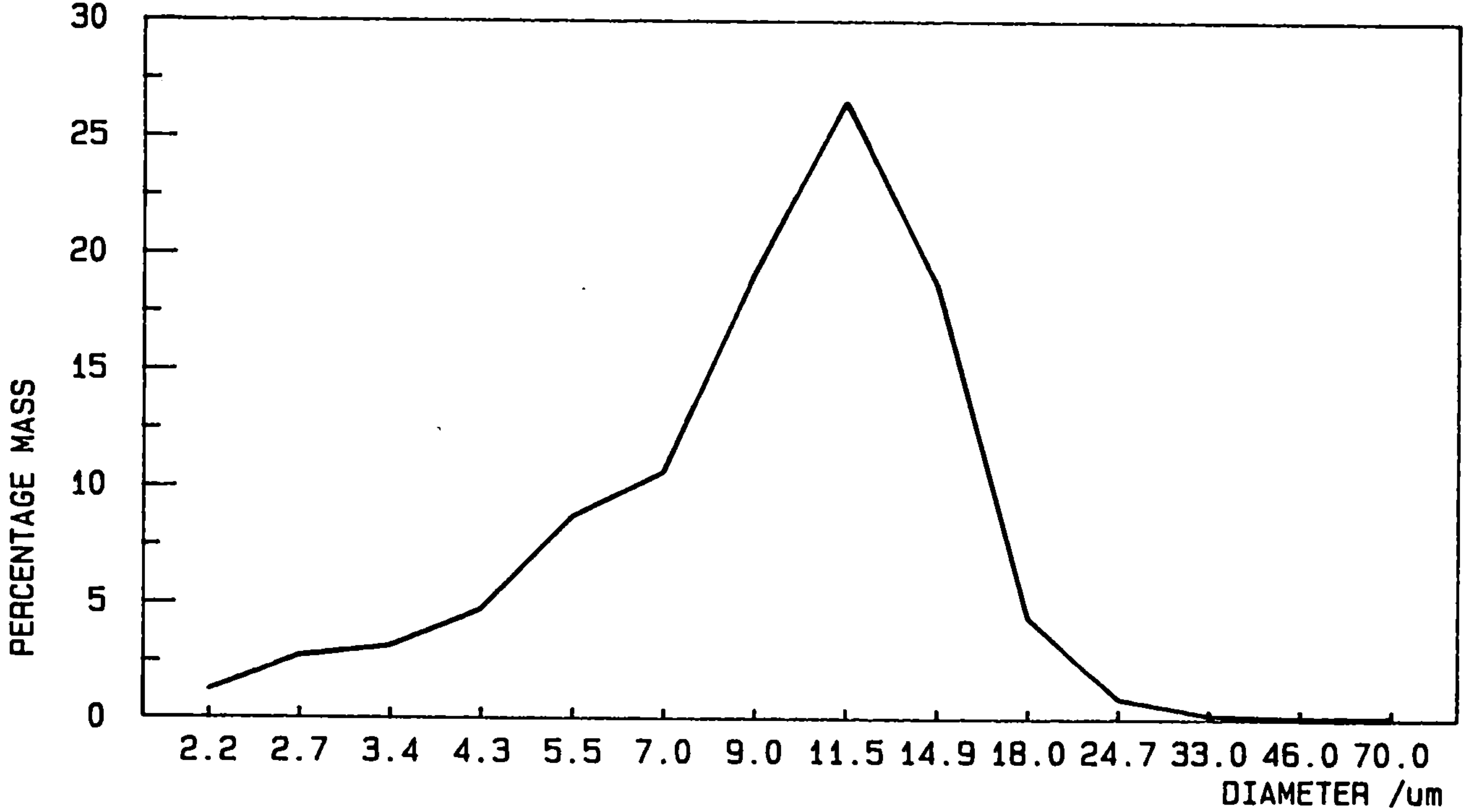


Figure 2.11 Particle size distribution of a 1% m/v slurry of Zeolite A as received

1% m/v slurries were made up in various dispersive agents (Table 2.3), left to stand overnight and placed in a sonic bath for 1 hour before being analysed.

The signal intensity of the iron 259.940 nm line was compared with the intensity of a control slurry containing only 1% m/v Zeolite A in distilled water. The equivalent blank dispersant solutions were made up to correct for reagent blank contamination. The pH of some of the dispersant containing slurries was varied using analytical grade nitric acid. Plasma operating conditions are shown in Table 2.4.

Table 2.4

Plasma Operating Conditions for Comparison of Various Dispersants.

Coolant gas/l min $^{-1}$	18
Auxillary gas/l min $^{-1}$	2.0
Injector gas/l min $^{-1}$	0.9
Forward power/kw	2.2
Reflected power/w	280
Observation height/mm	24
Sample uptake/ml min $^{-1}$	1.5

2.5.3.3

Results and Discussion

The results are shown in Table 2.3. These show that no improvement was obtained with any of the dispersants tried. When viewed under an optical microscope no difference could be seen between the control and the dispersant containing slurries. Four other dispersive agents were made up with 1% zeolite slurries and simply viewed under a microscope. These were Sodium Polyacrylate (dispex), sodium dodecylsulphate, Microclean (International Products Corporation, Chislehurst), and manitol (BDH Chemicals Ltd, Poole) but these also showed no sign of improved dispersion. Interestingly the 23-laurylether caused worse aggregation possibly due to the long chain ends entering the pore structure of the zeolite particles and linking them together or forming micell-type structures which attracted the zeolite particles into a less polar environment.

Table 2.3

Reagents investigated for the dispersion of Zeolite A

Reagent	Concentration %m/v	pH(1)	Id/Ic(2)
Cetyl Pyridinium bromide	0.5	7	1.03
	0.5	3	0.97
Triton-X100	0.5	7	0.96
	0.5	3	0.98
Ammonium hydroxide	1.5	-	0.95
	0.3	-	0.97
	0.006	-	0.97
23-Laurylether	0.5	-	0.86
Tetrasodium pyrophosphate	0.5	-	1.04
	0.1	10	1.02
	0.1	3	1.02
Sodium hexameta phosphate	2	-	1.05
	0.2	-	0.96

(1) pH values not quoted are not adjusted from natural pH of Zeolite A solution as prepared, usually approx pH11.

(2) Id = Blank corrected intensity of Iron 259.940 mm line for dispersant containing slurries.

Ic = Intensity of Iron 259.940 mm line for control slurry

2.5.4

Analysis of Zeolite A using a Thixotropic Slurry

Fuller and Thompson (116) described a method of producing gel based particulate suspensions for analysis by a slurry technique. It was considered that this method may produce improved analytical results since it made possible the preparation of stable homogeneous suspensions without the need for constant agitation during analysis.

2.5.4.1

Experimental

The method of slurry preparation is described in Appendix 1. and due to the higher viscosity of such a slurry the calibration standards were also made up in the same thixotropic media. The analysis was then carried out using the instrumentation described earlier (Section 2.5.2). Plasma operating conditions used in this analysis are shown in Table 2.5. Analytical wavelengths were chosen by scanning over lines to check for spectral interferences from other elements within the zeolite matrix.

To provide results for comparison 0.2 g of the sample was fused in a platinum crucible with 2 g of spectroflux 100B (Johnson Mathey Chemicals, Royston) followed by dissolution in 5% analytical grade nitric acid and dilution to 100 mls with the same acid. This solution was then analysed using the same analytical wavelengths and plasma operating conditions but using calibration by simple 5% nitric acid based standards matched in spectroflux concentration.

All standards were made up from high purity metals or from analytical grade salts and diluted using distilled water, acidified with analytical grade nitric acid to give stock solutions stored in 5% acid in plastic containers.

A third set of results was provided by the collaborating body on this project, ICI Mond Division. These results produced on the same sample were obtained by X-ray fluorescence spectrometry (XRF) using semi-quantitative analysis.

Table 2.5

Plasma operating conditions for the analysis of the thixotropic Zeolite A slurry.

Coolant gas/lmin^{-1}	20.0
Auxillary gas/lmin^{-1}	2.0
Injector gas/lmin^{-1}	0.9
Forward power/kw	2.2
Reflected power/w	280
Observation height/mm	26
Sample uptake/mlmin^{-1}	1.5
Coolant flow/lmin^{-1}	2.0

2.5.4.2

Results and Discussion

The results are shown in Table 2.6 including the analytical wavelengths used.

Table 2.6
Analysis of Zeolite A by various techniques.

Element*	Wavelength (type)	XRF	Fusion ICP-OES	Thixotropic Slurry ICP-OES
Si	288.12 (I)	42.7	44.4	1.16
Al	309.29 (I)	35.3	34.8	0.38
Cr	283.56 (II)	0.1	0.006	0.001
Fe	280.27 (I)	0.03	0.012	0.001

* Results given as %m/m of oxide.

Inspection of these results immediately shows the extent of the sample transport problem, which has in fact been made worse by the inclusion of the thickening agent. The XRF results are semi-quantitative which for lower concentration analytes can mean that they are only accurate to a factor of plus or minus times three. Hence the iron result by fusion is likely to be more accurate, but there is a problem with the chromium result which only further experiments can resolve.

2.5.5

Use of Organic Solvents for the Dispersion of Zeolite A Slurries

Mackey and Murphy (60) reported the suspension of zeolites in xylene for slurry introduction into the ICP, using xylene due to its better powers of dispersion of zeolites compared with water. An initial observation of a Zeolite A Slurry in xylene using an optical microscope did not show any great improvement in the dispersion of the solid. Hence a short visual evaluation of other organic solvents was performed.

2.5.5.1

Experimental

A variety of organic solvents were chosen on the basis of their compatability with aspiration into the ICP (117, 118). 10 ml volumes of 1% Zeolite A slurries were made up and left in a sonic bath for an hour (ice was added to the bath to prevent evaporation of the solvents). A drop of each slurry was then pipetted onto a microscope slide and observed using an optical microscope.

2.5.5.2

Results and Discussion

The organic solvents used are shown in Table 2.7.

Visually no significant difference could be seen in the dispersion of the zeolite except in the case of benzyl alcohol which appeared to give a slightly better dispersion.

Table 2.7

Organic Solvents Investigated for the Dispersion of Zeolite A.

Organic Solvent	Boiling Point/°C	Vapour Pressure at 20°C(mm Hg)
Benzyl alcohol	205.4	1
2-Methyl Cyclohexanol	166	—
Di-ethylene dimetheyl ether	—	—
p-toluene	110.8	21
Nitrobenzene	210.9	1
p-xylene	140.6	4

Benzyl alcohol was investigated further but it was found that the zeolite was acting as a drying agent for the organic solvent and as such the apparent improvement in dispersion was an antifact.

2.5.6

Conclusion of Preliminary Experiments

The agglomeration of the Zeolite A sample did not appear to be a simple problem of attraction between individual particles in solution as it originally appeared. Rather it was agglomerates which were present in the dry solid material and as such had forces of attraction which were too great to be overcome by simple action of dispersive agents or solvents.

Hence this sample, required particle size reduction to individual particles less than 8 μm. Although certain industrial materials such as clays, titanium dioxide, ceramics and some plastics are produced with particle sizes in the low micrometer range, the majority of materials are not. Thus for the technique of slurry sample introduction to be applied to a wide range of samples a technique for rapid, contamination free, particle size reduction must be developed.

2.6

The Reduction of the Particle Size of Solid Samples

Of the small number of ICP slurry atomisation publications the majority mention the reduction of particle size (1c, 59, 60, 61, 119, 120). Somewhat surprisingly none of them mention contamination from the mill or the grinding elements even though most of them mention trace analysis of common elements, such as first row transition metals, silicon, aluminium, calcium and lead. The general requirements of any milling technique should be that it is reasonably rapid, introduces a minimum of contamination into the sample with the option of a wide variety of grinding elements. It should also be flexible enough to grind sample amounts between 0.1 g and 100 g of material with quantitative sample recovery from the grinding vessel. In an ideal situation it should also be low cost and with the facility to grind several samples simultaneously. This is a very wide ranging set of criteria to satisfy and so an initial study into the performance of all readily available mills was undertaken.

2.6.1

Preliminary Investigation of Available Mills

There were two mills at Plymouth Polytechnic, a McCrone micronising mill (McCrone Research Associates Ltd, London) and a vibrating agate ball mill (Beckmann-RIIC, Glenrothes, Scotland) . At the collaborating body laboratories three other mills were investigated for the grinding of Zeolite A. A ball mill (Glen Creston, Stanmore), a planetary mill, a Fritz Pulverisette (Chistison Ltd, Gateshead), and a type of high speed mill/mixer generally used for preparing paint (Red Devil Incorp., Worcester, UK).

Table 2.8 shows a brief summary of the capabilities of these mills.

Table 2.8

General Description of Mills Investigated for the Particle Size Reduction of Zeolite A

Mill Type	Grinding Elements	Sample Size min	Sample Size max	Sample media
McCrone	Corundum	1g	100g	Wet or dry
Vibration	Agate, Stainless Steel	0.01g	0.5g	Wet or dry
Ball mill	Agate	20g	500g	Wet
Planetary	Agate, Stainless Steel	1g	50g	Wet or Dry
Red Devil	Glass	0.1g	500g	Wet

The vibration mill was not studied since it could only be used for very small sample masses and as such would be no use for a considerable number of studies. The McCrone micronising mill had previously (58) been shown as capable of milling samples to less than 5 μm in 10 minutes. In a short simple test 50 mls of water were placed in the mill and left milling for 30 minutes to give a blank. The mill had previously been suspected of introducing contanimation (58) and this was supported as the blank run produced approximately 0.2 g of a fine slurry which was from the corundnum grinding elements. Hence due to the lack of other grinding elements this mill was not studied further.

2.6.1.1

Experimental

The planetary mill was loaded with 2 g of dry Zeolite A and run using the agate grinding elements for 30 minutes. The ground material was then washed from the mill and made up to 50 mls with distilled water. The particle size distribution of the ground material shown in figure 2.12 (compare with unground figure 2.11) was obtained using the Malvern laser 3300 system.

The Red Devil was loaded with 2 g of Zeolite A, 30 g of 3 mm glass beads and 30 mls of distilled water. The mill was run for 20 minutes after which time the zeolite was washed from the beads and diluted to 50 mls before being analysed on the Malvern system. The particle size distribution is shown in Figure 2.13.

The ball mill was loaded with 20 g of Zeolite A and the mill 30% filled with 15 mm agate balls and 100 mls of distilled water. The mill was placed on its rollers and left running for 2 hours after which time the zeolite was washed from the mill and diluted to 500 mls with distilled water. The particle size distribution was again determined using the Malvern system and is shown in Figure 2.14.

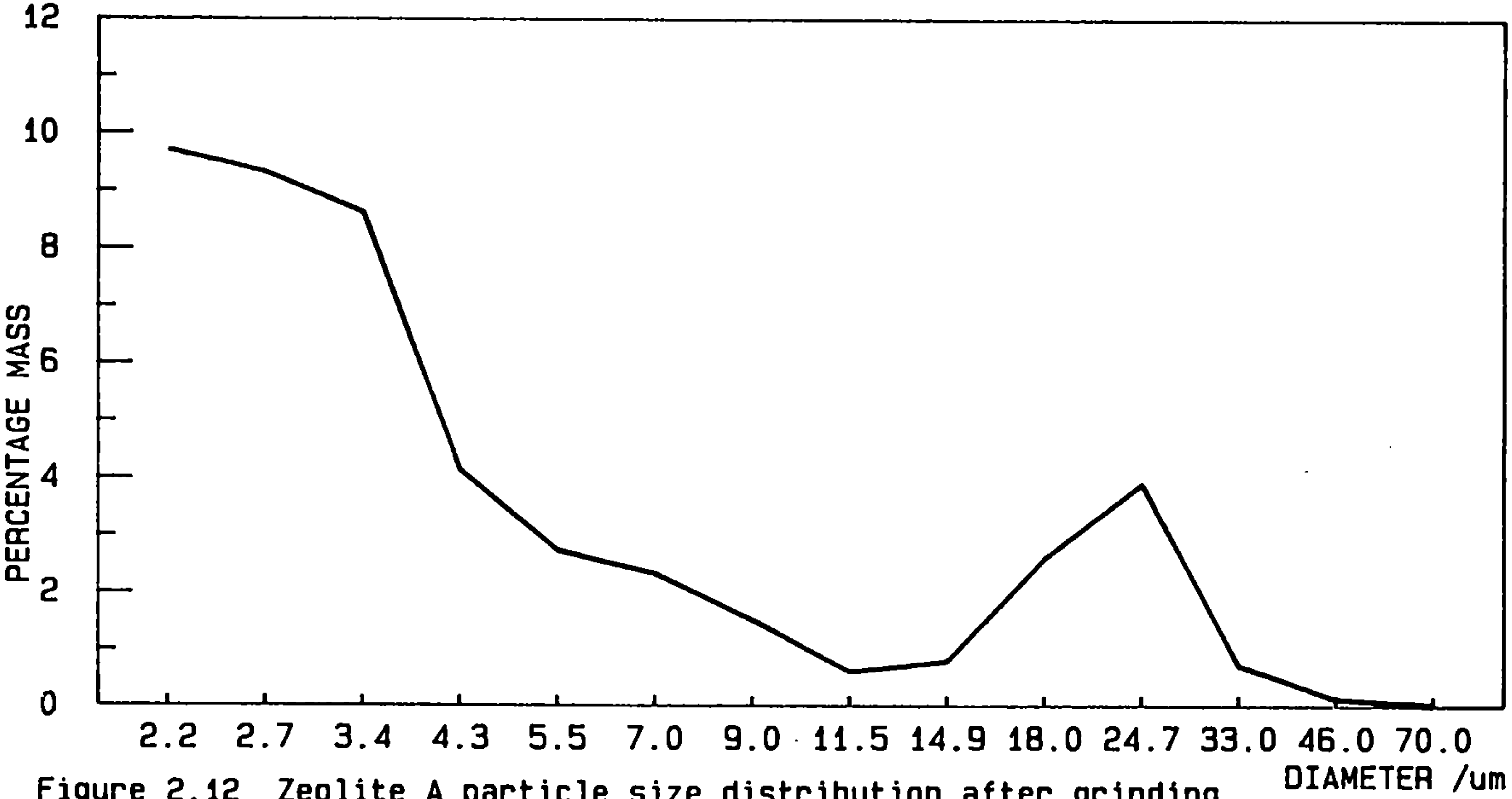


Figure 2.12 Zeolite A particle size distribution after grinding with the planetary mill

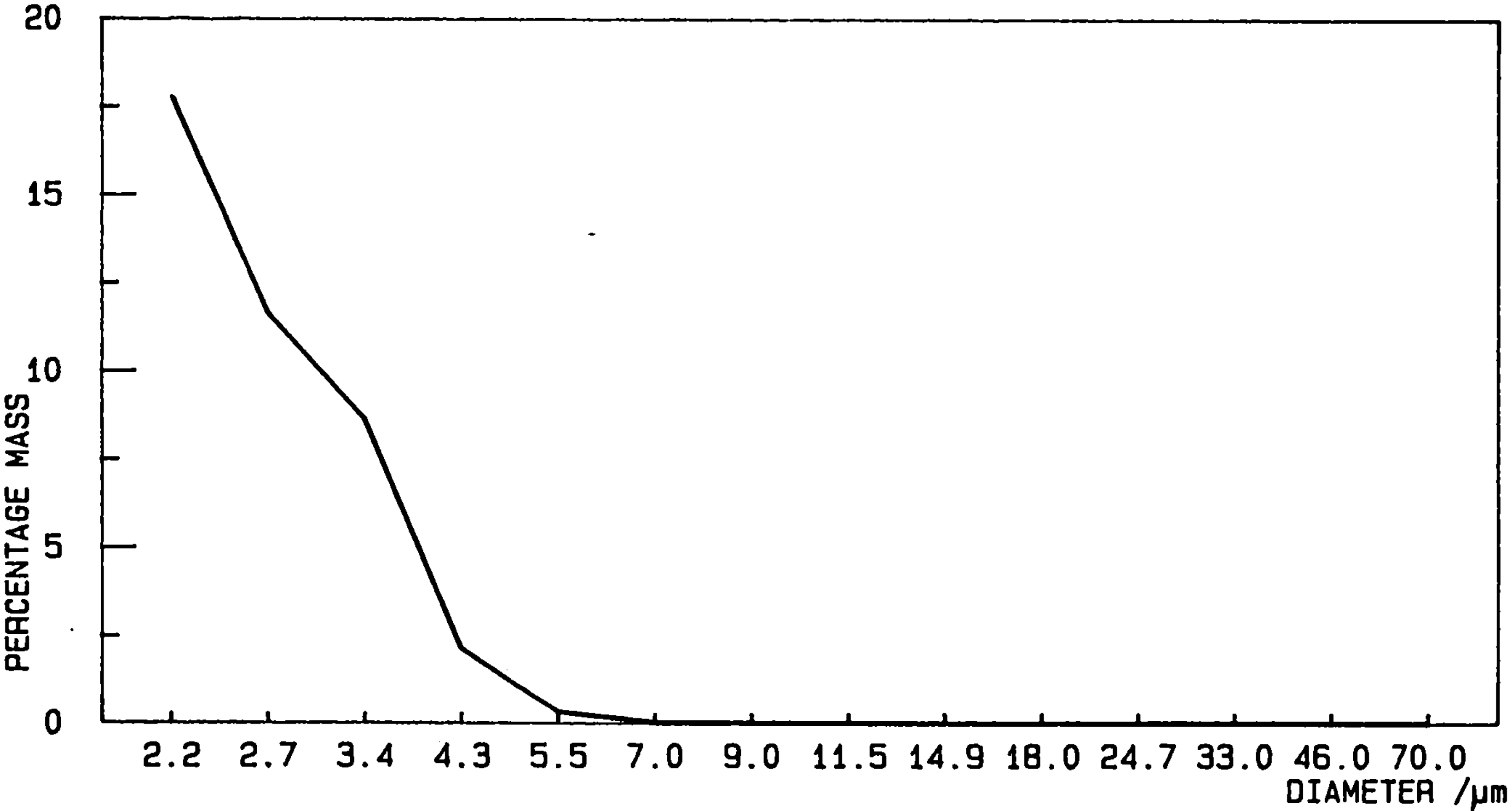


Figure 2.13 Particle size distribution of Zeolite A ground by the Red Devil.

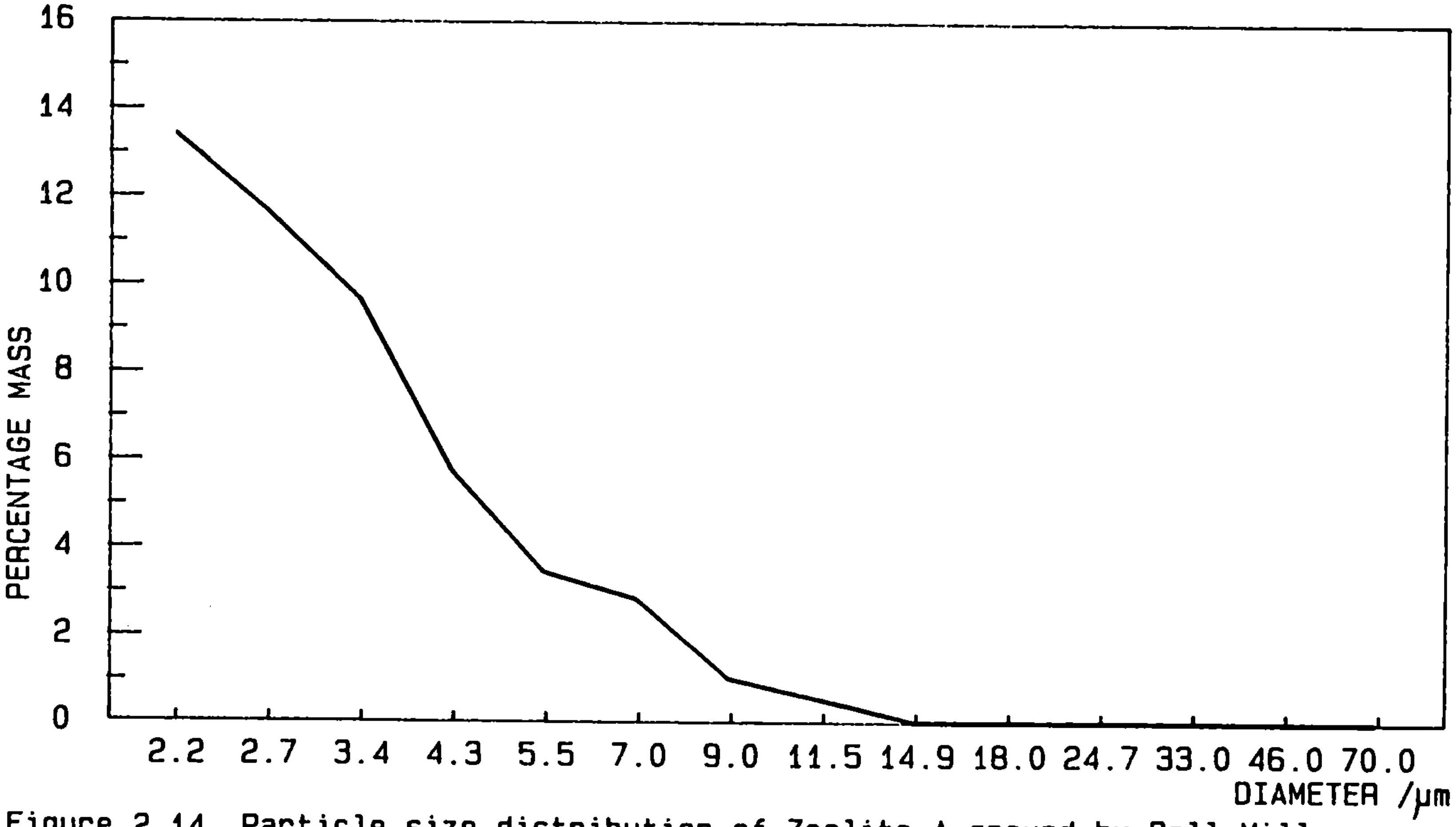


Figure 2.14 Particle size distribution of Zeolite A ground by Ball Mill.

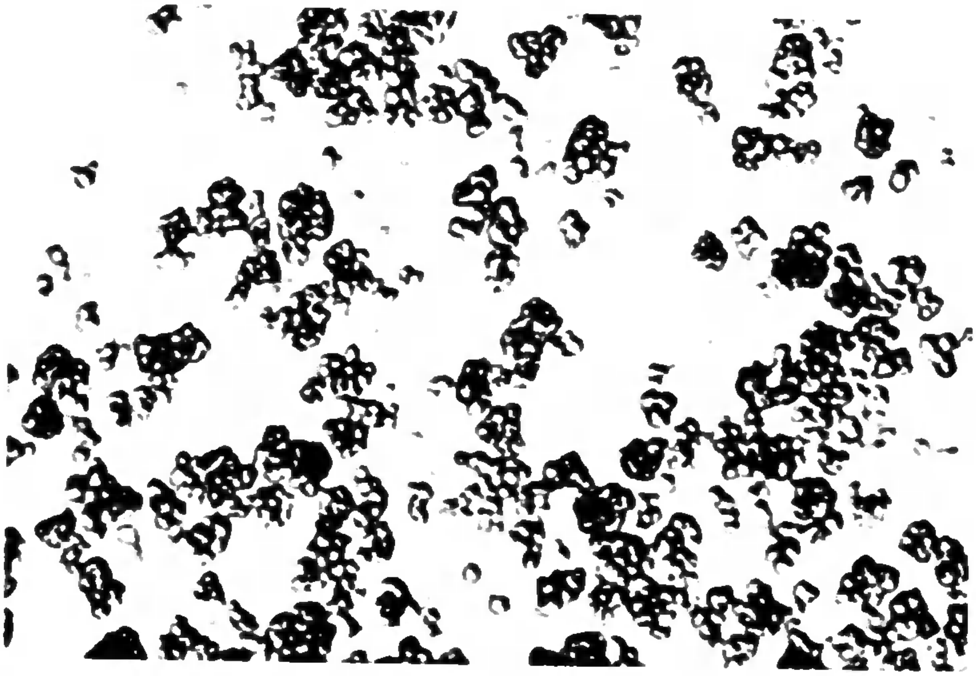
2.6.1.2

Results and Discussion

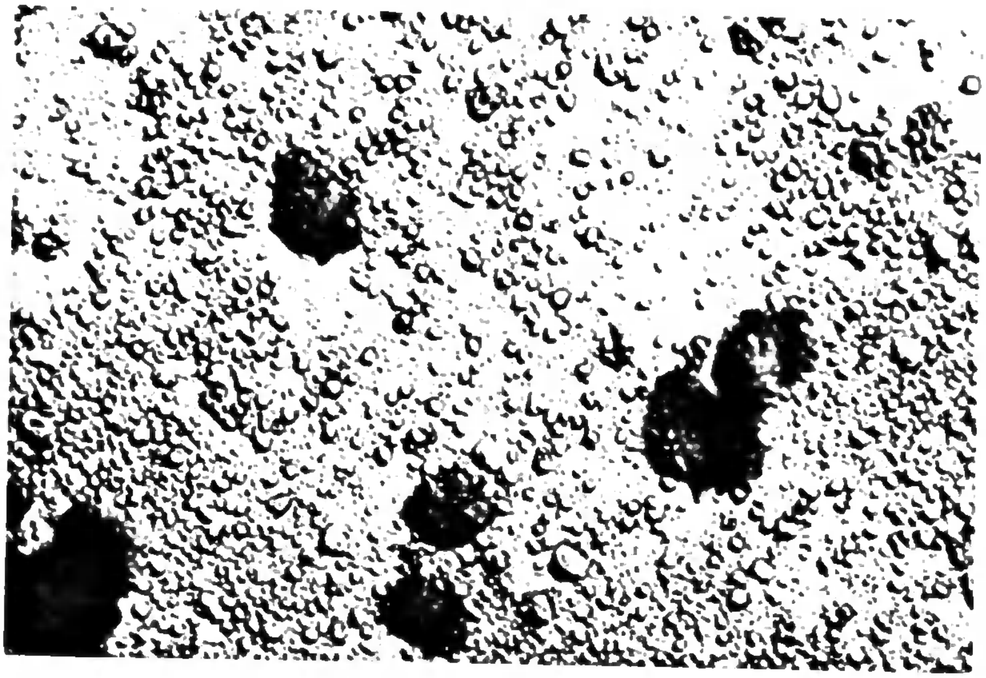
Of the three mills investigated the Red Devil was obviously the superior mill, producing a much finer slurry in a shorter time. In terms of contamination this preliminary study provided no information but further investigations are described in Section 2.6.2.1. The planetary mill produced an unusual result in that an apparent production of larger particles was observed (see Figure 2.12). This was further investigated by viewing the slurry under optical microscopy (Plate 2.1) and the results clearly show contamination of the zeolite slurry. On close inspection of both the mill and the slurry these larger particles were determined as being flakes of agate broken from the grinding elements.

The ball mill produced a reasonably fine slurry with low particle size and no visible signs of agate from the grinding elements, but the whole process was rather slow and limited to large sample sizes.

Unfortunately the Red Devil mill/mixer was very large and originally designed for much larger samples. Having a 3 kw electric motor and a large sample holding mechanism it was analogous to using a sledge hammer to crack a nut. Thus an attempt was made to use the same principle but to scale the apparatus down perhaps trading off some of the efficiency in order to have a more manageable piece of instrumentation.



BEFORE GRINDING



AFTER GRINDING SHOWING AGATE FLAKES

SCALE: 1 mm = 2 μm

Plate 2.1 Zeolite A before and after grinding with the Planetary mill.

2.6.2

Development of a Simple But Effective Milling Method

The principle on which the Red Devil mill worked, was simply the impaction of very large numbers of small beads upon the sample. The beads being fairly small and very violently aggitated they had enough energy on impact to break down not only the aggregates but also the primary particles. This was the action to be mimicked in order to produce an efficient mill and as such a flask shaker (Model SGL-705 Gallenkamp, Loughborough) was selected as the source of this violent shaking.

2.6.2.1

Experimental

A series of experiments involving various sizes of glass beads, length of grinding time and ratio of beads to sample were investigated. The flask shaker was investigated using a stroboscope and found to oscillate at 16 hz maximum, the amplitude being dependent on the load. In each of these experiments the quality of the slurry (i.e. its particle transport throught the sample introduction system) was assessed by analysing the silicon concentration by slurry introduction into the Kontron ICP, calibrating with simple aqueous standards. These results were compared with the actual silicon concentration in zeolite slurry and expressed as a ratio termed the atomisation efficiency (originally defined by Willis (123))

$$= \frac{\text{determined Si concentration}}{\text{actual Si concentration}} \times 100\%$$

All initial experiments were carried out using acid washed 125 ml Nalgene bottles. The plasma operating conditions used are shown in Table 2.9.

Table 2.9

Plasma operating conditions for the analysis of silicon in ground Zeolite A slurries.

Analytical wavelength/nm	251.432
Coolant flow/lmin^{-1}	23
Auxillary flow/lmin^{-1}	1.0
Injector flow/lmin^{-1}	0.9
Forward power/kw	2.5
Reflected power/w	300
Observation height/mm	32
Sample uptake/mlmin^{-1}	1.5

2.6.2.2

Effect of Bead Size and Grinding Time

Three sizes of glass bead were purchased (Jencons Scientific Ltd), 3, 5 and 8 mm diameter. Slurries were made up containing 10 g of Zeolite A, 10 g of beads and 30 mls of water. These were placed on the flask shaker and after one hour removed. The zeolite was washed from the beads and diluted to 100 mls followed by analysis as described in Section 2.6.2.1. This was repeated for grinding times of 3, 5 and 7 hours.

2.6.2.3

Results and Discussion

Table 2.10 shows the grinding results and clearly the 3 mm beads are superior. This shows that it is the number of collisions which is important and not the momentum of the impact.

Table 2.10

Atomisation efficiency of various ground zeolite slurries

	Bead Diameter		
Grinding Time	3 mm	5 mm	8 mm
1 hour	27%	20%	9%
3 hours	53%	43%	24%
5 hours	60%	45%	36%
7 hours	68%	57%	39%

The 3 mm beads were used for further studies, smaller beads were considered but as the beads got smaller separation of the ground slurry from the beads becomes increasingly difficult and quantitative recovery is not likely to be achieved.

2.6.2.4

Effect of Bead to Sample Ratio (Mass to Mass)

Using the 3 mm grinding beads slurries were made up containing 10 g of Zeolite A together with 20 mls of water with 10, 40 and 100 g of beads. These were all ground for 8 hours before being washed from the beads diluted to 100 mls with distilled water and analysed as described in Section 2.6.2.1.

2.6.2.5

Results and Discussion

The results below (Table 2.11) show two points, firstly that there is a problem of contamination from the beads. This was not unexpected since the beads began as clear spheres and ended up completely opaque showing that the surface of the beads was being chipped and scratched. This problem can be overcome in two ways, increasing the hardness of the beads by using a material stronger than glass (agate, tungsten carbide, zirconia) and by chosing grinding elements whose matrix elements are not required to be determined in the sample being ground.

Table 2.11

Atomisation efficiency of a function of sample to bead ratio

Sample/Bead ratio m/m	Atomisation efficiency
10/10	72%
10/40	86%
10/100	118%

The second point shown by the results is that the higher the bead/sample ratio the greater the efficiency of grinding. Again a compromise is reached since larger numbers of beads make it increasingly difficult to obtain quantitative recovery of the slurry. Hence the maximum ratio recommended of sample to beads is 1:10. This was the ratio used in all further experiments.

2.6.3

Conclusions

The method of grinding developed manages to meet most of the criteria described at the beginning of Section 2.6. It is perhaps not as rapid for refractory materials as some other milling techniques, but it is very simple, flexible and inexpensive. For less refractory materials, such as ion-exchange resins, the grinding time required to reach particle sizes optimal for slurry atomisation is only 15-30 minutes. The contamination problem has been overcome by the use of blown, hollow, zirconia beads (Glen Creston, Stanmore) and the grinding technique successfully applied to a wide variety of samples (112). In the long term it could obviously be improved upon especially since the flask shaker is used at the limit of its capabilities. It has been shown to work well for the preparation of slurries for DCP-OES (121), ICP-OES (121, Chapter 3) and ICP-MS (Chapter 4).

These preliminary investigations showed that analysis by slurry nebulisation ICP-OES was certainly viable provided certain criteria could be met. The injector tube of the plasma torch was identified as being a surprisingly important limitation in the sample introduction system and determined the maximum particle size of slurries which could be analysed. This limitation caused the investigation of methods of particle size reduction and a novel method was developed. Thus the substantiation of this work must obviously come from the analysis of various samples including certified reference materials and this work is described in the next chapter.

CHAPTER 3

THE ANALYSIS OF SOLID SAMPLES BY SLURRY ATOMISATION - ICP-OES

3.1

Introduction

The preliminary investigations into slurry sample analysis (Chapter 2) showed the limitations of the sample introduction system and a method of reducing particle size to overcome these was demonstrated. This chapter describes the practical application of those ideas and the results obtained with a variety of samples. To show the validity of the technique three standard reference materials were analysed together with three industrial inorganic materials.

3.2

The Analysis of Various Slurries Without Any Pre-Treatment

Certain industrial materials and natural samples can be considered as suitable for direct analysis by slurry atomisation - ICP-OES without any pre-treatment other than the addition of a suitable dispersive agent to the slurry. In general these samples must meet the criterion of particle size to negotiate the sample introduction system, but it has been shown (58) that a matrix element of known and constant concentration can be used as an internal standard to compensate for sample transport problems.

Early in this project three such samples were analysed and although only independent analysis results are available for one of the samples they are included as indicators of the type of applications which have been attempted.

3.2.1

The Analysis of Titanium Dioxide by Slurry Atomisation

An almost ideal sample for a slurry atomisation technique, titanium dioxide (Laporte Industries Ltd, Grimsby) is commercially produced in low micrometre and submicrometre particle sizes, having the majority of its mass arising from particles less than 2 μm in diameter (see Figure 3.1 for particle size distribution of the sample used in this experiment).

3.2.1.1

Experimental

A sample of titanium dioxide was sampled as received. Slurries ranging from 1 g to 20 g per 100 mls were readily dispersed in 0.1% (m/v) tetrasodium pyrophosphate (BDH Chemicals Ltd, Poole). The slurries were analysed after instrument calibration with simple acidified standards containing 1% (v/v) nitric acid and 0.1% (m/v) tetrasodium pyrophosphate. The slurries were kept homogenous during nebulisation by being continuously stirred with a magnetic stirrer. The operating conditions for the Kontron instrument used are shown in this analysis in Table 3.1.

3.2.1.2

Results and Discussion

The results obtained by slurry atomisation and the independent results (supplied by Laporte Industries Ltd, Grimsby) are shown in Table 3.2. The independent results are not certified values and no description of the methodology by which they were obtained is available nor is the uncertainty of the values.

Table 3.1

Plasma operating conditions for the analysis of titanium dioxide.

Coolant flow/$l$min^{-1}	20
Auxillary flow/$l$min^{-1}	1.0
Injector flow/$l$min^{-1}	0.9
Forward Power/KW	2.2
Reflected Power/W	280
Sample uptake/ml min^{-1}	1.5

Table 3.2

Analysis results for Titanium Dioxide by slurry atomisation.

Element	Wavelength /nm	Independant analysis	Slurry analysis
		% Oxide	
Al	309.271(I)	4.2	4.1
Si	288.158(I)	5.0	4.2
		$\mu g g^{-1}$ Oxide	
V	289.332(II)	3	18
Cr	283.563(II)	8	22
Fe	239.562(II)	91	25
Cu	224.700(II)	1	0.5
Ni	232.003(I)	29	12
Ca	393.366(II)	200	70

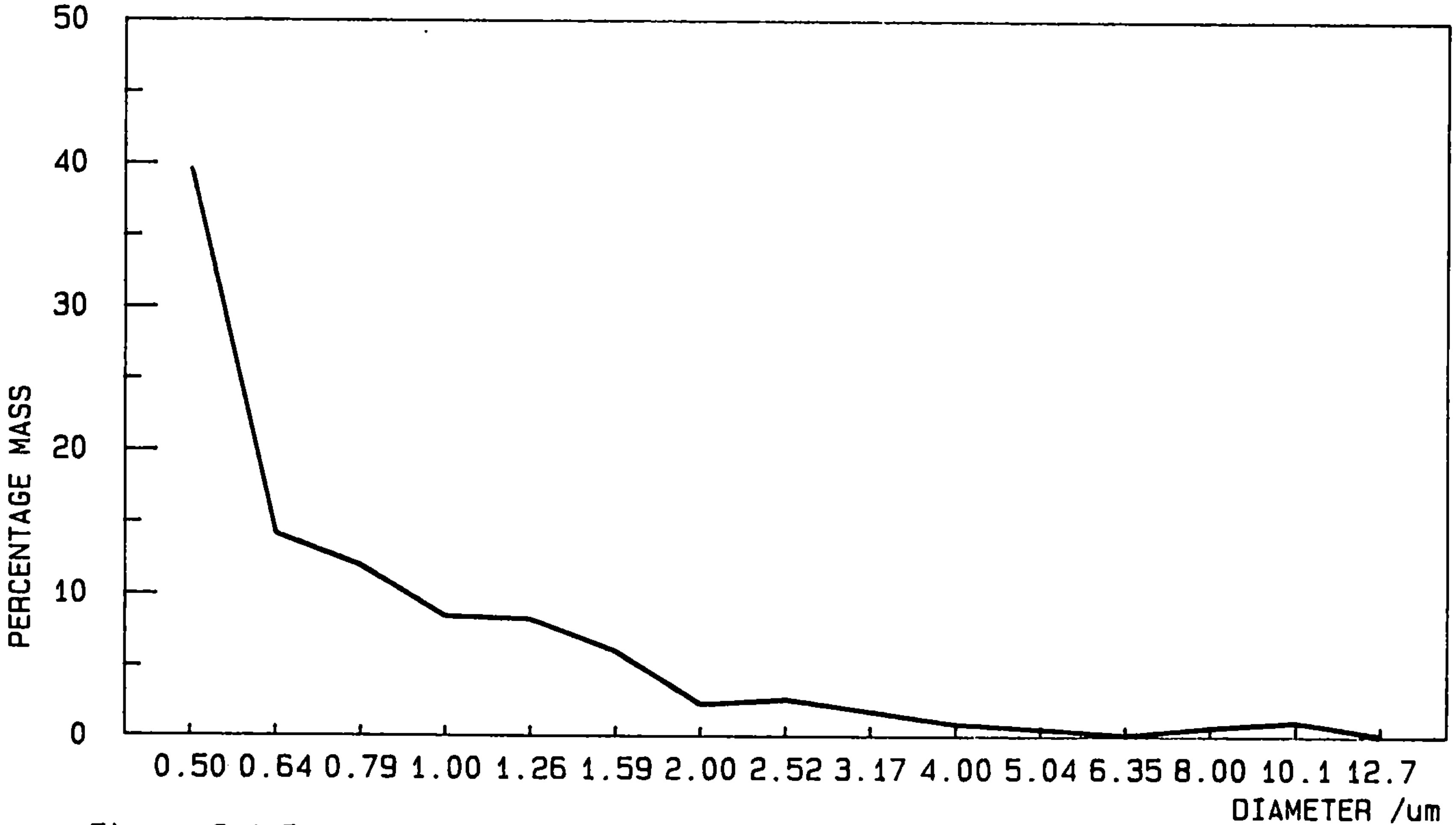


Figure 3.1 Particle size distribution of titanium dioxide slurry

The major disadvantage of this type of sample is the extremely line rich spectra produced by the titanium matrix. This caused many problems in line selection and is probably the main reason why the agreement between the two sets of results is not as good as desired. In several cases the lines used for the analysis were a compromise between loss of sensitivity for a particular element due to the low intensity line chosen and the acceptable amount of spectral interference which could be corrected for.

Due to those severe spectral interferences perhaps the use of slurries for atomic absorption measurements as carried out by Fuller (59) is more appropriate for this type of sample, alternatively the use of slurry atomisation ICP-MS might be the best method.

3.2.2

The Analysis of a River Water Sample

The analysis of a water sample (supplied by the South-West Water Authority) taken from a river in Cornwall heavily polluted by discharge from an old mine and containing a heavy loading of particulates was achieved using the slurry atomisation technique. The river had a very heavy loading of particulates which would usually be filtered off and dried before being taken into solution using a fusion technique. These results from the liquor and the particulates would then have to be combined to give average analysis figures for the sample as a whole. Using a slurry atomisation technique this analysis can be performed with a minimum of sample treatment.

3.2.2.1

Experimental

The water sample was received containing 1% (v/v) nitric acid in order to preserve the trace metal levels. Standards were prepared from analytical grade single element solutions in 1% (v/v) analytical grade nitric acid to match the sample. The sample was analysed while being stirred rapidly to keep the larger particulates dispersed throughout the solution. The Kontron plasma operating conditions are shown in Table 3.3 and the analysis results shown in Table 3.4.

3.2.2.2.

Results and Discussion

The results show the very high level of metal contamination in this river which has an extremely high particulate loading. Unfortunately no independent analysis results were supplied and the sample supplied was too small to allow two methods of analysis to be undertaken. A general comment can be made since, although the sample was not characterised by particle size analysis, the particulates in the sample were obviously too large for slurry atomisation to be accurate. Some of the particles blocked the peristaltic pump tubing (0.5 mm i.d.) and this tubing had to be replaced with 1 mm i.d. tubing in order to perform the analysis. The nebuliser significantly was not blocked by this excessive sample and this was a good indicator of the robustness of the design.

Table 3.3

Plasma operating conditions for the analysis of a natural water sample.

Coolant flow/$l min^{-1}$	20
Auxillary flow/$l min^{-1}$	1.0
Injector flow/$l min^{-1}$	0.9
Forward Power/kw	2.0
Reflected Power/w	280
Sample uptake/ml min^{-1}	2.2

Table 3.4

Analysis results for a natural water sample by slurry atomisation.

Element	Wavelength nm	Concentration $\mu g\ ml^{-1}$
Cd	214.438	0.9 ± 0.1
Cr	267.716	0.34 ± 0.02
Cu	324.754	10.0 ± 0.5
Fe	238.204	960.0 ± 0.2
Mn	293.306	10.5 ± 0.2
Ni	216.556	3.8 ± 0.1
Pb	220.353	4.5 ± 0.3
Zn	213.856	3.6 ± 0.1

3.2.3

The Analysis of P.T.F.E. Powder by Slurry Atomisation

P.T.F.E. is a notoriously difficult sample to analyse for trace elements due to its highly inert nature. It is resistant to all forms of wet chemical digestion and as such requires ashing prior to being taken into solution. During ashing large quantities of hydrogen fluoride gas are produced and many elements which form volatile fluorides are lost. Hence a slurry atomisation approach is one of the few options available for trace element analysis.

3.2.3.1

Experimental

The P.T.F.E. was received finely ground to less than micrometre particle size which could be dispersed in aqueous solution with a long chain fluorinated surfactant. Unfortunately, these dispersions could not be characterised by particle size analysis because the electrolyte solution used for the Coulter counter caused agglomeration of the P.T.F.E.

The dispersions were prepared by warming the P.T.F.E. powder in a 2% (m/v) solution of the dispersant (supplied by the Montgomery Plating Co Ltd, Coventry, the formulation of the surfactant is proprietary information) for several hours until visually the powder had formed a homogeneous slurry. Standards were prepared by diluting from acidic stock solutions into 2% (m/v) solutions of the surfactant with no further addition of acid. The slurries were kept homogeneous by rapid stirring during the analysis.

Table 3.5

Plasma operating conditions for the analysis of P.T.F.E. powder by slurry atomisation.

Coolant flow/lmin^{-1}	20
Auxillary flow/lmin^{-1}	1.0
Injector flow/lmin^{-1}	0.9
Forward Power/KW	2.2
Reflected Power/W	280
Sample uptake/ml min^{-1}	1.2

Table 3.6

Trace elements in P.T.F.E. powder by slurry atomisation.

	Sample Reference Number					
	840926B	840912	507H103	507H104	507H105	508H112
Element	(Concentrations µg/g)					
Cd	.2	.2	1.1	.25	.25	0.6
Co	.4	25	.25	.25	.25	.25
Cu	0.2	10	.25	8	.25	0.9
Fe	1.8	40	1	35	.25	.25
Mn	0.05	0.05	-	-	-	-
Ni	0.05	4	.25	.25	2	1.5
Pb	0.4	8	.25	.25	.25	.25
Sb	-	0.1	-	-	-	-
Zn	0.8	2.5	.25	.25	.25	.25

Table 3.5 shows the Kontron plasma operating conditions used for the analysis and Table 3.6 shows the results.

3.2.3.2

Results and Discussion

Unfortunately no alternative source of results was available for comparison purposes but perhaps this is not surprising considering the difficulty of this analysis. The first two samples (840926B and 840912) show the contamination introduced into the P.T.F.E. by a new stainless steel stirring system (identified by the sample suppliers after they were shown these results). The history of the other four samples is unknown, although cobalt contamination may arise from catalyst residues.

3.2.4

Conclusion

These three applications show some of the possibilities available with a slurry atomisation approach.

Other applications not detailed include the analysis of terephthalic acid samples, water soluble and insoluble organic dyes and several other samples which are described in Section 3.3 but which were ground prior to analysis.

The obvious problem in the direct analysis of samples without any pre-treatment is that the analysis has an increased number of potential problems compared to analysing solutions. The homogeneity of the sample is crucial since any element which is associated with larger than acceptable particles is going to produce erroneous results. If the sample is homogeneous but a correction factor is being applied because atomisation efficiency is low then the element chosen for the internal standard must be given very careful consideration as any fluctuation in the real concentration of this element will affect the accuracy of all the elements being determined. When all of these pitfalls have been considered and overcome slurry atomisation offers very real advantages for quality control and possibilities for continuous on-line monitoring.

3.3

Analysis of Various Samples After Particle Size Reduction

The majority of samples which any analytical chemist receives have particle sizes which are too large to be considered for direct analysis using a slurry atomisation technique. Some of these samples can be easily ground to a fine particle size and even those samples which may be fine powders can benefit from some grinding procedure to ensure that they are homogeneous.

The samples described in this section were chosen as a variety of samples which are typical of industrial materials as well as three standard reference soils to demonstrate the validity of the technique.

3.3.1

Instrumentation

Due to technical faults on the original Kontron plasma spectrometer another plasma system was assembled and used for all analyses described in this section.

The instrumentation was developed using a 2.5 kw R.F.A. generator (R.F.A. Ltd, Brighton, Sussex). The generator was a crystal controlled 27.12MH_Z system with automatic matching circuitry and a Scott-Fassel size torch in a 3-turn water-cooled load coil. The plasma torch was of 18 mm diameter with a tulip shape auxillary tube and a demountable injector of 3 mm internal diameter. This torch was used together with the in-house built double pass spray chamber (58) and all P.T.F.E. Babington-type nebuliser. The spectrometer was of the echelle type and was part of a Beckmann Spectrospan III D C Plasma system. The optical system and associated electronics have been well described by Sparkes (121) thus suffice to say that the image of the plasma was focused onto the entrance slit of the echelle using a quartz lens to give a slightly reduced image. This system provided only very poor control of viewing height by altering the position of the quartz lens but some adjustment was possible.

Signals from the spectrometer were fed to a chart recorder and all calibration and analysis was achieved by measurement from the chart paper.

3.3.2

Experimental

The samples analysed were:-

(a) Zeolite A molecular sieve (BDH Chemicals Ltd, Poole).

(b) Chromium III oxide catalyst pellets (ICI MOND Division, Runcorn).

(c) Mixed oxide catalyst (ICI MOND Division, Runcorn).

(d) Soil BCR 142 (Community Bureau of Reference, Brussels).

(e) Soil SO-1 (Canmet, Ottawa, Canada).

(f) Soil SO-2 (Canmet, Ottawa, Canada).

Each of these samples was ground for 8 hours by the method described previously (see Section 2.3) and made up as 0.1% to 10% (m/v) slurries in 0.5% (m/v) tetrasodium pyrophosphate (BDH Chemicals Ltd, Poole) as a dispersant. Standards were prepared from stock solutions and made up in 0.5% (m/v) tetrasodium pyrophosphate. All the samples were analysed using the same calibration curves except where concentrations of matrix elements had to be determined using low sensitivity lines and higher concentration standards. Certified values were available for the reference materials and fusions were carried out on the other 3 materials.

Zeolite A and the mixed oxide catalyst were both fused using the same method. This involved intimate mixing 0.2 g of the sample with 1 g of spectroflux 100B (Johnson Matthey Chemicals, Royston, Essex) in a platinum crucible. The fusion mix was then heated over a Bunsen burner until a clear melt was obtained. The melt was allowed to cool before being dissolved in 50 mls of 5% (v/v) analytical grade nitric acid. This solution was then made up to 100 mls with the same acid. Standards were prepared by matching the acid and spectroflux concentrations and determinations carried out using the ICP system described in Section 3.3.1.

Table 3.7

Plasma operating conditions for slurry analysis using the RFA system.

Coolant flow/$\mathrm{l\,min^{-1}}$	13
Auxillary flow/$\mathrm{l\,min^{-1}}$	1.0
Nebuliser flow/$\mathrm{l\,min^{-1}}$	1.0
Forward Power/kW	1.3
Reflected Power/W	5
Sample uptake/$\mathrm{ml\ min^{-1}}$	1.2

The chromium III oxide catalyst pellets were analysed after a fusion with sodium peroxide. Ten pellets (0.2 g each) were ground using an agate mortar and pestle and from this powder a 0.2 g sample was taken. The 0.2 g sample was mixed with 2 g of analytical grade sodium peroxide (BDH Chemicals Ltd, Poole) in a zirconia crucible and heated over a Bunsen burner until a clear melt was achieved. The melt was allowed to cool before being dissolved in 5% (v/v) nitric acid and diluted to 100 mls. This sample was analysed using the plasma system previously described with calibration using standards matched in acid and flux concentration.

The plasma operating conditions are shown in Table 3.7 and the results are shown in Tables 3.8, 3.9 and 3.10.

3.3.3

Results and Discussion

The agreement between the slurry results and the certificate values for the reference materials is very acceptable for most elements at major, minor and trace levels. There are a few results which are not in agreement but these are probably due to contamination or uncorrected spectral interferences since there is no general trend. The only element which does show generally low recovery is aluminium with values typically 10% lower than the certificate values. This problem has been observed previously (58, 121) and is not thought to be a sample transport problem since samples ground to sizes far lower than required for slurry introduction exhibit the same behaviour. This leads to the conclusion that perhaps an aluminium oxide species is

Table 3.8

Results of Analysis of Zeolite A by X.R.F., Solution ICP-OES and Slurry ICP-OES.

Element	X.R.F.*	Solution[a]	Slurry[b]
		Composition/%w/w	
SiO_2	42.7	44.4	44.0 ± 0.5
Al_2O_3	35.3	34.8	32.0 ± 0.6
Fe	0.03	0.012	0.027 ± 0.002
Cr	0.1	0.006	0.004 ± 0.001
		$\mu g\ g^{-1}$	
Cu	-	12	19 ± 2
Ni	-	10	4 ± 1
Mn	-	33	17 ± 2
V	-	-	28 ± 4
Co	-	15	18 ± 2
Mg	-	210	250 ± 30
Zn	-	15	-

* The X.R.F. values were obtained from ICI MOND Division and are semi-quantitative.

a Dissolution following tetraborate fusion and ICP-OES analysis.

b Slurry atomisation ICP-OES of 0.1% and 10% w/v slurries following 8 hours grinding.

Table 3.9

Analysis of Chromium III catalyst and a mixed oxide catalyst by disolution and slurry atomisation - ICP-OES.

Element	Cr_2O_3 Catalyst Solution[a]	Slurry[b]	Mixed Oxide Catalyst Solution[a]	Slurry[b]
		Major-Minor Elements/% w/w		
Al_2O_3	0.09 ± 0.01	0.1 ± 0.01	54 ± 2	49 ± 0.6
SiO_2	2.2 ± 0.2	2.00 ± 0.17	1.26 ± 0.08	1.31 ± 0.4
Fe	0.12 ± 0.01	0.09 ± 0.01	0.11 ± 0.05	0.08 ± 0.02
Cr_2O_3	91 ± 4	83 ± 4	50[c]	23 ± 6[c]
Mg	0.045 ± 0.003	0.022 ± 0.001	7.9 ± 0.2	7.78 ± 0.14
	Trace Elements/μg g^{-1}			
Mn	17 ± 3	19.5 ± 0.5	88 ± 14	70 ± 4
V	162 ± 24	155 ± 15	40	16 ± 1
Co	24 ± 16	18 ± 2	40	11 ± 4
Ni	24 ± 5	26 ± 4	37 ± 7	42 ± 3
Cu	112 ± 10	57 ± 2	18.7 ± 0.4[d]	13.5± 0.2[d]

a Dissolution following tetraborate fusion and ICP-OES analysis.

b Slurry atomisation of 0.1% and 10% m/v slurries following 8 hours grinding.

c μg g^{-1}

d % w/w

Table 3.10

Analysis of certified reference soils by slurry atomisation - ICP-OES.

Element	SO-1		SO-2		BCR	
	Slurry[a]	Certificate[b]	Slurry[a]	Certificate[b]	Slurry[a]	Certificate[b]
			Major - Minor Elements/%w/w			
Si	25.6 ± 0.23	25.72 ± 0.22	25.1 ± 0.23	24.99 ± 0.23	32.2 ± 0.23	(31.84)
Al	9.1 ± 0.3	9.38 ± 0.17	7.6 ± 0.3	8.07 ± 0.18	4.5 ± 0.3	(5.02)
Fe	5.8 ± 0.4	6.00 ± 0.13	5.4 ± 0.4	5.56 ± 0.16	2.0 ± 0.4	(1.96)
Mg	2.4 ± 0.4	2.31 ± 0.10	0.6 ± 0.05	0.54 ± 0.03	0.66 ± 0.05	(0.656)
Mn	0.069 ± 0.005	0.089 ± 0.003	0.056 ± 0.005	0.072 ± 0.002	0.047 ± 0.005	(0.057)
			Trace Elements/$\mu g\ g^{-1}$			
Cr	159 ± 6	160 ± 15	4 ± 1	16 ± 2	33 ± 5	(74.9)
V	160 ± 10	139 ± 8	48 ± 10	64 ± 10	65 ± 10	Not supplied
Ni	81 ± 5	94 ± 7	17 ± 5	8 ± 2	32 ± 5	29.2 ± 2.5
Cu	70 ± 2	61 ± 3	10 ± 2	7 ± 1	18 ± 2	27.5 ± 0.6
Co	8 ± 4	32 ± 3	23 ± 3	9 ± 2	8.4 ± 1.2	(7.9)

a Slurry atomisation of 0.1% and 10% m/v slurries following 8 hours grinding.

b Certified values, those values in brackets being indicated only.

sufficiently refractory to exist within the plasma. This hypothesis is supported by the work of Monnig and Koirtyohann (124) who used Mie scattering to follow sample aerosols into the ICP. They found that when aspirating 5000 μgml^{-1} aqueous solutions of aluminium signals for particles could be detected in the normal analytical zone whereas no signals were detected from equivalent solution of lithium, sodium, iron, cerium and europium. This would not affect the analysis of aqueous samples with aqueous standards as one would expect them to behave in an identical fashion generating desolvated salt clotlets of the same size. A slurry contains predefined particles which are probably larger than the clotlets formed from the aqueous standards and as such these do not show the same degree of atomisation as the aqueous standards. Thus it is likely that to obtain agreement between slurry and aqueous samples for aluminium the particle size of the slurry must be comparable with that of the desolvated aerosol rather than simply sufficient to negotiate the sample introduction system.

The results obtained for slurries of Zeolite A, the chromium III catalyst and the mixed oxide catalyst (Tables 3.8 and 3.9) show good agreement with the results obtained by sample dissolution. The trend of low aluminium results is again shown especially with the zeolite analysis.

The results obtained by slurry atomisation for trace elements generally have better precision since the analytical measurement is made using higher analyte concentrations than for fusion samples. This means that the signal has less contribution from background noise than those of fusion samples where the measurements are often made close to the limit of detection. Precision is also improved since the relative error on the weight of sample taken is less for a slurry method where typically 50 to 100 times more sample is taken than for a fusion. Also a more representative sample may be taken.

Sample preparation using a fusion method requires a reasonably high level of skill and experience expecially when dealing with samples not previously handled. Slurry preparation, on the other hand, is very simple with the same methodology being used for every sample. Hence it is easier to perform an analysis and get accurate results using slurry atomisation than from a fusion based method.

3.4

Conclusion

This chapter has shown the viability of analysis of solid samples by a slurry atomisation method. A variety of samples have been successfully analysed and a number of other applications briefly discussed. Thus having identified the methodology required and then proved the validity of the technique all that is now required is the application of slurry atomisation to a greater variety of samples in order that it gains wider acceptance. The technique may not be the answer to every problem the analytical chemist faces but it could be a useful tool for a variety of problems. The ease of carrying out such methodology being an attractive feature.

CHAPTER 4

SLURRY SAMPLE ANALYSIS BY INDUCTIVELY-COUPLED PLASMA - MASS SPECTROMETRY

4.1

Introduction

Inductively coupled plasma - mass spectrometry (ICP-MS) is a relatively new analytical technique (125, 267, 127) based on the coupling of a conventional ICP source, as used in optical emission and a quadrupole mass spectrometer. The ions produced at atmospheric pressure in the plasma are introduced into the mass spectrometer, maintained at low pressure (10^{-5} Torr) and analysed as a function of their mass to charge ratio. As a result of physically separating and counting ions formed rather than measuring the optional emission from the excited state, ICP-MS detection limits are generally one or two orders of magnitude better than ICP-OES (126).

The interest in this novel technique is growing very rapidly and as such a detailed review of the literature would be too large to be considered for this thesis. The reader is directed to the very informative paper by Date (128) as an introduction to the technique and to the papers by Gray (129, 130), and Houk et al. (125).

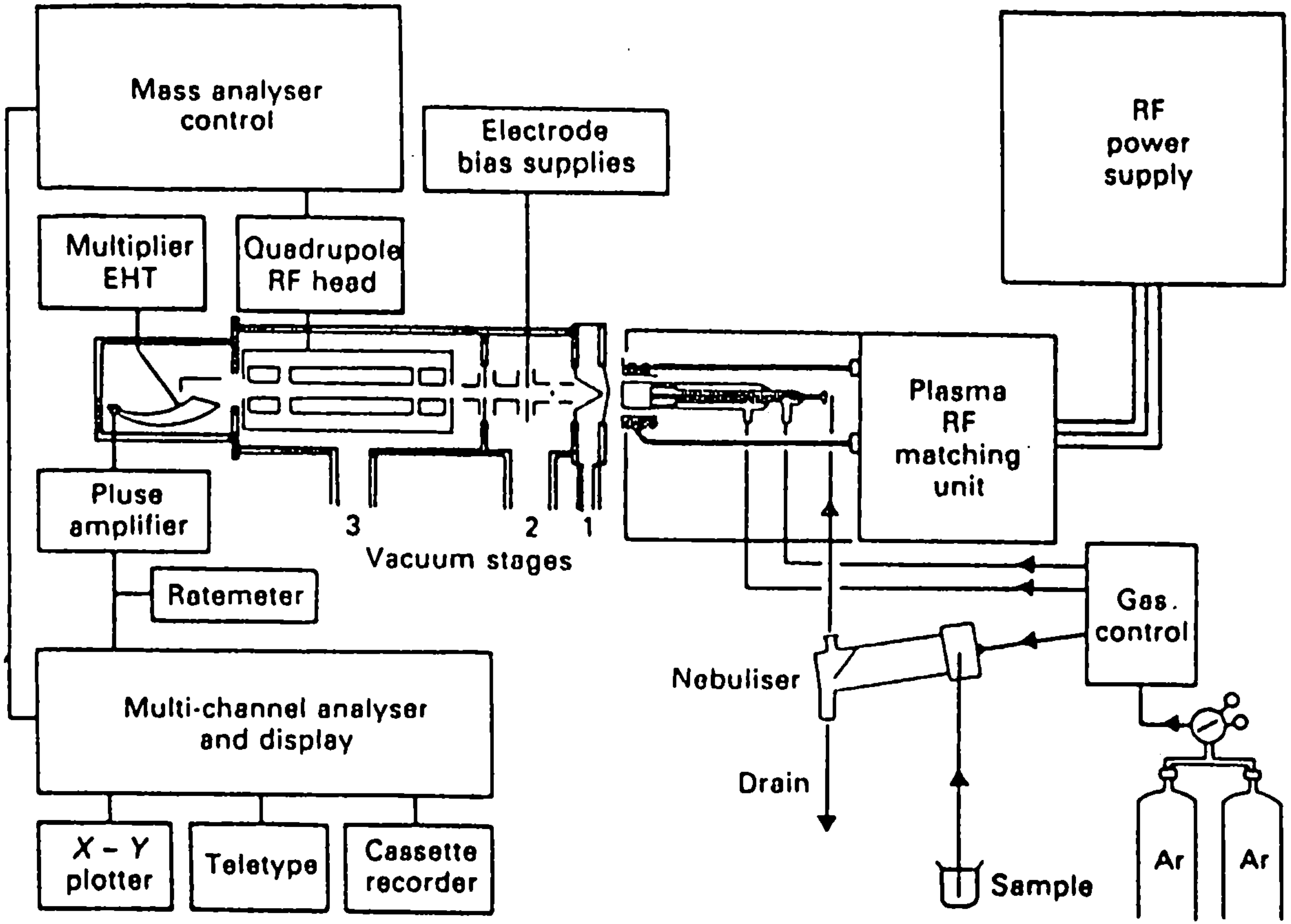


Figure 4.1 Schematic diagram of a basic ICP-MS system.

(taken from reference 126)

The basic ICP-MS system is shown in Figure 4.1 and consists of an inductively-coupled plasma with conventional pneumatic nebuliser, spray chamber and torch. The torch is mounted horizontally and ions are extracted from the centre of the plasma tailflame usually at a point between 5 and 10 mm from the load coil, by the primary aperture, of between 0.5-1.00 mm diameter, drilled in a shallow water-cooled cone. The core of the jet of gas formed by the supersonic expansion is extracted by a sharp skimmer cone about 10 mm behind the aperture into the high vacuum stages, the bulk of the entering gas being removed by a mechanical pump. No potentials are used in the first stage but an ion lens in the second and third stages focuses the ions into the mass analyser. Ions are separated by a quadrupole mass spectrometer and detected by a channel electron multiplier operated either as a pulse counter or a mean current detector.

Although initially developed for the analysis of solution samples, ICP-MS has recently been shown capable of the direct analysis of solid samples (131). In this technique aerosols of solid particles were generated from samples by laser ablation in the same manner as for ICP-OES (79, 81, 132) with the aerosol carried directly from the ablation cell to the injector by a stream of argon. This approach has several advantages including simple sample preparation, in which the sample has only to be ground to give a flat surface, or in the case of powders pelletted with a suitable binder. In this way the technique has similarities to spark sampling but has the advantage that the sample does not have to be conducting and hence the binding agent can be a simple organic resin. Unfortunately this technique suffers from problems of calibration in that very closely matched standards are required for accurate determinations. The main advantage is that no water or carrier solvent is used and hence the low mass elements usually obscured by oxygen and hydrogen species can be determined. This is very important since a large number of light elements cannot usually be determined even at high concentrations.

The demonstration of the capabilities of ICP-MS for solids suggested that perhaps the introduction of very finely ground slurries may be possible. Also the fact that slurry ICP-OES is viable using simple aqueous calibration suggests that complete atomisation and ionisation has occured and hence the ions are available for the mass spectrometer. The atomisation of particles generated by laser ablation should be identical to those introduced as slurries since desolvation occurs very rapidly a few millimeters below the initial radiation zone (125) and hence in both cases dry particles enter the plasma. Thus an initial investigation was performed to identify the potential for the analysis of solid samples by Slurry-ICP-MS.

4.2

Instrumentation

The ICP-MS system used was a commercial Plasma Quad instrument (V.G. Isotopes Ltd, Winsford, Cheshire) consisting of a 1.5 kw radio frequency generator and matching circuitry (Radio Frequency Applications Ltd, Eastbourne, Sussex), with a V.G. 12 + 12 quadr , mass spectrometer. The torch was of the demountable injector type with a 3 mm i.d. injector. An all P.T.F.E. Babington-type nebuliser

(P.S. Analytical, Kent) was used with an in-house constructed water-cooled spray chamber maintained at 13°C. Aqueous standards and slurries were pumped to the nebuliser using a Eyela peristaltic pump (Jencons Scientific Ltd, Leighton Buzzard, Beds). A technical description of the system is shown in Table 4.1.

Table 4.1

ICP-MS Technical Specifications

R.F. Generator	27.12 MHz Crystal controlled 1500W 3 turn, water-cooled, load coil Scott-Fassel quartz torch with 3 mm i.d. injector.
Mass Spectrometer	Quadrupole, V.G. Type 12-12S Nickel sampling cone 1 mm orifice diameter Nickel skimmer cone 0.7 mm orifice diameter Detector, continuous dynode election multiplier (Model 401, Detector Technology inc. USA) Multi-channel analyser, Tracor Northern, N7200 (Wisconsin, USA)
Data System	IBM PC/XT
Sample Introduction System	All P.T.F.E. Babington-type nebuliser (P.S. Analytical, Orpington, Kent) Water-cooled spray chamber (University of Surrey, Guildford, Kent) Peristatic Pump (Model Eyela, Jencons Scientific Ltd, Leighton Buzzard, Beds).

4.3

Experimental

The same materials as described in Chapter 3 were chosen for analysis so that comparative results were available. These were three certified reference soils together with a chromium III oxide catalyst, a molecular sieve zeolite and a mixed metal oxide catalyst. Slurries (1%m/v) were prepared in an identical fashion to that previously described (Section 3.3.2) except that the slurries were ground for 24 hours. No facilities were available for determining the particle size distribution of the slurries but from previous experience it was anticipated that the majority of the mass of each sample would be contained in particles of 2-3 um or less. The slurries were made up in 0.05% m/v tetrasodium pyrophosphate and all subsequent dilutions and calibration standards also contained this concentration of dispersant. The dispersant concentration used was a factor of ten less than that used for ICP-OES to reduce the intensity of the polyatomic interferences caused by the presence of phosphorous (133). Standards were prepared from acidic stock solutions but no further acid was added on dilution and fresh standards were prepared daily as required.

The use of 3 mm i.d. injector tube and a Babington-type nebuliser made it necessary to carry out a brief investigation of forward power and nebuliser pressure to assess the best compromise conditions for the instrumental parameters. Since the mass spectrometer has a virtually equal response to ions regardless of mass the ion lenses were set up using a standard containing cobalt and bismuth monitoring ^{59}Co and ^{209}Bi. Using a multi-element standard (containing Al, In, Co, and Bi at 100 ng ml^{-1}) the nebuliser flow rate and the r.f. power were adjusted to obtain the maximum signal with the minimum oxide and doubly charged ion peaks. It was intended that depending on the results obtained by slurry analysis further adjustment would be made in order to improve the atomisation efficiency obtained. This proved to be unnecessary as the conditions chosen gave very good agreement between aqueous calibration and slurry samples. These conditions are shown in Table 4.2 and were used for all subsequent analyses.

Initial experiments showed that 1% m/v slurries caused detectable sample cone blockage after about 30 minutes. This could be shown by a decreasing sensitivity and a gradual decrease in the pressure of the first vacuum stage. Thus slurries of 0.05% m/v were used for trace element determination and major elements were quantified using 0.0001% m/v slurries. No further blockage problems were detected over 4 days of analyses involving approximately 4 hours of aspiration.

Table 4.2

ICP-MS operating conditions using a 3 mm i.d. injector and Babington-type nebuliser

Forward power/w	1500
Reflected power/w	25
Nebuliser flow/lmin^{-1}	0.75
Auxillary flow/lmin^{-1}	0.6
Coolant flow/lmin^{-1}	14
Sample uptake/mlmin^{-1}	1.5

Table 4.3

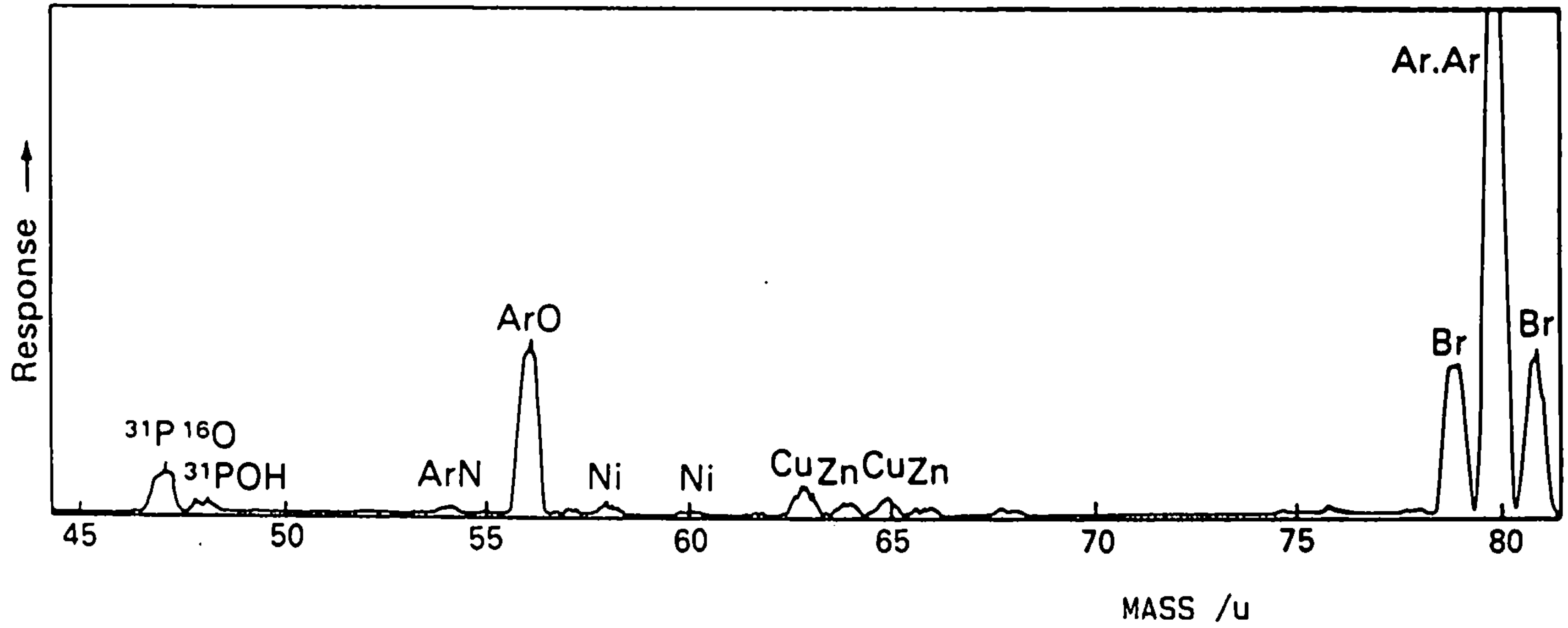
The isotopes used for the analysis of various slurries by ICP-MS

Element	Isotopic Mass amu	Percentage Isotopic abundance
Al	27	100
Si	30	3.12
Mg	26	11.29
Ca	44	2.13
Ti	49	5.51
Mn	55	100
Fe	56	91.5
V	51	99.76
Cr	52	83.76
Co	59	100
Ni	60	26.16
Cu	63	69.09
Zn	66	27.81

4.4

Results and Discussion

The determination of all elements was achieved using simple aqueous calibration and the careful choice of appropriate isotopes. The choice of isotopes for the determination of the major elements involved not only finding isotopes free from interfering ions but also ensuring that the detector was not saturated due to the very high count rate. It was decided that to analyse a slurry of less than 0.0001% m/v may cause problems in achieving a representative sample and hence where possible low abundance isotopes were monitored to avoid this saturation problem. The elements which were determined, the isotopes used and their relative abundance is shown in Table 4.3. All results were obtained after subtraction of a dispersant blank, a mass spectrum of which is shown in Figure 4.2. The peaks at 47 and 48 mass units are the polyatomic species $^{31}P^{16}O$ and $^{31}P^{16}OH$ respectively and arise from the phosphorous in the dispersant. These would interfere with the determination of titanium but fortunately there are three other titanium isotopes available. Tetrasodium pyrophosphate is not an ideal dispersant for ICP-MS but the selection of a suitable dispersive agent which does not cause polyatomic interferences requires more extensive study. It does have the possible advantage of buffering out any easily ionisable element interferences due to the high sodium content of the dispersant. Examples of the aqueous calibration curves are given as Figures 4.3 and 4.4 for silicon and manganese respectively.



NICKEL IS PRESENT AS CONTAMINATION FROM THE SAMPLING CONE.
THE SIGNAL FOR ArO IS APPROXIMATELY 1500 COUNTS SEC-1

Figure 4.2 Mass spectrum of 0.05% m/v Tetrasodium Pyrophosphate.

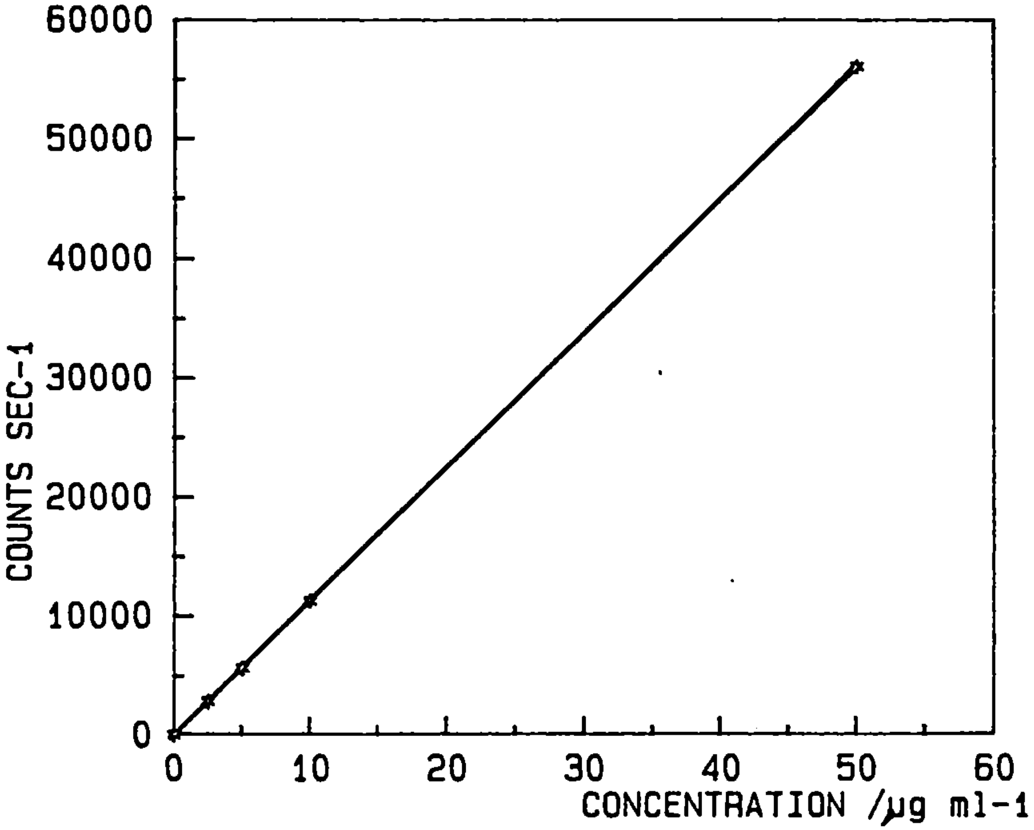


Figure 4.3 Aqueous calibration for silicon 30 by ICP-MS

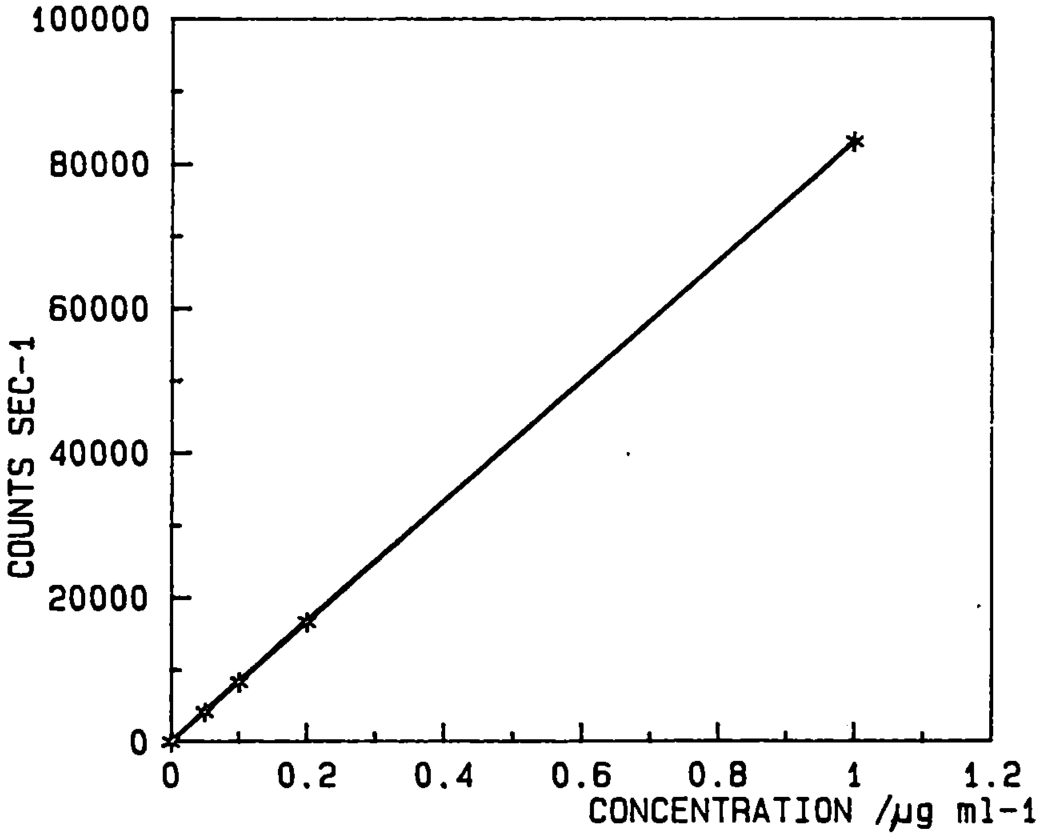


Figure 4.4 Aqueous calibration for manganese 55 by ICP-MS

The slurry ICP-MS results for all six materials for major, minor and trace elements are shown in Tables 4.4 to 4.7 together with the certificate values and those obtained by ICP-OES.. The agreement between the results is very good for almost all elements for all the samples. Most of the disagreement in results can be readily explained as for the copper result for CRM142. This high value was identified as coming from cross contamination from the mixed oxide catalyst (13.5% copper) due to insufficient washout time between samples. The residual copper was probably due to small amounts of particles remaining in the peristaltic pump tubing and the deposition of copper on the sampling cone.

The zinc values obtained for the reference soils are 10-20% higher than the certified values. This is almost certainly due to the low signal level in relation to the blank (shown in Figure 4.2) which contains significant signals at both the 64 and 66 mass units. The blank contained significant concentration of zinc, copper and bromine and with these levels of background accurate trace determinations for these elements were much more difficult.

The analysis results for aluminium for all the samples are lower than the certified values or those obtained by sample dissolution. This agrees with the trend observed in slurry-ICP-OES and was expected. The same explanation as put forward in Chapter 3 is equally valid for ICP-MS whereby the refractory nature of alumina is such that not all of the sample is atomised in the plasma. Incomplete atomisation could have been indicated by the identification of AlO^+ at mass 43

Table 4.4 Analysis of CRM SO-1 by slurry atomisation Inductively-coupled Plasma - Mass Spectrometry

Element	Certificate Value*	ICP-MS[a]	ICP-OES[b]
	Soil SO-1 (% m/m)		
Si	25.72 ± 0.22	25.9	25.6
Al	9.38 ± 0.17	8.10	9.10
Fe	6.00 ± 0.13	5.70	5.80
Mg	2.31 ± 0.11	2.21	2.40
Mn	0.089 ± 0.003	0.08	0.07
	Soil SO-1 (μg g-1)		
Cr	160 ± 15	166	159
V	139 ± 8	140	160
Ni	94 ± 7	92	81
Cu	61 ± 3	70	70
Co	32 ± 3	37	8
Zn	146 ± 5	182	-

* Values in parentheses are indicated values only.

a Slurry atomisation of 0.05% and 0.0001% m/v slurries following 24 hours grinding.

b Slurry atomisation of 0.1% and 10% m/v slurries following 8 hours grinding.

Table 4.5 Analysis of CRM SO-2 by slurry atomisation Inductively-coupled Plasma - Mass Spectrometry

Element	Certificate Value *	ICP-MS [a]	ICP-OES [b]
	Soil SO-2 (% m/m)		
Si	24.99 ± 0.23	25.9	25.1
Al	8.07 ± 0.18	7.00	7.60
Fe	5.56 ± 0.16	5.40	5.40
Mg	0.54 ± 0.03	0.45	0.60
Mn	0.072 ± 0.002	0.06	0.06
	Soil SO-2 (μg g-1)		
Cr	16 ± 2	19	4
V	64 ±10	65	48
Ni	8 ± 2	16	17
Cu	7 ± 1	14	10
Co	9 ± 2	20	23
Zn	124 ± 5	139	-

* Values in parentheses are indicated values only.

a Slurry atomisation of 0.05% and 0.0001% m/v slurries following 24 hours grinding.

b Slurry atomisation of 0.1% and 10% m/v slurries following 8 hours grinding.

Table 4.6 Analysis of CRM 142 by slurry atomisation Inductively-coupled Plasma - Mass Spectrometry

	CERTIFICATE VALUE*	ICP-MS[a]	ICP-AES[b]
	Soil CRM 142 (% m/m)		
Si	(31.9)	32.6	32.2
Al	(5.02)	4.20	4.50
Fe	(1.98)	1.96	2.00
Mg	(0.66)	0.59	0.66
Mn	(0.057)	0.05	0.05
	Soil CRM 142 (μg g-1)		
Cr	(75)	90	33
V	-	67	65
Ni	29.2 ± 2.5	32	32
Cu	27.5 ± 0.6	482	18
Co	(8)	21	8
Zn	92.4 ± 4.4	100	-

* Values in parentheses are indicated values only.

a Slurry atomisation of 0.05% and 0.0001% m/v slurries following 24 hours grinding.

b Slurry atomisation of 0.1% and 10% m/v slurries following 8 hours grinding.

Table 4.7 Analysis of Zeolite A, Chromium III Oxide and a Mixed Oxide Catalyst by slurry atomisation ICP-MS

Element	Slurry ICP-MS	Slurry ICP-OES	Solution ICP-OES
Mixed Oxide Catalyst (% oxide m/m)			
Al	53	49	54
Si	1.2	1.3	1.3
Mg	7.9	7.8	7.9
Cu	-	14	19
Mixed Oxide Catalyst ($\mu g\ g^{-1}$)			
Mn	100	70	88
Fe	700	810	1100
V	16	16	<40
Cr	16	23	<50
Co	15	11	<40
Ni	41	42	37
Zeolite A (% oxide m/m)			
Al	33	32	35
Si	40	44	44
Zeolite A ($\mu g\ g^{-1}$)			
Mg	123	250	210
Mn	40	17	33
Fe	330	270	120
V	30	28	-
Cr	32	40	60
Co	17	18	15
Ni	<16	4	<10
Cu	12	19	12
Chromium (III) Oxide Catalyst (% oxide m/m)			
Si	2.5	2.0	2.2
Cr	-	83	91
Chromium (III) Catalyst ($\mu g\ g^{-1}$)			
Al	870	1000	900
Mg	250	215	450
Mn	20	20	17
Fe	1030	900	1200
V	179	155	162
Co	17	18	24
Ni	<16	26	24
Cu	52	57	112

but no significant number of counts were recorded at this mass. This is rather difficult to explain and requires a more in-depth study perhaps using higher concentration slurries in order that other species might be identified. This problem probably arises because of the cooler central channel of the plasma and may well be made worse by the small sampling orifice of the ICP-MS by which only the middle of the central channel is sampled. In ICP-OES the hotter edges of the channel are also viewed as well as the actual centre which could explain the slightly better results obtained by slurry-ICP-OES. The use of a 3 mm i.d. injector may well also enhance this problem by creating a cool channel wider than obtained by using a 1 or 2 mm i.d. injector. Unfortunately there is a 'trade-off' with the sample transport problems which prevents the use of a narrower injector although an experiment involving very finely ground slurries and a narrower injector may produce higher atomisation efficiencies not only for aluminium but also iron which shows some similar behaviour.

Overall the results are very good especially when it is considered that this is the first time that slurry samples have been introduced into an ICP-MS instrument and that this work was carried out as a preliminary investigation on a non-optimised system. The elements determined are also all in the lower mass region (below 80 mass units) where the ICP-MS has most interference problems from polyatomic species. A semi-quantitative analysis of the rare earth elements was carried out for the three reference soils, the results of which are shown in Table 4.8 and a sample mass spectrum for

Table 4.8 Semi-quantitative analysis of the rare earth elements for the CRM soils SO-1, SO-2 and CRM142

ELEMENT	CRM142	SO-1	SO-2	SO-2*
		Concentration /μg g^{-1}		
La	26	34	39	46 ± 1
Ce	68	83	124	111 ± 3
Pr	7.7	9.5	15	13.4 ± 0.4
Nd	31	41	66	57 ± 1
Sm	7.0	6.8	13	12.2 ± 0.1
Eu	1.2	1.5	3.7	3.43 ± 0.02
Gd	8.4	5.9	11	10.3 ± 0.2
Tb	1.8	0.88	2.4	1.3 ± 0.2
Dy	15	4.6	17	8.6 ± 0.1
Ho	4.3	1.5	3.8	1.7 ± 0.05
Er	19	5.6	12	4.1 ± 0.1
Tm	3.1	0.56	2.5	0.54 ± 0.02
Yb	23	6.5	15	3.39 ± 0.01
Lu	4.7	1.2	3.7	0.47 ± 0.4

* Results for comparison taken from Crock, J.G., and Lickte, F.E., Anal. Chem., 1982, 54, 1329.

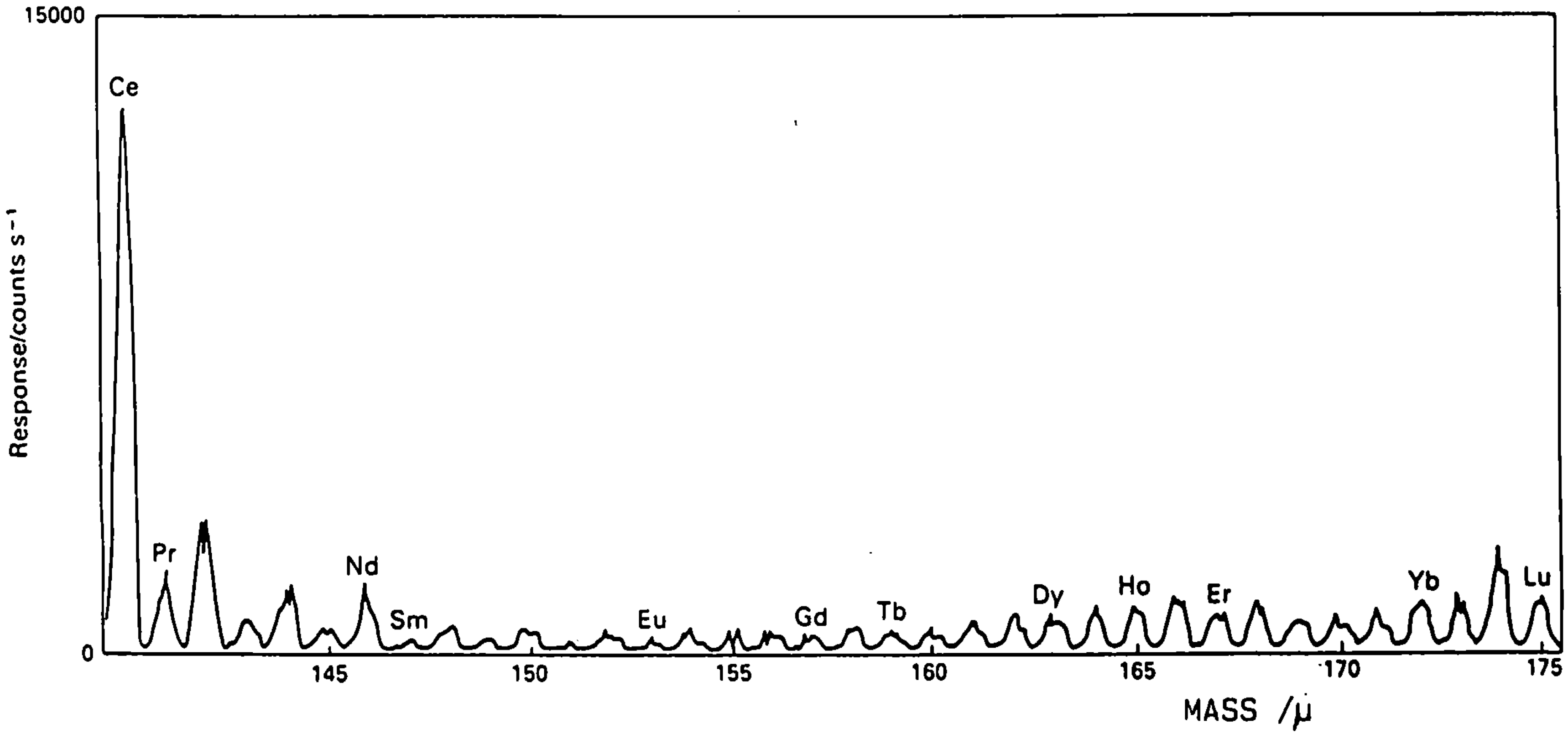


Figure 4.5 Mass spectrum of CRM142 for the rare earth mass region

CRM142 shown in Figure 4.5. This is the mass region for which the ICP-MS produces the lowest detection limits and has the greatest freedom from interferences. Unfortunately there are no certified or indicated values for these elements for the reference soils.

4.5

Conclusion

The analysis of slurry samples by inductively-coupled plasma mass spectrometry proved to be less problematical and far more successful than expected. It was anticipated that slurry samples would cause sample cone blockage and give very poor atomisation efficiencies due to the close proximity of the sample cone to the load coil. These problems did not occur (apart from low atomisation efficiencies for aluminimum and iron) and this may be due to the very fine particle size of these slurries. The water cooled spray chamber also helped by reducing the solvents loading in the plasma, thus raising its temperature and probably increasing the atomisation efficiency of the slurry.

For a preliminary study the results obtained were remarkably good and with further investigation into the effects of particle size, slurry concentration and operating conditions this technique could prove to be very powerful. A combination of the high solids loading capability of slurries and the sensitivity of ICP-MS could lead to extremely low limits of detection for solid samples if cone blockage problems can be overcome. Thus it seems likely that analysis by slurry-ICP-MS may be a very powerful technique which could gain acceptance within the analytical community.

CHAPTER 5

SIMPLEX OPTIMISATION

5.1

Introduction

The Simplex optimisation algorithm was originally described by Spendley *et al*. in 1962 (42). It is an optimisation method which is guided by rules, calculations and decisions that are rigorously specified but are almost trivially simple. The algorithm is based on an adaptive approach in that information gathered during the optimisation procedure is used to direct and guide the progress of the experiment. Thus the method has the ability to cope with the unexpected during the optimisation process and does not depend on any assumptions about the response surface of the system under investigation. This makes the simplex algorithm particularly attractive for the optimisation of novel systems where little if anything is known about the response surface.

5.2

The Sequential Simplex Algorithm

A simplex is a geometric figure described by a number of points (vertices) equal to one more than the number of factors, or variables being optimised. Hence a simplex for two factors is a triangle and for three factors is a tetrahedron. This series can obviously be extended to higher dimensions but then the simplexes are difficult to visualise. The complexity of the mathematics does not however increase with more dimensions as each dimension is treated in an identical manner.

The iterative nature of the simplex algorithm is controlled by a set of simple rules. Figure 5.1 shows a two variable system and the identification of the optimum using the basic simplex algorithm. The objective of the sequential simplex procedure is to force the simplex to move away from regions of low response and hence towards the optimum response. Each experiment commences with the identification and evaluation of an initial set of simplex vertices. In Figure 5.1 these would be vertices 1, 2 and 3 and could be any three points within factor space. The next and subsequent steps are made according to the following "rules":-

RULE 1

The vertex with the lowest response in the current simplex set is rejected. A new vertex is generated by reflection of the rejected vertex though the mid-point of the hyperface formed by the remaining vertices. This new vertex is experimentally evaluated and joins the simplex set.

Thus in Figure 5.1, vertex 1 is rejected and reflection of this point though the hyperface formed by vertices 2 and 3 generates a new vertex 4. The simplex set now consists of vertices 2,3 and 4.

RULE 2

If the newest vertex in the simplex set has the lowest response, do not reapply rule 1 but instead reject the next to worst point in the simplex.

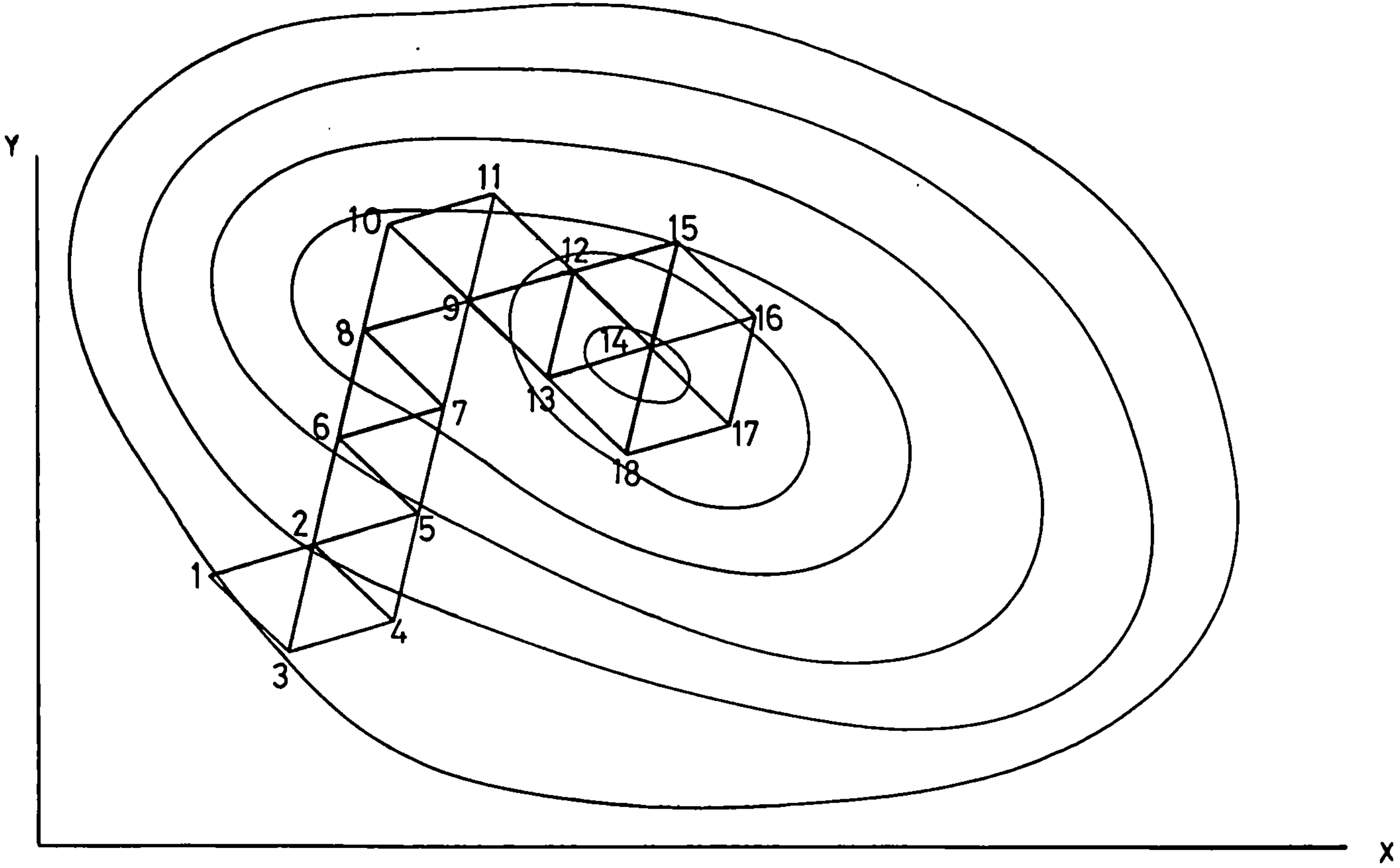


Figure 5.1 Fixed step size simplex identification of a two variable optima.

This rule prevents simplex oscillation and is demonstrated in Figure 5.1 by the vertices 9, 10 and 11. Vertex 11 is the newest point in the simplex but has the lowest response in the current simplex set. Rejection of vertex 11 would regenerate vertex 8 and oscillation about the hyperface 9-10 would occur with the experiment failing. Implementation of rule 2 prevents this and causes the simplex to reject vertex 10, generating vertex 12 and thus avoiding oscillation. This kind of failure is most likely to occur where the response surface forms a ridge.

RULE 3

If a vertex remains in the simplex set for n + 1 successive iterations (where n is the number of parameters in the optimisation) then re-evaluate the response of this vertex before continuing with the next iteration.

This rule stops an erroneously high result from preventing the correct movement of the simplex. This rule is essential in the evaluation of real systems where errors and noise will always occur and simplex movement could easily be prevented by an erroneous result.

RULE 4

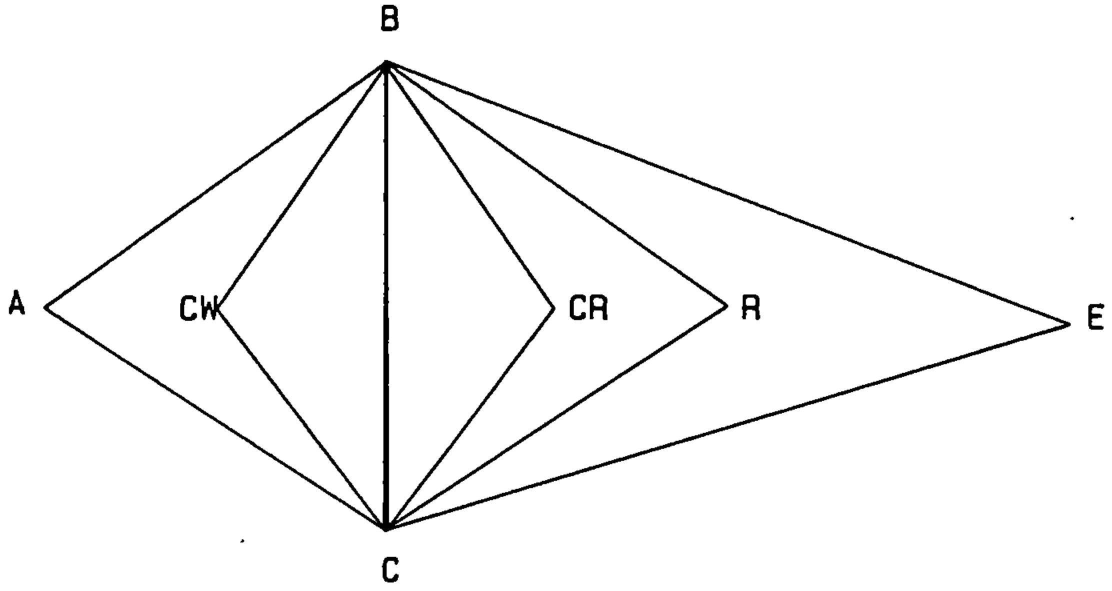
If a vertex is generated which falls outside the boundary of one or more parameter then assign this vertex an arbitary low response and continue as before.

This rule allows the experiment to continue rather than being terminated due to an impossible vertex being generated.

The above set of rules describe the original simplex algorithm which has several important limitations. The main limitations being that the size of the initial simplex has an important influence on how factor space is explored. Too small a simplex and the risk of finding a local rather than the global optimum is increased as well as increasing the number of iterations required to find an optimum. Too large an initial simplex and any optimum found is only vaguely identified. This leads to the necessity of running several optimisations using a progressively smaller simplex to accurately identify the optimum.

Nelder and Mead (43) proposed a change to the original simplex method which overcomes this size limitation. The change was that of allowing the simplex to expand or contract depending on the response surface. This version of the algorithm is known as the variable step size simplex algorithm, or more commonly, the Modified Simplex Method. The movement of the simplex is still governed by the same basic rules with the ability to expand or contract incorporated into the generation of new vertices.

Consider Figure 5.2. The points A, B and C represent the current simplex set with vertex A having the lowest response. Reflection of vertex A through B/C produces the new vertex R and the response of R is evaluated in the usual way. Dependent on the response of the new vertex there are now four possible outcomes.



Starting simplex = ABC

Reflection vertex = R

Expansion vertex = E and is double the distance of R from BC

Contraction vertices CR and CW are half the distance of R from BC

Figure 5.2 A variable step size simplex iteration

(a) The response of R is higher than any of the previous vertices which suggests that the simplex is moving in a direction of increasing response. In this case an expansion in this direction could be advantageous and a vertex E is generated which is double the distance from the centroid (see Figure 5.2). E is evaluated and compared with R. If the response of E is greater than R then E enters the simplex set and the simplex has changed shape expanding towards a direction of improving response. If E is less than R then R is retained and no change in simplex size occurs. In this way the simplex can accelerate towards regions of higher response and hence search an optimum in fewer iterations.

(b) The response of vertex R is lower than the best response in the simplex set but not as low as the lowest (not including the rejected vertex). In this case neither expansion nor contraction is indicated and vertex R is accepted into the simplex set without further vertices being generated.

(c) The response of vertex R is lower than any of the current vertices but not as low as the rejected vertex. This implies that higher response lies between the centroid of the hyperface and the vertex R. Thus a vertex CR is generated which lies half way between the centroid of the hyperface and R (see Figure 5.2). This vertex is evaluated and regardless of its response it is incorporated into the simplex set.

(d) The response of vertex R is lower than any of the vertices in the simplex set including the vertex being rejected. This response for R implies that higher response lies between the previously rejected vertex and the hyperface. A vertex CW is generated which lies half way between the rejected vertex A and the centroid of the hyperface. After this vertex is experimentally evaluated it is automatically incorporated into the simplex set as with the contraction vertex CR in case (c).

The contractions of the simplex which occur in cases (c) and (d) allow an initially large simplex to more precisely define the optimum of the response surface. Since CW and CR can be the lowest in the simplex set they would naturally be rejected in the next iteration and further contraction of the simplex may well occur. To prevent this undesirable rapid contraction a new rule is introduced into the algorithm which states that any contraction vertex must stay in the simplex set for at least one iteration.

Nelder and Mead made other changes to the original algorithm which were later rejected as other workers added to and changed the algorithm to form the modified simplex method which is now most commonly used. An important contribution was made by Yarbro and Deming (44) who advocated the use of a large initial simplex in order that factor space is thoroughly explored. The development of the modified simplex method has been described by Betteridge et al. (49), other versions of the simplex algorithm were also discussed.

A comparison of the performance of three simplex based algorithms has been given by Parker et al. (53) and an early review of the use of simplex optimisation in analytical chemistry is given by Deming and Parker (51).

5.3

Application of Simplex Techniques to Inductively-Coupled Plasma Spectrometry

Since its conception in the early 1960's the inductively-coupled plasma has been the subject of many disagreements over which operating conditions give the best analytical performance. The situation was greatly clarified when Greenfield and Burns (134) demonstrated that two or more plasmas could be directly compared on a given spectrometer using the criteria of net signal to background ratio (SBR). This factor of criterion merit can be used to make a direct comparison of high and low power plasmas as well as differing torch/sample introduction designs and various plasma gases. These various plasma systems can only be rigorously compared if each system is operating at the maximum of its capabilities. Hence there is a need to optimise novel plasma systems to determine the analytical capability of the plasma by whatever criterion of merit is chosen. Ebdon et al. (45) compared the performance of alternative plasmas after each system had been optimised using the modified simplex method. Cave et al. (135) used the modified simplex method for single element optimisation and interference reduction. Moore et al. (46) and Leary et al. (136) concentrated on using simplex techniques to identify compromise, optimised conditions for multi-element analysis.

Simplex optimisation can be an extremely useful tool in developing novel systems or methodology. Initial work on the introduction of slurry samples into the inductively-coupled plasma (58) indicated that the use of simplex optimisation experiments may help to bring about a viable method of analysis. Although the mathematics of this iterative procedure can be performed manually it is an extremely laborious and time consuming task. Hence to assist any further development work a computer program to perform these calculations was constructed for the Apple IIe microcomputer.

5.4

Development of a BASIC Program for the Modified Simplex Method

Although initially written as a dedicated five variable program for use during ICP experiments only, the program was greatly modified to incorporate up to ten variables. This extensive modification was performed because of the potential use of such a program in many other research projects.

A complete listing of the program is given as Appendix 2.

5.4.1

Instrumentation

The software development involved the use of an Apple IIe micorcomputer (Apple Computer Inc, Cupertino, California, USA). An 80 column text extension card in interface slot 3 and a suitable printer interface in slot 1 are essential for running the program.

5.4.2

Software Description

A schematic diagram for the program is shown as Figure 5.3 all programming being in Applesoft BASIC.

The initial simplex set is generated using the matrix and equations as described by Yarbro and Deming (44). The program then follows the modified simplex rules described earlier (Section 5.2) the user driving the program from a menu format.

The software has been constructed to accommodate up to 10 parameters, this limitation arising from screen formatting and data display requirements, using the 80 column text extension card, rather than memory space problems.

During each iteration the program generates each reflection vertex followed by contraction or expansion vertices as required. The user is prompted to experimentally evaluate each vertex and enter the response factor. Between iterations the operator is returned to a menu of options which includes a routine to correct input errors, print a copy of all vertices which have previously been in the simplex set or view the progress of the experiment graphically. The graphs available are:

(a) Response factor versus vertex number. This shows the improvement being made by each iteration;

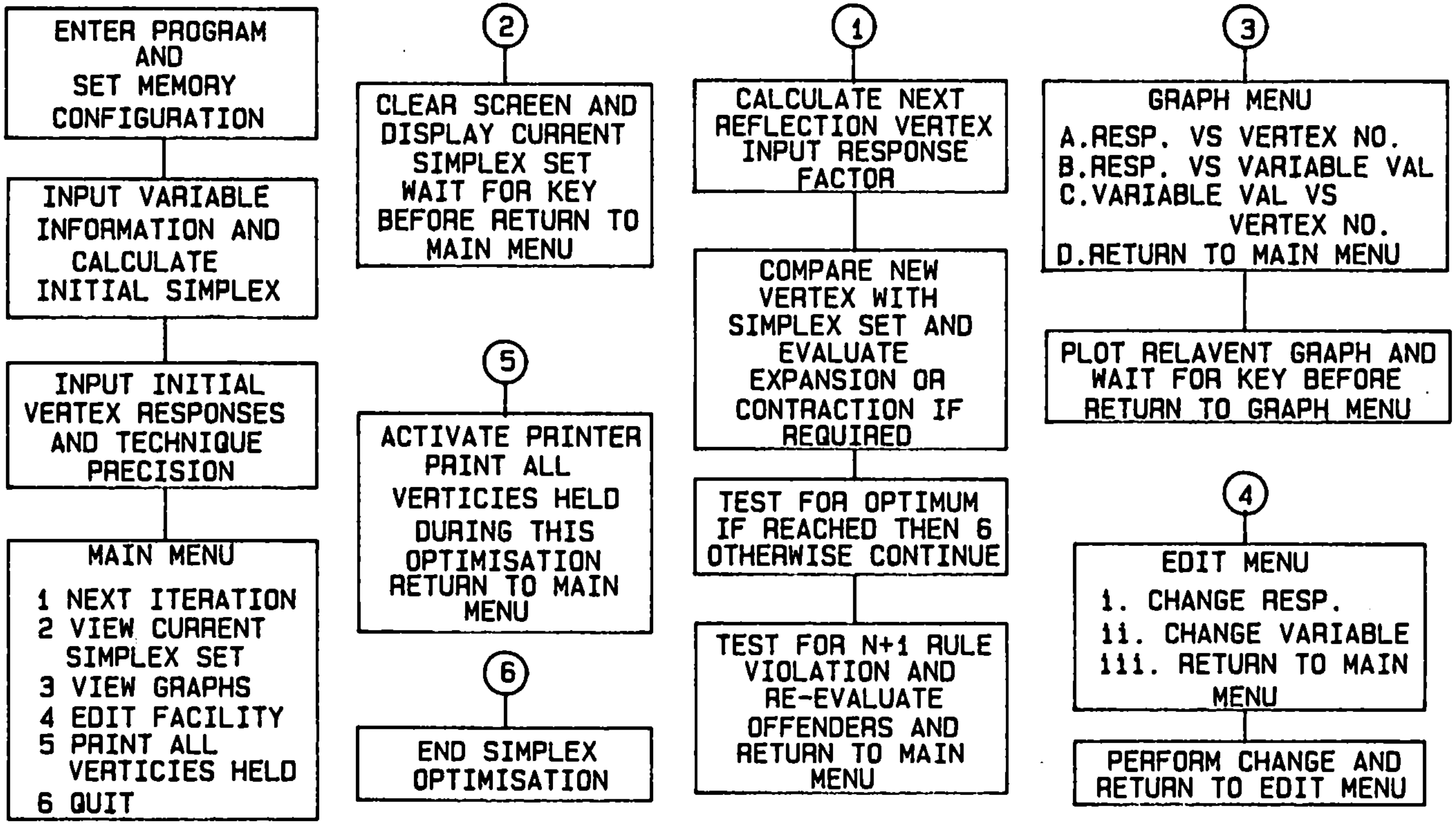


Figure 5.3 Schematic diagram of Apple IIe Simplex program.

(b) Response factor versus variable value. This shows the correlation (or lack of it) between the value of any of the variables being considered and the response of the system under investigation;

(c) Variable value versus vertex number. This graph gives an indication of how each variable is converging towards a single value as an optimum is reached.

The software identifies the end of the optimisation experiment as being when successive iterations cause the response of all of the vertices in the simplex set to converge. When the response of all of the vertices falls within twice the measurement precision as given by the operator an optimum is indicated. The operator is given the opportunity of changing the entered measurement precision and hence continuing the experiment or ending the experiment.

There is always concern that the optimum identified may not be the global optimum. This can only be rigorously confirmed by repeating the simplex optimisation using new starting vertices. However by performing a univariate search for each variable, holding the other variables at their optimal values a check may be made on the optimisation and considerable information on the influence of each parameter on the optimum obtained. The program does not contain any instructions to perform such a search this being left to the discretion of the operator.

A univariate search involves holding n-1 variables (where n is the number of variables or parameters in the experiment) at the level indicated by the centroid of the final simplex set. The nth variable is then incremented through its working range and the response of the system evaluated at each point. The maximum response should be obtained when the variable has the value indicated by the centroid of the simplex if not then a local rather than a global optimum has been obtained. This search is repeated for each variable in turn and if none of the searches shows that a local optimum has been identified then the optimisation has successfully identified the global optimum. If a local optimum has been identified then the experiment must be restarted with the variables reordered such that the simplex shape has a different orientation and thus hopefully will not get caught on the local optimum. This must be repeated every time a local optimum is identified.

5.4.3

Experimental Use of the Simplex Program

The development of the slurry atomisation procedure progressed into an area of practical methodology where it was impractical to use optimisation experiments. Hence the applications discussed are part of other research projects which had specific need of optimisation experiments.

5.4.3.1

Optimisation of ICP Operating Conditions for Slurry Atomisation of B P Kaolin

The Apple II simplex program was used to identify optimum plasma operating conditions of the S35 Plasmakon for the analysis of B P Kaolin (Boots Co Ltd, Nottingham, England) slurries (58). The five plasma parameters, 3 gas flows, viewing height and radio-frequency power were optimised to obtain the best signal to background ratio (SBR) for the magnesium 280.270 nm ion line. The experiment was performed whilst aspirating a 0.5% w/v kaolin slurry using an in-house constructed Babington-type nebuliser (58).

Table 5.1

Optimum conditions for the analysis of B.P. Kaolin slurries by ICP-OES

Parameter	Optimal Range	Centroid
Coolant gas/$l min^{-1}$	14.5 - 17.5	16
Plasma gas/$l min^{-1}$	3.3 - 3.9	3.6
Nebuliser gas/$l min^{-1}$	2.5 - 2.7	2.6
Power/kw	1.23 - 1.68	1.48
Observation Height/mm	22 - 25	23

The experiment successfully identified the optimum set of operating conditions for best SBR for the slurry (shown in Table 5.1), confirmed by a univariate search investigation. The experiment took approximately 2 hours to perform as opposed to approximately 6 hours for earlier experiments where all calculations were evaluated using a hand held calculator. Gray has reported (58) several other optimisation experiments of similar type to identify optimum plasma operating conditions using this computer program.

5.4.3.2

Simplex Optimisation of a Direct Current Plasma for Atomic Emission Spectrometry

A short piece of collaborative work was performed on the optimisation of a direct current plasma (DCP). Aspects of this work have been reported elsewhere (140). The optimisation involved the four important operating parameters of the DCP, vertical and horizontal viewing position, nebuliser gas flow and sleeve gas flows. The plasma was optimised for the analysis of aqueous solutions with the SBR obtainable at various analytical lines as the criterion of merit. The results of optimisation experiments for four different elements are given in Table 5.2. The experments were again verified by the univariate search method.

The Apple IIe simplex program was later used on a wide variety of optimisation experiments including the generation and analysis of various metal hydrides and the analysis of slurries by DCP-OES (121).

Table 5.2

Optimum conditions for the analysis of aqueous solutions by DCP-OES

Element	Wavelength/nm (type)	Viewing Position /mm		Sleeve Gas Flow /lmin^{-1}
		Horizontal	Vertical	
B	249.77(I)	0	+0.6	3.2
Mg	280.27(II)	0	+0.2	2.8
Co	345.35(I)	0	+0.9	2.5
Mo	386.41(I)	0	+0.7	3.0

5.4.3.3

Optimisation of a Fluorescence Detection System for High Performance Liquid Chromatography

A post column derivatisation system for the fluorescence detection of aluminium using Mordant blue 9 was optimised using the Apple IIe simplex program. This work was an extension of another project and involved identifying the greatest peak height to base line noise ratio. The chromatographic conditions were not part of the experiment and remained constant while the detection system was optimised using 20 ml injections of a 5 ngml^{-1} aluminium solution. A diagram of the higher performance liquid chromatography (HPLC) system is shown as Figure 5.4.

The detection system variables considered were pH (controlled by the volume of 5 M ammonium hydroxide solution added to a fixed volume of reagent), concentration of Mordant blue 9 chelating agent, post column reaction temperature and fluorescence excitation wavelength. Optimised conditions were successfully identified (Table 5.3) as confined by a univariate search.

This type of optimisation experiment was considerably slower than the systems described previously due to the time taken to evaluate each new vertex. The optimisation involved 30 iterations and took approximately 8 hours to complete.

Table 5.3

Optimum conditions for the post column derivitisation/detections of aluminium using Mordant blue 9 chelating agent

Fluorescence Excitation Wavelength	530 nm
Mordant blue 9 concentration	70 μ molar[a]
Ammonia concentration	70 m molar[a]
Water bath temperature	60°C

a Concentration in the post column reagent stream.

5.5

Conclusion

Simplex optimisation was shown to be capable of identifying optimal conditions for a variety of instrumental systems. The Apple IIe computer program was shown to be mathematically and logically valid by its practical application to several independent systems. This is perhaps a more conclusive test of a computer program than the optimisation of mathematically generated response surfaces as performed by other workers (137, 138, 139). In real systems software has noise and human error to overcome as well as mathematics to calculate.

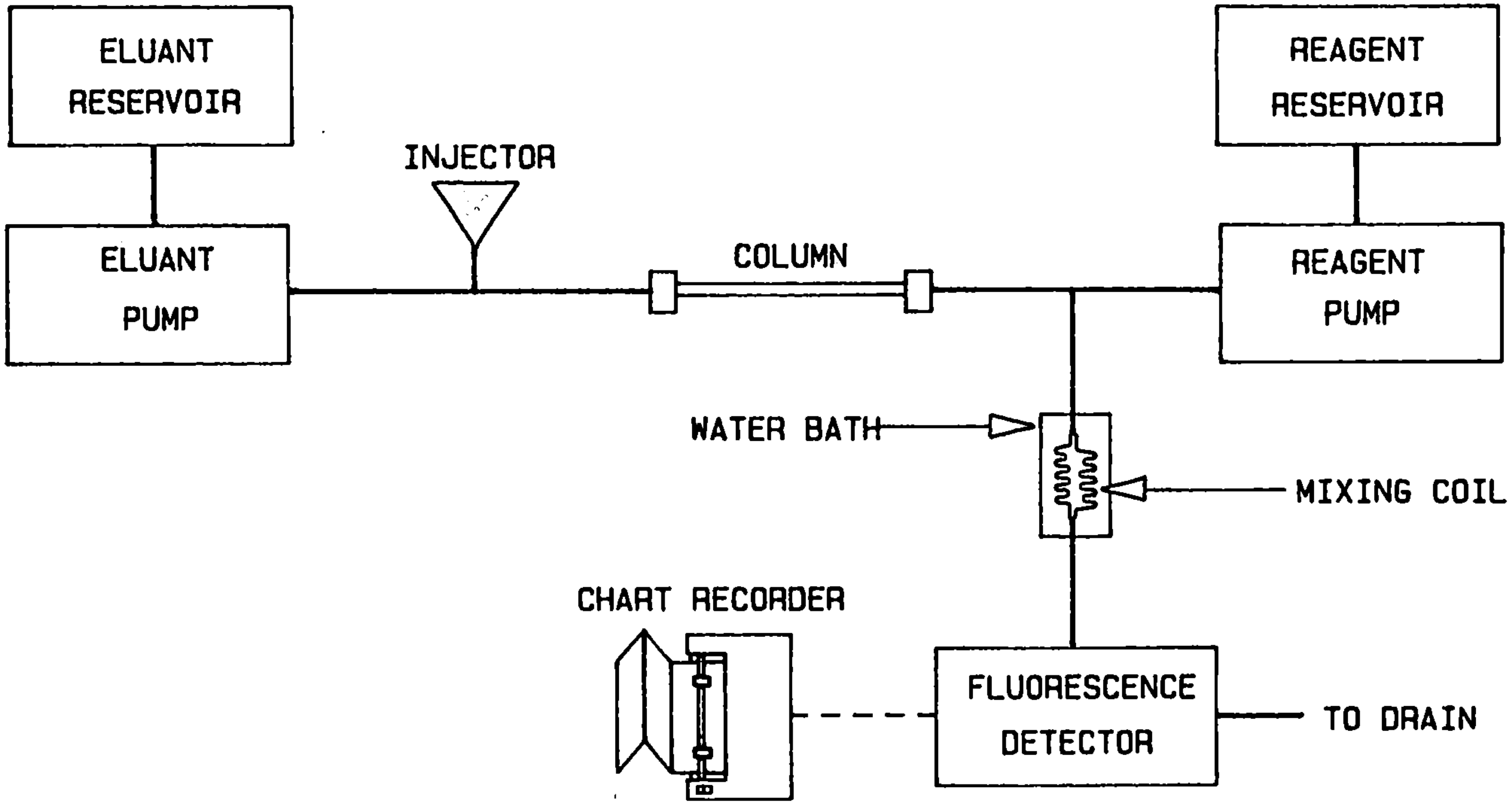


Figure 5.4 HPLC system for the analysis of aluminium using post column derivatisation and fluorescence detection.

5.6

Automated Simplex Optimisation

Optimisation experiments using a microcomputer program to assist with mathematical calculations still require the scientist to perform the experiment. The optimisation of a novel ICP system can occupy the scientist for a period of two hours or more. His time is spent doing a simple repetitive task which could be performed by a computer on a fully automated instrument. This would make experiments more reproducible and remove the possibility of human error as well as release the scientist for other more demanding tasks.

A programme of work was started to bring the Kontron S35 Plasmakon under full computer control. The objective being to incorporate a simplex program into the existing software which could perform completely automated simplex optimisation experiments.

5.6.1

Hardware Modifications of the S35 Plasmakon

The instrument (described in Chapter 2) was supplied with a computer controlled height of observation system and therefore only the three gas flows and the radiofrequency power control needed to be brought under computer control.

The system of gas flow control supplied on the instrument consisted of 3 ten turn, linear, ten thousand ohm potential dividers (pots). Each pot supplying between 0V and 5V control to drive the mass flow controllers. It was decided that two options were initially viable. Firstly to replace these pots with equivalent stepper motor driven pots which could either be manually adjusted or computer controlled via a suitable interface. Or secondly the mass flow controllers could be driven from an interface with digital to analogue output and control switched between the interface and the pots via a rapid relay system. This second option was chosen to avoid excessive cost and complexity and consisted of two separate printed circuit boards as shown in Figures 5.5 and 5.6.

The first of the two boards allows 8 bit binary values output from the central processor to be decoded, in terms of which gas flow they are intended for, and converted to an analogue signal between 0V and 2.25V This voltage then goes to the second board where it is amplified to give a maximum output of 5 volts. There is also an offset facility which allows a minimum output voltage to be set. This was used only on the coolant gas flow where a voltage equivalent to a flow of 5 litres per minute was set (0.6V). The minimum being set to give some protection to the plasma torch in the event of a software failure.

Optimised coolant conditions were not envisaged as ever being less than 5 litres per minute with the torch types being used. The two board design was adopted to give some measure of isolation between the computer system and the rest of the plasma instrument. Initially problems were encountered with radio frequency (r.f.) noise feeding back to the gas flow and power control system. This was identified as being instability in the operational amplifier (op-amp) used to generate the final control voltage. The TTL 741 op-amp then being used was replaced with its low noise equivalent the 351. This made a

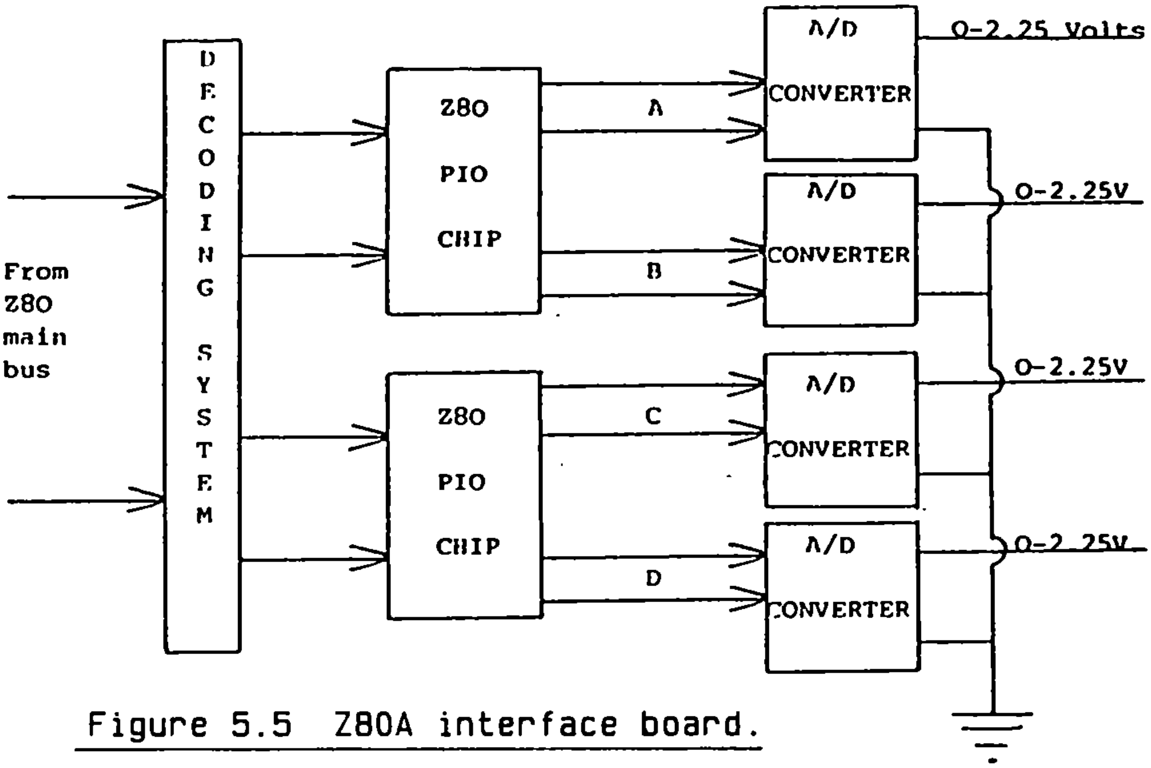


Figure 5.5 Z80A interface board.

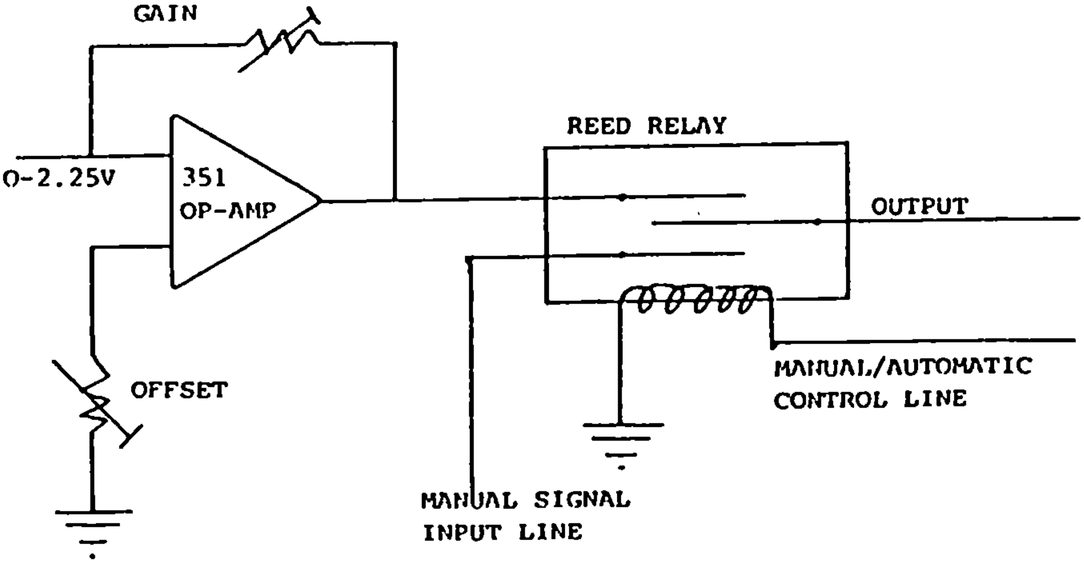


Figure 5.6 Control switching and r.f. buffer board.

significant improvement but final stability was achieved only after grounding the gain and offset lines with 10 picofarad capacitors to remove as much of the 27 MHz interference as possible.

The radio frequency power was initially controlled via a similar system but the pot supplied between 0V and 8V. Hence automated control was achieved in the same way. The only difference being that the gain of the final output was increased to give a maximum of 8 volts and the offset was adjusted to give a minimum r.f. generator output of 500 watts. It was found that control of the r.f. power level could only be switched if the system taking control had a slightly higher power setting than the operating system. If the system taking control was at the same or slightly lower power then the plasma was always extinguished. This was thought to be due to the r.f. matching network but the problem was never conclusively identified but in practice could be simply overcome.

The control system described above provided adjustment of the gas flows and r.f. power level with 8 bit accuracy. Thus the injector gas flow could be set between 0 l min^{-1} and its maximum of 3 $lmin^{-1}$ in 256 steps of 11.7 cm^3 min^{-1}. Control of the other variables was as follows:

	Range	Step size
Coolant gas flow	5-40 $lmin^{-1}$	136 cm^3 min^{-1}
Auxillary gas flow	0-10 $lmin^{-1}$	39 cm^3 min^{-1}
Radio frequency power	0.5-2.5 kw	7.8 watts

This control was thought to be sufficiently accurate since previous workers (58) had shown that optimum conditions for ICP systems are usually quite broad regions.

If at a later date a greater degree of control was required the interface could be replaced for one giving 16 bit accuracy which would reduce the step size by a further factor of 256.

5.6.2

Software Modifications to the S35 Plasmakon

The original software for the instrument was written in a version of Fortran-80 (Image Analysis Systems, distributed by Lifeboat Associates, New York, USA) and compiled. In addition a large number of routines were written in Z80 assembler language and also compiled. The size of the whole program code when compiled was approximately 74 kilobytes, without run time data storage. The on-board computer of the instrument, based on a Z80 A microprocessor, had a total random access memory (RAM) of 64 kilobytes and as such could not hold all the required software in memory simultaneously. Thus the software had been linked together using a two-pass linkage editor, Plink-II (Phoenix Software Associates, distributed by Lifeboat Associates, New York, USA) and the memory divided into 4 overlay areas.

Overlays are simply sections of the program which are defined to use the same memory areas. When overlays are specified an overlay module is automatically included into the program. The loader reads files from disk into memory as required by the executing program.

Since portions of the program share the same memory space during run time the memory requirement of the program is reduced.

The software to perform a simplex experiment would require many of the routines which already existed. Expecially those to select wavelengths, drive the monochromator, read files from the floppy disc drives, integrate spectral intensities and perform many other smaller tasks. Hence it was decided that due to the complexity of these routines and their interaction with each other, they could not easily be rewritten. Therefore, the simplex software would have to be included into the existing software and any additional routines would have to be fitted into the overlay structure. To do this the size and memory location of each overlay and each file within those overlays would have to be determined so that new files would not disrupt or overwrite the overlay structure. Where possible it was preferable to enlarge or modify existing files to incorporate simplex routines as this was easier than trying to include new routines into an already overcrowded memory system. Figure 5.7 shows the memory map including the 3 simplex routines SIML, RAMP and EVAL. Modifications were made to several of the existing routines, a description of which follows.

5.6.2.1

New Assembler Routines

Routines written in Z80 assembler were required to initialise the new interface board and to transfer information to it. The existing software already contained a Macro library of Z80 assembler routines called INTUP.MAC. The two new assembler routines TRIT (routine to initilise the Z80 PIO integrated circuits) and PIOWR (routine to write

BYTES to each PIO port) are given in Appendix 3. These were added to the existing library of routines, an exact description of how these routines work is beyond this thesis and the reader is directed to any book on Z80A assembler for more details. The routine TRIT is called only once at the very start of any simplex optimisation and the routine P1OWR is used every time a signal is output to one of the four output locations.

5.6.2.2.

New Fortran Routines

The software to perform automated simplex optimisation was broken down into sub routines. The main routine SIML shown in Appendix 4, is called from the existing software and executes the simplex process. This involves calculating and evaluating the initial simplex set according to the method of Yarbro and Deming (44), followed by the usual iterative improvement cycle until an optimum solution is reached.

The initialisation of the interface and the determination of the boundary conditions for each variable is performed by the routine NUP (Appendix 5). This routine allows the operator to input boundary conditions for each variable or to use a set of default conditions. It also calls the assembler routine which initialises the interface ready for software control.

Adjustment of variable settings is achieved through the routine RAMP (Appendix 6) which steps each variable from its old setting to the new setting. This is essential for adjustment of the radio frequency power level where sudden changes cause the plasma to be extinguished.

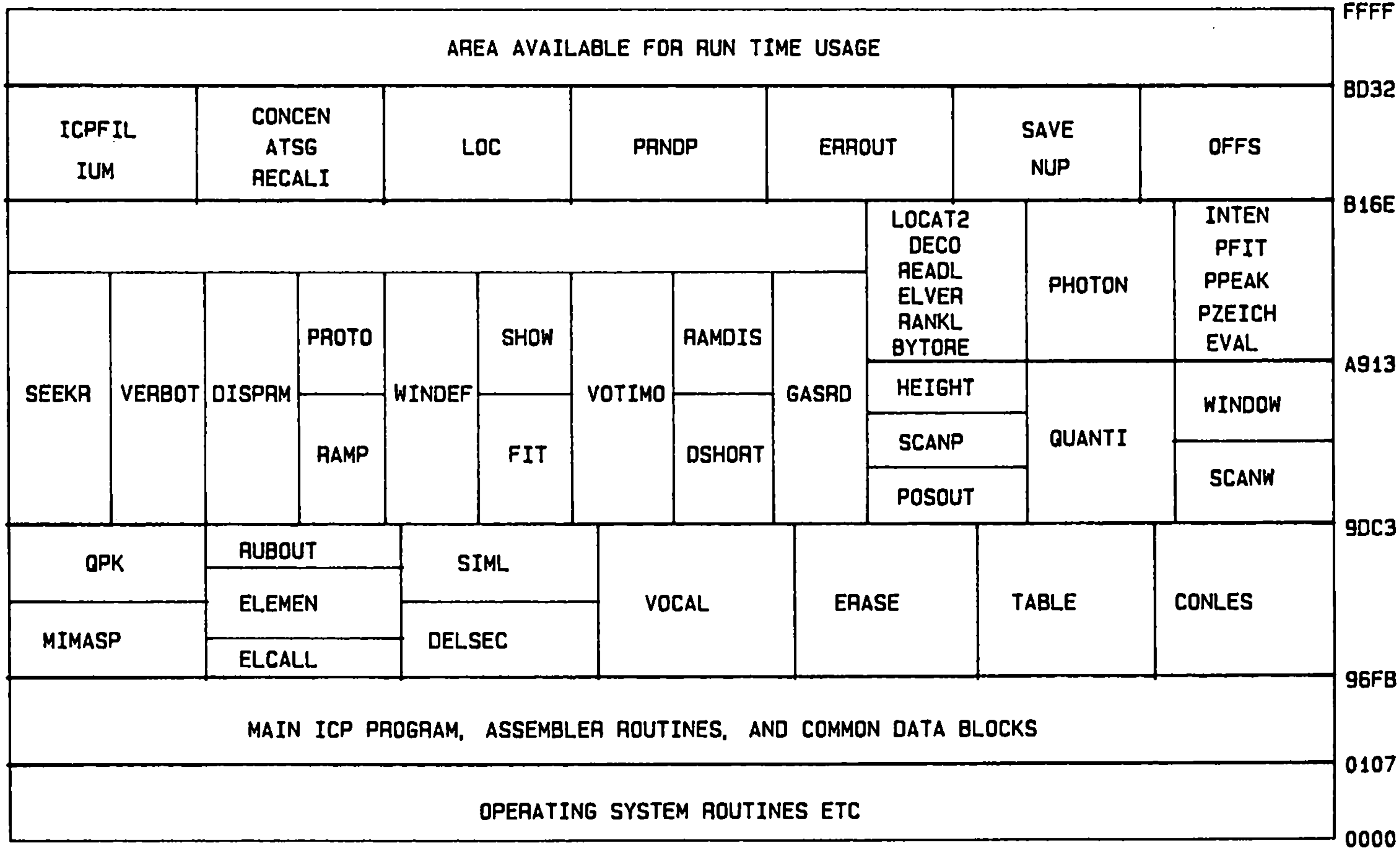


Figure 5.7 Memory overlay map of the S35 Plasmakon software.

The signal to background ratio for each vertex is calculated by the routine EVAL (Appendix 7) which uses a modified version of an exisitng routine QUANTI, to drive the monochromator and collect data regarding signal intensities. The background signal was calculated from the mean of the intensity at two wavelengths set on either side of the analytical line.

To check for violations of boundary conditions a short routine, RNGCK (Appendix 8) compares calculated vertex values with the boundary limits. Boundary violations are dealt with by assigning the vertex a very low response factor. This treatment of boundary violations could easily be changed to that used by Bettridge et al. (50) whereby the variable out of range is reset to its boundary limit. A FORTRAN function MIMA existed in the software to perform this variable readjustment.

Changes were made to the existing files ICPPQ, ICPBS, DRIVE, PHONEU and QUANTI. These files are very large and the changes to ICPBS, DRIVE and PHONEU were fairly small, thus none of these files are included in this thesis for reasons of space. SIML was included as a routine called from the main software program ICPPQ and control returns to the that routine once an optimum has been reached.

The subroutine QUANTI performs wavelength adjustment and collects peak and background intensities. Hence this routine received the greatest modification such that it could be called and used by the new routine EVAL.

5.6.3

Discussion

Software development was often severely hampered. Initially problems were encountered in obtaining the correct FORTRAN source files from the instrument manufacturer. Several updates of the software had been made and no record had been kept as to which software revision was running on the instrumentation used. This problem was finally overcome by the manufacturer reconfiguring the instrument for the latest software version and supplying the relevant source files.

The actual development itself was slow due to the length of time taken to compile and link the software. The double-pass linkage editor typically took 45 minutes to generate the overlay defined executable code. Compilation time obviously depended on the number of files modified, since not every file had to be compiled every time. Even so, changes to two or three files could take 30 minutes to compile and transfer to the correct floppy discs for linking. Hence the development cycle for software changes including time taken to run the program and assess the impact of any changes was usually 1½ to 2 hours. Unfortunately this cycle could not be shortened by running routines individually since no interpretive system existed.

The greatest problem was that of instrument stability and reliability. The stability problem arose from a faulty radio frequency generator which could not easily be repaired. Signal drift was at times as bad as 50% per hour with signal to background ratios halving in a 60 minute period. A simplex experiment cannot cope with such rates of signal change. New vertices which are superior to those in the simplex set achieve worse signal to background ratios because the system has changed since the previous vertices were evaluated. Finally the instrument suffered a series of major faults which effectively prevented operation for the last eight months of the project. Unfortunately due to the highly instrument specific nature of the software it was not possible to transfer to other available plasma instrumentation.

At times during the eight month period of instrument failure it was possible to operate the computer system. During these periods software development continued in the hope that it could be properly evaluated at a later date. The simplex software was shown to perform an iterative cycle and successfully control the monochromotor and gas flows. This was mainly tested by putting text printing statements into the software to assess its progress.

5.6.4

Conclusion

The hardware and software modifications to the S35 Plasmakon showed that it was feasible to automate the instrument to perform simplex experiments. No intrinsic problems were encountered which could not be overcome. Hence provided that the problems of stability and reliability can be overcome the instrument can be made to perform automated simplex experiments. Since completion of this work the generator and tuning network of the Plasmakon instrument used have been completely redesigned and refurbished and should now offer the necessary stability and performance characteristics to allow a full evaluation of the software and hardware developments described here.

Previous work using simplex optimisation has shown the usefulness of optimisation in the field of plasma spectrometry. This has been generally accepted and confirmed by the introduction of commercial instruments capable of self optimisation. As the cost of computer hardware and software is reduced it is highly likely that more and more "intelligent" inductively-coupled plasma instruments will be constructed.

CHAPTER 6

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

The project was successful in meeting some, if not all, of its objectives. Solid samples were successfully introduced into the inductively-coupled plasma for analysis by both optical emission and mass spectrometry. The technique was shown to be valid by the analysis of several sample types including certified reference materials.

Study of the Scott-type spray chamber and Greenfield style torch sample introduction system has produced a better understanding of the role and importance of each part of the system. This work highlighted the important role of the internal diameter of the injector tube in limiting the size of particles reaching the plasma. The maximum injector bore size consistent with forming an annular plasma was found to be 3 mm for this system which prevented particles of greater than 8 µm diameter from searching the plasma.

Recent work carried out by Snook and Davies (17) has suggested that a laminar flow torch system can maintain a stable plasma while using wider bore injector tubes. Hence a study of such systems for the introduction of slurries would be interesting from several viewpoints. larger slurry particles could be nebulised thus reducing the need for particle size reduction. Introduction of larger particles should eventually allow the state whereby the plasma was no longer capable of total atomisation to be reached. This may already have been reached with alumina which has been shown to exist as solid particles even within the normal analytical zone (124). The introduction of large mono-dispersed particles may reveal interesting mechanistic information by causing a change of atom/ion ratios when compared with aqueous solutions. These ratios could easily be measured spectroscopically and some spatial resolution within the plasma would be possible.

Further work on applications of slurry nebulisation is obviously essential in establishing the technique and attention should be paid to the grinding technique which is capable of increased sophistication. Simplex optimisation experiments have wide applicability and may well help in modifying and improving future slurry nebulisation developments.

Automated simplex experiments are very heavily dependant on the reliability and stability of the instrumentation used. This constraint should ease as the quality and cost of ICP equipment improves, but will always require a very significant software input. The current modification to the Kontron Plasmakon should be capable of driving the instrument through a simplex experiment. The main problems facing a continuation of this work are the complexity of the existing software and the difficulty in driving the already over-worked computer system to a higher level of operation. Newer computer systems, especially those based on 16 bit microprocessors, would obviously be of great assistance in attempting such automation on other ICP instruments.

Meetings of the Royal Society of Chemistry

i. Analytical Diversion symposium, 12th April, 1984, Annual Reports on Analytical Atomic Spectroscopy, 'Automation - is it cost effective?', Sheffield City Polytechnic.

ii. Analytical Division meeting, 26th and 27th June, 1984, 'Research and Development Topics in Analytical Chemistry', UMIST, Manchester.

iii. Analytical Division meeting, 10th-13th July, 1984, 'Second Biennial National Atomic Spectroscopy Symposium', University of Leeds.

iv. Analytical Division symposium, 2nd April, 1985, 'Annual Reports on Analytical Atomic Spectroscopy', Sheffield City Polytechnic.

v. Joint Analytical Division and the Atomic Spectroscopy Group meeting, October, 1985, 'Sample Introduction and the ICP', University of Bristol.

vi. Analytical Division symposium, 15th April, 1986, 'Atomic Spectroscopy Updates', Sheffield City Polytechnic.

vii. Analytical Division meeting, 16th and 17th April, 1986, 'Research and Development Topics in Analytical Chemistry', UCL, London.

viii. Analytical Division joint meeting, 'SAC 86 International Conference and Exhibition on Analytical Chemistry' together with 'Third Biennial National Atomic Spectroscopy Symposium', 20th-26th July, 1986, University of Bristol.

Lectures and associated studies

i. RSC meeting, 28th October, 1983, Plymouth Polytechnic, Prof J P Riley, 'Analytical Chemistry Applied to Marine Pollution Problems'.

ii. RSC AGM and lecture, 13th January 1984, Bristol University, Mr J G Jones, 'Death of the Analyst'.

iii. RSC lecture, 17th February, 1984, Plymouth Polytechnic, Prof J N Miller, 'Hunting the Snark - Recent Developments in Ultra Sensitive Molecular Spectroscopy'.

iv. Series of lectures on 'Advanced Analytical Atomic Spectroscopy', June - August 1984, Plymouth Polytechnic.

v. RSC lecture, 16th November, 1984, Plymouth Polytechnic, Dr D Woodcock, 'Fungicides and the Environment'.

vi. Departmental Colloquium, 8th February, 1985, Plymouth Polytechnic, Dr C Corfield, 'Gas Cromotography - Mass Spectrometry, Useful Applications of a Technique Come of Age'.

vii. RSC lecture, 15th March, 1985, Plymouth Polytechnic, Dr P S Liss, 'The Role of the Oceans in the Chemistry of the Atmosphere'.

viii. Departmental Colloquium, 10th September, 1985, Plymouth Polytechnic, Dr J M Harnly, 'Recent Developments in Analytical Atomic Spectroscopy'.

ix. Departmental Symposium, 24th and 25th September 1985, 'The First Surrey Conference on ICP-MS', Unversity of Surrey.

x. RSC lecture, 1st November 1985, Plymouth Polytechnic, Dr T E Hunt, 'Trace Element Speciation in Aquatic Systems'.

xi. RSC lecture, 7th February, 1986, Plymouth Polytechnic, prof A F Fell, 'Snapshot Chromatography-Biomedical Applications of New Technology in HPLC'.

xii. RSC lecture, 7th March, 1986, Plymouth Polytechnic, Dr P Campion, 'The Chemistry of PWR and AGR Nuclear Power Reactor Coolant'.

Presentations and Publications

Resulting from the work reported in this thesis the following papers have been presented and published.

(a) Presentations

1. 'Computer Controlled Optimisation of an Inductively-Coupled Plasma'.

   Poster presentation at Research and Development Topics in Analytical Chemistry meeting, UCL, London, April 1986.

2. 'Analysis of Zeolites and other Minerals by ICP-OES using Slurry Atomisation'.

   Paper presented at the Third Biennial National Atomic Spectroscopy Symposium, Unversity of Bristol, July 1986.

(b) Publications

1. Ebdon, L., Norman, P., Sparkes, S.T.
   'Simplex Optimisation of a Direct Current Plasma for Atomic Emission Spectrometry'.

   Spectrochim Acta. 1987, 42B, 619.

2. Williams, J. G., Gray, A.L., Norman, P., Ebdon, L.
   'Feasibility of Solid Sample Introduction by Slurry Nebulisation for ICP-MS'.

   J. Anal. At. Spectrom. 1987, 2, 469.

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Appendix 1 Thixotropic slurry preparation.

1. Accurately weigh 1g of sample and place into a 150 ml beaker containing 50 mls of distilled water.

2. While stirring the solution vigorously with a magnetic stirrer add 3.0 mls of 0.1% v/v sodium hexametaphosphate solution*.

3. Add 0.1 mls of antifoaming, H2(Allied Colloids, Bradford) followed by 1 ml of thixotropic thickening agent Viscalex HV30 (Allied Colloids, Bradford).

4. Stirring gently adjust the pH to 7.5 by addition of a few drops of aqueous ammonia solution. Allow gel to form before transferring to a 100 ml volumetric flask and diluting to volume. Use the suspension within 24 hours as the gel tends to degrade fairly rapidly with only 1% v/v of the Viscalex HV30 thickening agent.

* Standards can be made up in an identical fashion except that when diluting from acidic stock solutions the pH should be adjusted to above 3 at this point as the thickening agent degrades at low pH.

Appendix 2 Simplex Optimisation program for the Apple IIe

```
1  PRINT  CHR$ (4);"PR#0"
2  HOME
3  PRINT  CHR$ (17)
10  POKE 103,1
20  POKE 104,64
30  POKE 16384,0
40  PRINT  CHR$ (4);"RUN K2"
```

```
100  REM  NB=no. of variables consi STR$ ered
110  REM  NT=no. of worst vertex in simp tab
120  REM  Z=output format parameter
130  REM  VNUM=vertex number
140  HOME
150  REM  NS=no.of substitution:if=3 then R:if=6 then S
160  VTAB 10: HTAB 10: PRINT "SIMPLEX OPTIMISATION"
170  PRINT
180  HTAB 17: PRINT "BY"
190  PRINT
200  HTAB 11: PRINT "PHILIP NORMAN"
210  HTAB 25: PRINT "1984"
220  FOR I = 1 TO 2000: NEXT I
221  HOME
222  PRINT  TAB( 7);"This program is designed to assist": PRINT
     "the user in the Simplex Optimisation": PRINT : PRINT "of
      any system which has several inter-": PRINT : PRINT "rel
     ated variables."
224  PRINT
227  PRINT : PRINT : PRINT
230  PRINT  CHR$ (4);"RUN K33"
```

```
100  PRINT  CHR$ (4)"BLOAD HGR FONT,A$800 "
230  HOME
240  PRINT : PRINT
250  PRINT  TAB( 3);"Please enter the number of variables": PRINT
: PRINT " that are going to be considered during": PRINT : PRINT
" this optimisation."
252  PRINT : PRINT : PRINT
254  PRINT "The maximum permissable number being 10."
255  PRINT
256  PRINT  TAB( 15);
260  INPUT NB
280  IF NB < 10 GOTO 320
285  PRINT
290  PRINT "Too many variables for screen size"
300  PRINT
310  GOTO 250
320  DIM SIMP(NB + 4,NB + 4)
330  DIM OPT(NB + 3,6)
340  DIM HOLD(NB + 4,75)
350 VNUM = 0
360 XX = 1
370 STV = 0
380 HPT =  INT (NB / 2)
400  HOME
401  PRINT  TAB( 1);"You now have the following choice:-"
403  PRINT : PRINT : PRINT
405  PRINT  TAB( 3);"1. Starting a new simplex optimisation"
407  PRINT : PRINT
409  PRINT  TAB( 3);"2. Restarting an old optimisation by": PRINT
: PRINT " typing in the starting simplex matrix."
410  PRINT
415  PRINT : PRINT
420  PRINT  TAB( 18): PRINT "Input your choice ?";
425  GET G
430  IF G = 1 GOTO 1040
440 CC = 2
450 CH = 65
470  HOME
480  PRINT " To use previous verticies simply input the values
      for each variable as they are requested in the following
      format"
490  PRINT : PRINT
510  PRINT "Vertex No.,"; CHR$ (CH);"1,"; CHR$ (CH);"2,...,"; CHR$
(CH);"n,Response Factor"
520  PRINT : PRINT
540 CT = 2
550  INPUT "Vertex No.=";SIMP(1,CC)
560  IF SIMP(1,CC) < STV GOTO 580
570 STV = SIMP(1,CC)
580  PRINT
590  PRINT "   "; CHR$ (CH);CT - 1;
600  INPUT SIMP(CT,CC)
```

```
610 CT = CT + 1
620  IF CT = NB + 2 GOTO 640
630  GOTO 580
640  PRINT
650 CT = 2
660  INPUT "Response Factor =";SIMP(NB + 2,CC)
680 CH = CH + 1
690 CC = CC + 1
700  IF CC = NB + 3 GOTO 730
710  HOME
720  GOTO 490
730  HOME
740  IF NB > 4 THEN  PR# 3
750 Z = 40 / (NB + 2)
760  IF NB > 4 THEN Z = 80 / (NB + 2)
770  PRINT  SPC( (Z * HPT) + 5);"Variable"
780  PRINT
790 ZZ = STV - (NB + 1)
800  FOR I = 1 TO NB + 2
810  FOR A = 0 TO NB + 1
820 SIMP(A + 1,1) = A
830 HOLD(A + 1,ZZ) = SIMP(A + 1,I)
840 A$ =  STR$ (SIMP(A + 1,I))
850  IF A = 0 THEN A$ = "   " +  STR$ (SIMP(A + 1,I))
860  IF I = 1 AND A = 0 THEN A$ = "Vertex"
870  IF A = NB + 1 THEN A$ = " " + A$
880  IF I = 1 AND A = NB + 1 THEN A$ = "Resp."
890  PRINT A$; SPC( Z -  LEN (A$))
900  NEXT A
910 ZZ = ZZ + 1
920  PRINT
930  IF NB > 3 AND NB < 6 THEN  PRINT
940  NEXT I
950  PRINT : PRINT
970  PRINT "Are above verticies satisfactory"
980  GET B$
990  IF B$ = "N" GOTO 440
1010 VNUM = STV + 1
1020 XX = STV - (NB + 1)
1030  GOTO 1590
1040  HOME
1041  PRINT "  You have chosen to start a new": PRINT : PRINT
     "optimisation and thus we must start by": PRINT : PRINT "
     constructing the initial Simplex matrix"
1045  PRINT : PRINT : PRINT
1046  PRINT "  To do this the usable range of each": PRINT : PRINT
"variable is required.Please input the": PRINT : PRINT "lowest
      and the highest possible values": PRINT : PRINT "for eac
     h variable"
1050 STV = 2
1070  PRINT
1080  PRINT  TAB( 15);"eg. Variable 3= 0.05,25.0"
1090  PRINT : PRINT : PRINT
```

```
1100  FOR I = 1 TO NB
1110 SIMP(I + 1,1) = I
1120  PRINT "Variable ";I;
1121  INPUT "=";SIMP(I + 1,2),SIMP(I + 1,NB + 4)
1140  PRINT
1150 SIMP(I + 1,NB + 3) = SIMP(I + 1,NB + 4) - SIMP(I + 1,2)
1160  NEXT I
1170  FOR I = 2 TO NB + 1
1180  FOR N = 3 TO NB + 2
1190 SIMP(I,N) = SIMP(I,2) + (SIMP(I,NB + 3) / ((I - 1) * 1.41
     4214)) * (I ^ 0.5 - 1)
1200  NEXT N
1210 SIMP(I,I + 1) = SIMP(I,2) + (SIMP(I,NB + 3) / ((I - 1) *
     1.414214)) * (I ^ 0.5 + I - 2)
1220  NEXT I
1230  HOME
1240  IF NB > 4 THEN  PR# 3
1250 Z = 40 / (NB + 1)
1260  IF NB > 4 THEN Z = 80 / (NB + 1)
1270  PRINT "The initial simplex verticies are :-"
1280  PRINT
1300  PRINT
1310  PRINT  SPC( (Z * HPT) + 5);"Variable"
1320  PRINT  SPC( (Z * HPT) + 5);"--------"
1330  FOR I = 1 TO NB + 2
1340 SIMP(1,I) = VNUM
1350 VNUM = VNUM + 1
1360  FOR N = 1 TO NB + 1
1370 HOLD(N,I) = SIMP(N,I)
1380 SIMP(N,I) = (( INT (SIMP(N,I) * 100)) / 100)
1390  NEXT N
1400  FOR A = 0 TO NB
1410 A$ =  STR$ (SIMP(A + 1,I))
1420  IF A = 0 THEN A$ = "   " +  STR$ (SIMP(A + 1,I))
1430  IF I = 1 AND A = 0 THEN A$ = " "
1431 LS =  LEN (A$)
1435  IF A = 0 THEN LS = LS - 3
1440  PRINT A$; SPC( Z - LS)
1450  NEXT A
1455 PL =  INT (Z) * NB + 1
1460  PRINT  TAB( 80 - PL)
1480  IF I = 1 THEN  PRINT "VERTEX"
1481  FOR J = 1 TO  INT ((Z * (NB + 1)) + 0.3): PRINT "-";
1482  NEXT J
1490  IF NB > 4 AND NB < 7 THEN  PRINT
1500  NEXT I
1510  PRINT
1520  PRINT "Input the RESPONSE FACTOR as given by   the ini
    tial simplex verticies"
1530  FOR I = 2 TO NB + 2
1540  PRINT
```

```
1550  PRINT " RESPONSE FACTOR for vertex ";I - 1;" = ";
1560  INPUT SIMP(NB + 2,I)
1570 HOLD(NB + 2,I) = SIMP(NB + 2,I)
1580  NEXT I
1590  PRINT
1600  HOME
1605  PRINT  CHR$ (17)
1610  PRINT "This program assumes the optimum to have": PRINT
     "been reached when the RESPONSE FACTORS": PRINT : PRINT "
     for all the verticies are within twice": PRINT : PRINT "t
     he PRECISION of the technique."
1620  PRINT
1630  PRINT
1640  PRINT "  Hence please input your estimate for ": PRINT :
      PRINT "     precision of the RESPONSE FACTOR": PRINT : PRINT
"      as a percentage value";
1650  INPUT XB
1660  HOME
1670 NT = 2
1680 TEMP = SIMP(NB + 2,2)
1690  FOR I = 3 TO NB + 2
1700  IF TEMP < SIMP(NB + 2,I) THEN 1730
1710 TEMP = SIMP(NB + 2,I)
1720 NT = I
1730  NEXT I
1740  FOR I = 1 TO NB + 2
1750 OPT(I,1) = 0
1760  NEXT I
1770  FOR I = 1 TO NB
1780  FOR N = 2 TO NB + 2
1790  IF N = NT THEN 1810
1800 OPT(I,1) = (OPT(I,1) + SIMP(I + 1,N) / NB)
1810  NEXT N
1820 OPT(I,2) = OPT(I,1) - SIMP(I + 1,NT)
1830 OPT(I,3) = ( INT ((OPT(I,1) + OPT(I,2)) * 100)) / 100
1840  NEXT I
1850  HOME
1860  PR# 3
1870  PRINT  TAB( 14);"MASTER MENU"
1880  PRINT
1890  PRINT
1900  PRINT "  You now have a choice of the following"
1910  PRINT
1920  PRINT
1930  PRINT  TAB( 8);"1. Continuing the simplex optimisation b
     y considering the next vertex."
1940  PRINT
1950  PRINT
1960  PRINT  TAB( 8);"2. Graphically inspecting the progress o
     f the optimisation."
1970  PRINT
1980  PRINT
```

```
1990  PRINT  TAB( 8);"3. Displaying the current simplex matrix
     ."
2000  PRINT
2010  PRINT
2020  PRINT  TAB( 8);"4. Obtaining a printed copy of all verti
     cies held in the simplex matrix": PRINT : PRINT  TAB( 50)
     ;"during this optimisation."
2030  PRINT
2040  PRINT
2050  PRINT  TAB( 8);"5. Quiting the program thus ending this
     optimisation."
2060  PRINT : PRINT
2061  PRINT  TAB( 8);"6. Change any value within the simplex m
     atrix."
2062  PRINT  SPC( 55)
2063  INVERSE
2064  PRINT "Input your choice ?";
2067  NORMAL
2070  GET CNUM
2080  IF CNUM = 1 GOTO 2300
2090  ON CNUM GOSUB 2300,4300,2110,4005,8000,9000
2100  GOTO 1850
2110  HOME
2118  PRINT  CHR$ (27); CHR$ (17)
2120 Z = 40 / (NB + 2)
2130  IF NB > 4 THEN Z = 80 / (NB + 2)
2135  IF NB > 4 THEN  PR# 3
2140  PRINT  SPC( (Z * HPT));"Variable"
2150  PRINT
2160  FOR I = 1 TO NB + 2
2170  FOR A = 0 TO NB + 1
2180 A$ =  STR$ (SIMP(A + 1,I))
2190  IF A = 0 THEN A$ = "   " +  STR$ (SIMP(A + 1,I))
2200  IF I = 1 AND A = 0 THEN A$ = " "
2210  IF A = NB + 1 THEN A$ = "  " + A$
2220  IF I = 1 AND A = NB + 1 THEN A$ = "       "
2230  PRINT A$; SPC( Z -  LEN (A$))
2240  NEXT A
2250  PRINT
2260  IF NB > 3 AND NB < 6 THEN  PRINT
2270  IF I = 1 THEN  PRINT "Vertex"; SPC( Z * NB);"    Resp."
2280  NEXT I
2281  PRINT
2283  PRINT  TAB( 10);"To return to the main menu press any ke
     y"
2285  GET B$
2290  RETURN
2300  HOME
2305 SIMP(1,NT) = VNUM
2310 VNUM = VNUM + 1
2320  PRINT
2330  PRINT ; SPC( 5);"Reflection Vertex equals:-"
2340  PRINT
```

```
2350  FOR A = 0 TO NB
2360 A$ =  STR$ (OPT(A,3))
2370  IF A = 0 THEN A$ = " "
2380  PRINT A$; SPC( Z -  LEN (A$))
2390  NEXT A
2400  PRINT
2410  PRINT
2420  PRINT
2430  PRINT "Input the RESPONSE FACTOR for the          Reflectio
     n Vertex"; SPC( 3)
2440  INPUT OPT(NB + 1,3)
2450  IF OPT(NB + 1,3) =  - 99 THEN  GOTO 4020
2460 JT = 0
2470  FOR I = 2 TO NB + 2
2480 SIMP(NB + 3,I) = SIMP(NB + 3,I) + 1
2490  IF OPT(NB + 1,3) > SIMP(NB + 2,I) THEN 2510
2500 JT = JT + 1
2510  NEXT I
2520  IF JT = 0 THEN 2880
2530  IF JT <  = NB - 1 THEN  GOTO 2700
2540  IF JT = NB THEN 2720
2550  FOR I = 1 TO NB
2560 OPT(I,5) =  INT ((OPT(I,1) - 0.5 * OPT(I,2)) * 100) / 100

2570  NEXT I
2580  PRINT
2590 Z = 40 / (NB + 2)
2600  IF NB > 4 THEN Z = 80 / (NB + 2)
2610  PRINT "Contraction vertex Cw ="
2620  PRINT
2630  FOR A = 0 TO NB
2640 A$ =  STR$ (OPT(A,5))
2650  IF A = 0 THEN A$ = "  "
2660  PRINT A$; SPC( Z -  LEN (A$))
2670  NEXT A
2680 NS = 5
2690  GOTO 3130
2700 NS = 3
2710  GOTO 3080
2720  FOR I = 1 TO NB
2730 OPT(I,4) =  INT ((OPT(I,1) + 0.5 * OPT(I,2)) * 100) / 100

2740  NEXT I
2750  PRINT
2760  PRINT "Contraction vertex Cr ="
2770  PRINT
2780 Z = 40 / (NB + 2)
2790  IF NB > 4 THEN Z = 80 / (NB + 2)
2800  FOR A = 0 TO NB
2810 A$ =  STR$ (OPT(A,4))
2820  IF A = 0 THEN A$ = "  "
```

```
2830  PRINT A$; SPC( Z -  LEN (A$))
2840  NEXT A
2850 NS = 4
2860  GOTO 3130
2870 Z = 40 / (NB + 1)
2880  IF NB > 4 THEN Z = 80 / (NB + 1)
2890  FOR I = 1 TO NB
2900 OPT(I,6) =  INT (OPT(I,3) + OPT(I,2) * 100) / 100
2910  NEXT I
2920  PRINT
2930  PRINT "Expansion vertex E ="
2940  PRINT
2950 Z = 40 / (NB + 2)
2960  IF NB > 4 THEN Z = 80 / (NB + 2)
2970  FOR A = 0 TO NB
2980 A$ =  STR$ (OPT(A,6))
2990  IF A = 0 THEN A$ = " "
3000  PRINT A$; SPC( Z -  LEN (A$))
3010  NEXT A
3020  PRINT
3030  PRINT
3040  PRINT "Input the RESPONSE FACTOR for the Expansion verte
     x"; SPC( 3)
3050  INPUT OPT(NB + 1,6)
3060 NS = 6
3070  IF OPT(NB + 1,3) > OPT(NB + 1,6) THEN NS = 3
3080  FOR I = 1 TO NB + 2
3090 HOLD(I,VNUM) = SIMP(I,NT)
3100 SIMP(I + 1,NT) = OPT(I,NS)
3110  NEXT I
3120  GOTO 3220
3130  PRINT
3140  PRINT
3150  PRINT " Input  the  RESPONSE FACTOR  for  this vertex";
3160  INPUT OPT(NB + 1,NS)
3170  FOR I = 1 TO NB + 2
3180 HOLD(I,VNUM) = SIMP(I,NT)
3190 SIMP(I + 1,NT) = OPT(I,NS)
3200  NEXT I
3210 SIMP(NB + 3,NT) = 1
3220 TEMP = SIMP(NB + 2,2)
3230  FOR I = 2 TO NB + 1
3240  IF TEMP > SIMP(NB + 2,I) THEN 3270
3250 TEMP = SIMP(NB + 2,I)
3260 NT = I
3270  NEXT I
3280  REM
3290  REM  TESTING FOR OPTIMUM
3300  REM
3310 RAVE = 0
3320  FOR M = 2 TO NB + 2
3330 RAVE = RAVE + SIMP(NB + 2,M) / (NB + 1)
3340  NEXT M
```

```
3350 LRAVE = RAVE - (RAVE / 100) * XB
3360 HRAVE = RAVE + (RAVE / 100) * XB
3370  FOR M = 2 TO NB + 2
3380  IF SIMP(NB + 2,M) > HRAVE GOTO 3450
3390  IF SIMP(NB + 2,M) < LRAVE GOTO 3450
3400  NEXT M
3410  GOTO 3750
3420  REM
3430  REM  TESTING FOR N+1 VIOLATION
3440  REM
3450  FOR I = 2 TO NB + 2
3460  IF SIMP(NB + 3,I) < NB + 1 THEN 3640
3470  PRINT
3480  HOME
3490  PRINT ; SPC( 5);"N+1 rule violated by vertex";SIMP(1,I)
3500  PRINT
3510 Z = 40 / (NB + 2)
3520  IF NB > 4 THEN Z = 80 / (NB + 2)
3530  FOR A = 1 TO NB + 1
3540 A$ =  STR$ (SIMP(A,I))
3550  PRINT A$; SPC( Z -  LEN (A$))
3560  NEXT A
3570  PRINT
3580  PRINT
3590  PRINT  SPC( 13);"Please check and input the RESPONSE FAC
     TOR for this vertex";
3600  INPUT SIMP(NB + 2,I)
3610 HOLD(NB + 2,SIMP(1,I) + 1) = SIMP(NB + 2,I)
3620  PRINT
3630 SIMP(NB + 3,I) = 0
3640  NEXT I
3650  IF NS = 3 OR NS = 6 THEN 1670
3660 NT = 2
3670 TEMP = 1000
3680  FOR I = 2 TO NB + 2
3690  IF OPT(NB + 1,NS) = SIMP(NB + 2,I) THEN 3730
3700  IF TEMP < SIMP(NB + 2,I) THEN 3730
3710 TEMP = SIMP(NB + 2,I)
3720 NT = I
3730  NEXT I
3740  GOTO 1740
3750  HOME
3760  PRINT "The optimal solution has been obtained"
3770  PRINT
3780  PRINT
3790  PRINT "If you consider that a better degree of precision
      should have been entered"
3800  PRINT "you can now continue the optimisation by entering
      a smaller value"
3810  PRINT
3820  INPUT " Do you wish to enter a new degree of precision?"
     ;B$
```

```
3830  IF  LEFT$ (B$,1) = "N" THEN 1860
3840  PRINT
3850  INPUT " Simply type in your new PRECISION and press RETU
     RN.";XB
3860  GOTO 1860
4005  HOME
4010  PRINT
4020  PRINT "Is a hard copy of all verticies held required ";
4030  INPUT B$: PRINT :
4040  IF  LEFT$ (B$,1) = "N" THEN 1850
4041  PRINT " Please ensure that the printer is switched on an
     d contains PAPER"
4044  PRINT "Press any key to continue";
4045  GET B$
4049  PR# 0
4050  PR# 1
4052  PRINT  CHR$ (9);"80N"
4060  PRINT  CHR$ (17)
4070  HOME
4082  PRINT
4100  PRINT "The verticies held during this optimisation were
     :-"
4110  PRINT
4114 Z = 40 / NB + 3
4120  PRINT  SPC( (Z * HPT) + 5);"Variable"
4130  PRINT
4140  FOR I = XX TO VNUM
4150  FOR A = 1 TO NB + 2
4160 HOLD(A,I) =  INT (HOLD(A,I) * 100) / 100
4170 A$ =  STR$ (HOLD(A,I))
4180  IF I = XX AND A = 1 THEN A$ = " "
4190  IF A = NB + 2 THEN A$ = " " + A$
4200  IF I = XX AND A = NB + 2 THEN A$ = " "
4210  PRINT A$; SPC( Z -  LEN (A$))
4220  NEXT A
4230  PRINT  TAB( 1)
4240  PRINT
4250  IF I = XX THEN  PRINT "Vertex"; SPC( (Z * NB) + 3);"Resp
     ."
4260  PRINT
4270  NEXT I
4280  PR# 0
4290  RETURN
4300  HOME
4310  PRINT : PRINT
4330  PRINT "You can display either :-"
4340  PRINT : PRINT
4360  PRINT  TAB( 8);"1. Responce Factor vs Vertex No."
4370  PRINT
4380  PRINT
4390  PRINT  TAB( 8);"2. Parameter value vs Vertex No."
4400  PRINT : PRINT
4420  PRINT  TAB( 8);"3. Parameter value vs Response"
4430  PRINT
4440  PRINT  TAB( 34);"Factor."
4450  PRINT
```

```
4460  PRINT  TAB( 8);"4. Return to the main menu."
4470  PRINT
4490  PRINT
4500  PRINT
4510  PRINT  SPC( 55): INVERSE
4511  PRINT "Input your choice ?";
4512  NORMAL : GET CNUM
4520  IF CNUM < 1 OR CNUM > 4 GOTO 4545
4530  IF CNUM = 4 THEN  RETURN
4540  ON CNUM GOSUB 5000,6000,7000,4550
4545  GOTO 4300
4550  RETURN
5000 TEMP = HOLD(NB + 2,2)
5010  FOR I = 2 TO VNUM + 1
5020  IF TEMP > HOLD(NB + 2,I) GOTO 5040
5030 TEMP = HOLD(NB + 2,I)
5040  NEXT I
5050 YF = 160 / TEMP
5060 XF = 280 / VNUM
5062  PRINT  CHR$ (27); CHR$ (17)
5070  HGR
5071  HPLOT 0,0 TO 0,159 TO 279,159
5075 CTR = 0
5080  HPLOT XF,(160 - YF * HOLD(NB + 2,2))
5090  FOR I = 2 TO 280 STEP XF
5091 CTR = CTR + 1
5100  HPLOT  TO I,(160 - YF * HOLD(NB + 2,CTR))
5110  NEXT I
5112  VTAB 22: PRINT "Press any key to return to the graphics
     menu.";: GET B$
5130  TEXT
5140  RETURN
6000  HOME : PRINT : PRINT
6010  PRINT "Input the number of the variable which you requir
     e displayed."
6020  INPUT CNUM
6030 YF = 160 / (SIMP(CNUM + 1,NB + 4))
6040 XF = 280 / VNUM
6050  HGR
6060  HPLOT 0,0 TO 0,159 TO 279,159
6062  GOSUB 8000
6070 CTR = 0
6080  HPLOT XF,(160 - YF * HOLD(CNUM + 1,2))
6090  FOR I = 2 TO 280 STEP XF
6100 CTR = CTR + 1
6110  HPLOT  TO I,(160 - YF * HOLD(CNUM + 1,CTR))
6120  NEXT I
6140  VTAB 22: PRINT " Press any key  to return to the menu.":
      GET B$
6160  TEXT
6170  RETURN
7000  HOME
7010  PRINT "Input the number of the variable which you requir
     e displayed."
```

```
7020 TEMP = SIMP(NB + 2,2)
7030  FOR I = 1 TO NB + 2
7040  IF SIMP(NB + 2,I) < TEMP GOTO 7060
7050 TEMP = SIMP(NB + 2,I)
7060  NEXT I
7070  INPUT CNUM
7080  HGR
7090  HPLOT 0,0 TO 0,159 TO 279,159
7100 XF = 280 / SIMP(CNUM + 1,NB + 4)
7110 YF = 159 / TEMP
7120  FOR I = XX + 1 TO VNUM
7130 X = XF * HOLD(CNUM + 1,I)
7140 Y = YF * HOLD(NB + 2,I)
7150  HPLOT X,Y TO X + 1,Y TO X + 1,Y + 1 TO X,Y + 1
7160  NEXT I
7180  VTAB 25: PRINT " Press any key to return to the graphics
     menu": GET B$
7200  RETURN
8000  PRINT "BUM"
8010  POKE 232,1: POKE 233,2
8020  HCOLOR= 7
8030  SCALE= 1
8040  ROT= 0
8050  FOR I = 1 TO VNUM
8060 H = I:V = 19:S$ =  STR$ (I): GOSUB 8080
8070  RETURN
8080 L =  LEN (S$): FOR X = 1 TO L
8090 S =  ASC ( MID$ (S$,X,1)): IF S < 32 OR S > 94 THEN 8120
8100 S = S - 31
8110  DRAW S AT (X + H - 2) * 7,6 + (V - 1) * 8
8120  NEXT X
8130  NEXT I
8140  RETURN
9000  HOME
9010  PRINT : PRINT  TAB( 14);"ALTERATIONS MENU "
9020  PRINT : PRINT
9030  PRINT "  You now have a choice of the following"
9040  PRINT : PRINT
9050  PRINT  TAB( 8);"1.Displaying the current simplex matrix.
"
9060  PRINT : PRINT
9070  PRINT  TAB( 8);"2.Altering one of the verticies' RESPONS
     E FACTORS."
9080  PRINT : PRINT
9090  PRINT  TAB( 8);"3.Altering the value of any variable wit
     hin a given vertex."
9100  PRINT : PRINT
9110  PRINT  TAB( 8);"4.Return to the main menu."
9120  PRINT : PRINT  SPC( 55)
9130  INVERSE
9140  PRINT "Input your choice ?";
9150  NORMAL
```

```
9160  GET CNUM
9170  IF CNUM < 1 OR CNUM > 4 GOTO 9000
9180  IF CNUM = 4 THEN  RETURN
9190  ON CNUM GOSUB 2110,9200,9500
9195  GOTO 9000
9200  HOME
9210  PRINT : INPUT " Input the vertex number which is to be c
     hanged ?";CNUM
9220  PRINT : PRINT "The RESPONSE FACTOR for vertex";CNUM;" is
      ";HOLD(NB + 2,CNUM + 1)
9230  PRINT : PRINT "Please type in the new RESPONSE FACTOR fo
     r this vertex."
9240  FOR I = 2 TO NB + 2
9250  IF SIMP(1,I) = CNUM GOTO 9270
9260  NEXT I
9270  INPUT SIMP(I,NB + 2)
9280 HOLD(NB + 2,CNUM + 1) = SIMP(I,NB + 2)
9300  RETURN
9500  HOME
9510  PRINT : INPUT " Input the vertex number which is to be c
     hanged ?";CNUM
9520  FOR I = 2 TO NB + 2
9530  IF SIMP(1,I) = CNUM GOTO 9560
9540  NEXT I
9550  PRINT " That vertex is not within the current simplex ma
     trix"
9551  PRINT : PRINT " Press any key to return to the menu"
9552  GET B$
9553  RETURN
9560  HOME
9570  PRINT : PRINT " Input the number of variable whos' value
      you wish to alter in this vertex"
9580  PRINT : INPUT CNUM
9590  HOME : PRINT " The current value of that variable in ver
     tex ";SIMP(1,I);" is ";SIMP(CNUM + 1,I)
9600  PRINT : PRINT " Please input the new value you wish this
      variable to have in this vertex"
9610  INPUT SIMP(CNUM + 1,I)
9620  PRINT : PRINT " The change has been made,press any key t
     o return to the alterations menu";
9630  GET B$
9640  RETURN

]
```

Appendix 3 Z80 assembler routines for the S35 Plasmakon.

```
        .Z80
;                          INITIALISE INTERFACE
        ENTRY TRIT
TRIT:
        LD    C,X'D0'
        SET   1,C
;                          SAVE REGISTERS
        PUSH  AF
;                          PROGRAM PORT A1
        XOR   A
        OUT   (C),A
        OUT   (C),A
        LD    A,X'0F'
        OUT   (C),A
        LD    A,X'0F'
        OUT   (C),A
;                          PROGRAM PORT A2
        LD    C,X'D1'
        SET   1,C
        LD    A,X'0F'
        OUT   (C),A
        LD    A,X'07'
        OUT   (C),A
;                          PROGRAM PORT B1
        LD    C,X'D4'
        SET   1,C
        LD    A,X'0F'
        OUT   (C),A
        LD    A,X'07'
        OUT   (C),A
;                          PROGRAM PORT B2
        LD    C,X'D5'
        SET   1,C
        LD    A,X'0F'
        OUT   (C),A
        LD    A,X'07'
        OUT   (C),A
;                          RECOVER REGISTERS AND RETURN
        POP   AF
        RET
;
        END
;
;
;
;
;CALL PIOWR(ICHA,OUT)      WRITE OUT TO ADDRESS ICHA
;
        ENTRY PIOWR
PIOWR:
        LD    A,(DE)
        LD    C,(HL)
        RES   1,C
        OUT   (C),A
        RET
;                          RETURN TO CALLING CODE
        END
```

Appendix 4 Main simplex routine for the S35 Plasmakon

```
C
C
C
      SUBROUTINE SIML
C
C     SIMPLEX OPTIMISATION ROUTINE DEDICATED TO THE KONTRON S35 PLASMAKON
C
      BYTE INN,FLOR,FLAGE,NA
C
      INTEGER HN,DEST
      REAL OLD(5),LAVE
C
      DIMENSION INTL(5),ISTP(5),NGST(3)
C
      COMMON /SPVS$$/BMIN(5),BMAX(5),SET(8,7),CALS(7;7)
     *       /MESS$$/EL(2),NRE,FLAGAU,WVL,WIN(3),TIM,PKI,PKS,
     *              BGI,BGS,CON,BG,STD,CS(2,5),NCS,QUMO,BGKO,
     *              FAK,INTS,FSTO,NRVO,CNR,NRPR,PHI,CMNT(16),BGLR
     *       /COM2$$/INN,IREC,IANF,IEND,FLAGE,IRECA
C
C
      DATA OLD/50.0,50.0,5.0,50.0,0.0/
C
      CALL CLGR
C
      WRITE(1,1)
1     FORMAT(' THE WAVELENGTH OF BOTH THE PEAK AND THE BACKGROUND-LOW
     * POSITIONS USED FOR THIS OPTIMISATION MUST HAVE BEEN PREVIOUSLY
     * SELECTED'/)
C
      WRITE(1,2)
2     FORMAT(//' HAVE THESE WAVELENGTHS BEEN SELECTED Y OR N ?')
      CALL KEYIN(INN)
      IF(INN.EQ.78) GOTO 1000
C
      CALL NUP(P)
C
C     USE DATA TO CONSTRUCT THE INITIAL SIMPLEX SET
C      AND USE RNGCK TO SET BOUNDARY LIMITS
C
C
C
      DO 10 J=1,5
      SET(1,J)=J
      SET(1,6)=6.0
      B=(SET(J+1,7)-SET(J+1,1))/(J*(2**0.5)
      DO 5 N=2,6
      SET(J+1,N)=SET(J+1,1)+B*((J+1.0)**0.5-1.0)
5     CONTINUE
      SET(J+1,J+1)=SET(J+1,1)+B*((J+1.0)**0.5+J-1.0)
10    CONTINUE
C
C     SET UP INITIAL SIMPLEX VERTICIES AND EVALUATE S/B'S
C
      DO 50 N=1,6
C
      DO 15 J=1,3
      DEST=J
      CALL RAMP(DEST,OLD(J),SET(J+1,N))
      OLD(J)=SET(J+1,N)
15    CONTINUE
      DEST=4
```

```
        CALL RAMP(DEST,OLD(4),SET(5,N))
        OLD(4)=SET(5,N)
C
C       CHANGE VIEWING HEIGHT
C
        A=SET(6,N)/10.0
        NA=PHI(A)
        SET(6,N)=CENTI(NA)
        CALL MIRROR(NA)
C
        WRITE(1,17)
17      FORMAT(/' GOT PAST MOVING MIRROR')
C
C       EVALUATE S/B
C
        RESP=0.0
        CALL EVAL(RESP)
C
        WRITE(1,20) RESP
20      FORMAT(/' RESPONSE =',F10.5)
        SET(7,N)=RESP
C
50      CONTINUE
C
C       IDENTIFY WORST AND CALCULATE CENTROID AND HENCE REFLECTION VERTEX
C
100     NT=1
        TEMP=10000
        DO 180 L=1,6
        IF((NN.EQ.5.OR.NN.EQ.4).AND.L.EQ.HN)GOTO 180
        IF(TEMP.LT.SET(7,L))GOTO 180
        TEMP=SET(7,L)
        NT=L
180     CONTINUE
C
C       CALCULATE NEW VERTEX
C
C       CLEAR CAL
C
        DO 190 J=1,7
        CALS(J,1)=0.0
190     CONTINUE
C
        DO 250 J=1,5
        DO 200 K=1,6
        IF(K.EQ.NT)GOTO 200
        CALS(J,1)=CALS(J,1)+SET(J+1,K)/5.0
200     CONTINUE
        CALS(J,2)=CALS(J,1)-SET(J+1,NT)
        CALS(J,3)=CALS(J,1)+CALS(J,2)
        SET(J,7)=CALS(J,3)
250     CONTINUE
C
C       CHECK FOR OUT OF BOUNDARY ERRORS
C
        FLOR=0
        CALL RNGCK(FLOR)
        IF(FLOR.EQ.1)JT=7
        IF(FLOR.EQ.1)GOTO300

C
C
```

```
C       READ NEW RESPONSE AND CALCULATE CW,CR OR E AS REQUIRED
C
C
        DO 255 M=1,4
        DEST=M
        CALL RAMP(DEST,OLD(M),CALS(M,3))
        OLD(M)=CALS(M,3)
255     CONTINUE
C
C       ALTER VIEWING HEIGHT
C
        A=CALS(5,3)/10
        NA=PHI(A)
        CALL MIRROR(NA)
C
        RESP=0.0
        CALL EVAL(RESP)
        CALS(6,3)=RESP
        WRITE(1,260) CALS(6,3)
260     FORMAT(/' REFLECTION RESPONSE = ',F10.5)
C
C       IDENTIFY QUALITY OF NEW VERTEX
C
        JT=1
        DO 300 M=1,6
C
C       UPDATE NUMBER OF TIMES HELD FOR OLD VERTICES
        SET(8,M)=SET(8,M)+1
C
        IF(CALS(6,3).GT.SET(7,M))GOTO300
        JT=JT+1
300     CONTINUE
        NN=3
        GOTO ( 500,600,600,600,600,400,320),JT
320     CONTINUE
C
C       CALCULATE CW
C
        DO 350 M=1,5
        CALS(M,5)=CALS(M,1)-0.5*CALS(M,2)
        DEST=M
        IF(M.EQ.5)GOTO350
        CALL RAMP(DEST,OLD(M),CALS(M,5))
        OLD(M)=CALS(M,5)
350     CONTINUE
        A=CALS(5,5)/10.0
        NA=PHI(A)
        CALL MIRROR(NA)
        RESP=0.0
        CALL EVAL(RESP)
        HN=NT
        NN=5
        GOTO 600
C
C       CALCULATE CR
C
        DO 450 M=1,5
        CALS(M,4)=CALS(M,1)+0.5*CALS(M,2)
        DEST=M
        IF(M.EQ.5)GOTO450
        CALL RAMP(DEST,OLD(M),CALS(M,4))
```

```
        OLD(M)=CALS(M,4)
450     CONTINUE
        A=CALS(5,4)/10.0
        NA=PHI(A)
        CALL MIRROR(NA)
        RESP=0.0
        CALL EVAL(RESP)
        HN=NT
        NN=4
        GOTO 600
C
C       CALCULATE E
C
        DO 550 M=1,5
        CALS(M,6)=CALS(M,3)+CALS(M,2)
        DEST=M
        IF(M.EQ.5)GOTO450
        CALL RAMP(DEST,OLD(M),CALS(M,6))
        OLD(M)=CALS(M,6)
550     CONTINUE
        A=CALS(5,6)/10.0
        NA=PHI(A)
        CALL MIRROR(NA)
        RESP=0.0
        CALL EVAL(RESP)
        HN=NT
        IF(RESP.GT.CALS(6,3)) NN=6
        GOTO 600
C
C       EXCHANGE NEW VERTEX FOR WORST VERTEX
C       AND WRITE REJECTED VERTEX TO PRINTER
C
600     CONTINUE
        WRITE(2,610)(SET(M,NT),M=1,7)
610     FORMAT(/,7(2X,F10.5))
C
        DO 650 M=1,7
        SET(M,NT)=CALS(M,NN)
650     CONTINUE
C
C       HAS END POINT BEEN REACHED?
C
        AVE=0.0
        DO 700 M=1,6
        AVE=AVE+(SET(7,M)/6.0)
700     CONTINUE
        LAVE=AVE-(AVE*P)/100.0
        HAVE=AVE+(AVE*P)/100.0
        FLOP=0
        DO 710 M=1,6
        IF(SET(7,M).LT.LAVE.OR.SET(7,M).GT.HAVE) FLOP=1
710     CONTINUE
        IF(FLOP.NE.0) GOTO50
C
        WRITE(1,750)
750     FORMAT(' OPTIMUM HAS BEEN OBTAINED')
C
1000    CONTINUE
        CALL CLGR
        RETURN
        END
```

Appendix 5 Simplex FORTRAN Routine NUP

```
B>TYPE NUP.FOR
C
        SUBROUTINE NUP(PRE)
C
        BYTE INN,ICHA
C
        REAL IMIN(5),IMAX(5)
C
        COMMON /SPVS$$/AMIN(5),AMAX(5),SET(8,7)
C
        DATA IMIN/0.0,0.0,0.0,0.0,0.0/
     *  IMAX/999.0,999.0,999.0,999.0,60.0/
C
C   INITIALISE BOARD D
C
        CALL TRIT
C
C   SET INITIAL POWER LEVEL FOR TRANSFER TO COMPUTER CONTROL
C
        ICHA=X'D0'
        NOUT=60
        CALL PIOWR(ICHA,NOUT)
C
C   SET COOLANT GAS FLOW
C
        ICHA=X'D1'
        NOUT=50
        CALL PIOWR(ICHA,NOUT)
C
C   SET AUX GAS FLOW
C
        ICHA=X'D4'
        NOUT=50
        CALL PIOWR(ICHA,NOUT)
C
C   SET INJ GAS FLOW
C
        ICHA=X'D5'
        NOUT=5
        CALL PIOWR(ICHA,NOUT)
C
C       END OF BOARD SETUP
C       ENTER PRECISION
        WRITE(1,2)
2       FORMAT(/,' Enter the % precision you require of the optimum')
        READ(1,4)PRE
4       FORMAT(F5.2)
C       SET UP SIMPLEX RANGE
C
10      WRITE(1,20)
20      FORMAT(' Do you wish to  1. enter boundary conditions or '/)
        WRITE(1,30)
30      FORMAT(' 2. allow the full range of each variable '/)
        CALL KEYIW(INN)
        IF(INN.EQ.50)GOTO 200
        IF(INN.NE.49)GOTO 10
C
40      CONTINUE
```

```
      WRITE(1,50)
50    FORMAT(' Please enter power range as integer pot settings')
      WRITE(1,52)
52    FORMAT(/' Enter minimum power  *NOTE minimum level 300 ')
      READ(1,190)SET(6,1)
      AMIN(4)=SET(6,1)
      WRITE(1,54)
54    FORMAT(/' Enter maximum power ')
      READ(1,190)SET(6,7)
      AMAX(4)=SET(6,7)
C
C     GAS FLOWS
C
      WRITE(1,60)
60    FORMAT(/' Now enter the gas flow ranges')
      WRITE(1,62)
62    FORMAT(/' Minimum coolant  *NOTE minimum level 300 ')
      READ(1,190)SET(2,1)
      AMIN(1)=SET(2,1)
      WRITE(1,64)
64    FORMAT(/' Maximum coolant ')
      READ(1,190)SET(2,7)
      AMAX(1)=SET(2,7)
      WRITE(1,66)
66    FORMAT(/' Minimum plasma ')
      READ(1,190)SET(3,1)
      AMIN(2)=SET(3,1)
      WRITE(1,68)
68    FORMAT(/' Maximum plasma ')
      READ(1,190)SET(3,7)
      AMAX(2)=SET(3,7)
      WRITE(1,70)
70    FORMAT(/' Minimum injector ')
      READ(1,190)SET(4,1)
      AMIN(3)=SET(4,1)
      WRITE(1,72)
72    FORMAT(/' Maximum injector ')
      READ(1,190)SET(4,7)
      AMAX(3)=SET(4,7)
      WRITE(1,74)
74    FORMAT(//' Now enter the viewing height in millimeters')
      WRITE(1,76)
76    FORMAT(/' Minimum viewing height ')
      READ(1,190)SET(6,1)
      AMIN(5)=SET(6,1)
      WRITE(1,78)
78    FORMAT(/' Maximum viewing height ')
      READ(1,190)SET(6,7)
      AMAX(5)=SET(6,7)
```

```
79      WRITE(1,80)
80      FORMAT(//' Is the information correct? ')
        CALL KEYIW(INN)
        IF(INN.EQ.78) GOTO 10
        IF(INN.NE.89) GOTO 79
C
190     FORMAT( F6.1)
C
        GOTO 310
C
200     CONTINUE
        DO 300 J=1,5
        AMIN(J)=IMIN(J)
        AMAX(J)=IMAX(J)
        SET(J+1,1)=IMIN(J)
        SET(J+1,7)=IMAX(J)
300     CONTINUE
310     CONTINUE
        RETURN
        END
```

Appendix 6 Simplex FORTRAN Routine RAMP

```
C
       SUBROUTINE RAMP(DEST,VOLD,VNEW)
C
       INTEGER DEST
C
       WRITE(1,1)
1      FORMAT(' THE START OF RAMP')
C
       IF(DEST.EQ.1)ICHA=X'D1'
       IF(DEST.EQ.2)ICHA=X'D4'
       IF(DEST.EQ.3)ICHA=X'D5'
       IF(DEST.EQ.4)ICHA=X'D0'
C
       IF(DEST.LT.1.OR.DEST.GT.4)RETURN
C
       NWT=50
       WRITE(1,5)VOLD,VNEW
5      FORMAT(2X,F6.2,2X,F6.2)
       IF((VOLD-VNEW).LT.1.AND.(VNEW-VOLD).LT.1) GOTO 30
       IF(VOLD.EQ.0.0)VOLD=VOLD+1.0
       IF(VNEW.EQ.0.0)VNEW=VNEW+1.0
       K=-4
       IF(VOLD.LE.VNEW)K=4
       JO=VOLD
       JN=VNEW
       DO 10 I=JO,JN,K
       N=I/4
       CALL PIOWR(ICHA,N)
10     CONTINUE
       WRITE(1,20)
20     FORMAT(' END OF RAMP')
30     CONTINUE
       RETURN
       END
```

Appendix 7 Simplex FORTRAN Routine EVAL

```
B) TYPE EVAL.FOR
C
C       SUBROUTINE TO COLLECT PEAK AND BG INTENSITY TO EVALUATE A VERTEX
C
        SUBROUTINE EVAL(ARSP)
C
        BYTE CURS, INV, MESS(128), CNR
C
C
        COMMON  /SPVS$$/CMIN(5), CMAX(5), SET(8,7)
     *          /PIOA$$/PIOA(4), PIOB(4), IEOS
     *          /PIOS$$/PREC
     *          /NCNR$$/NCNR(8), COUNT
     *          /MESP$$/ISYM, MP(128,1)
     *          /MESS$$/EL(2), NRE, FLAGAU, WVL, WIN(3), TIM, PKI, PKS,
     *                  BGI, BGS, CON, BG, STD, CS(2,5), NCS, QUMO, BGKO,
     *                  FAK, INTS, FSTO, NRVO, CNR, NRPR, PHI, CMNT(16), BGLR
     *          /CURS$$/CURS(8)
     *          /DRIV$$/SZEIL1, SZEIL2
     *          /MONI$$/ALGR
     *          /COM2$$/INN, IREC, IANF, IEND, FLAGE
     *          /COMD$$/LU, KNR
C
C
        WRITE(1,10)
10      FORMAT(' THE START OF EVAL')
C
        RES=0
C
        ALGR=.TRUE.
        LPROC=6
        CALL QUANTI(LPROC, RES)
C
        WRITE(1,12) RES
12      FORMAT( F8.3)
        ARSP=RES
C
        CALL SWAL$(ALGR)
C
        WRITE(1,20)
20      FORMAT(' THE END OF EVAL')
        RETURN
        END
```

Appendix 8 Simplex FORTRAN Routine RNGCK

```
B) TYPE RNGCK.FOR
C         ROUTINE TO CHECK THAT NEW VERTICIES ARE WITHIN WORKING LIMIT
C
          SUBROUTINE RNGCK(FLOR)
C
          BYTE FLOR, I
C
          COMMON /SPVS$$/DMIN(5),DMAX(5),SET(8,7)
          WRITE(1,1)
1         FORMAT(' THE START OF RNGCK')
C
          FLOR=0
          DO 100 I=1,5
          IF(SET(I+1,7).LT.DMIN(I))FLOR=1
          IF(SET(I+1,7).GT.DMAX(I))FLOR=1
100       CONTINUE
          WRITE(1,110)
110       FORMAT(' THE END OF RNGCK')
          RETURN
          END
C
          SUBROUTINE DELSEC(N)
          DO 10 I=1,N
          DO 10 J=1,10000
          NC=10
10        CALL DELAY(NC)
          RETURN
          END
```