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FIELD SAMPLING AND MICROCOLUMN PRECONCENTRATION TECHNIQUES IN INDUCTIVELY COUPLED PLASMA SPECTROMETRY

presented by

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ABSTRACT

Thesis Title:
Field Sampling and Microcolumn Preconcentration Techniques in Inductively Coupled Plasma Spectrometry

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This thesis is concerned with analytical studies on the trace analytes barium, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, vanadium and zinc, present in high purity and highly complex matrices. The technique utilises activated alumina microcolumns in a flow injection (FI) system, to perform analyte enrichment and matrix removal. The analytes, after retention on the microcolumn are subsequently eluted and quantified by inductively coupled plasma-emission spectrometry (ICP-ES).

Initial studies focus on trace analytes in caesium iodide, however a selection of the alkali metal salts, lithium nitrate, potassium bromide, sodium fluoride and sodium chloride, are investigated. New methodology for the ultratrace determination of high purity alkali metal salts is thus provided. The microcolumn enrichment technique with ICP-ES detection is robust, utilises limited sample handling and simultaneously preconcentrates and separates the analytes from matrix components. Hence possible matrix interferences are eliminated and limits of detection are significantly improved, in comparison to conventional ICP-ES analysis.

A technique for the determination of the total content of eleven trace analytes present in natural waters (mineral, reservoir), using microcolumns of activated alumina in a FI-ICP-ES is investigated. The use of the complexing agent tartaric acid is shown to be effective in improving analyte retention. The procedure is successfully applied to determination of these analytes in a certified river water reference material (SLRS-1). Due to low retention and elution efficiencies, the total content of the analytes Fe and V present in Buxton, Redmires and Langsett samples could not be accurately determined by this technique.

Activated alumina microcolumns are utilised as a new field sampling tools. Samples are collected in the field and processed through the alumina microcolumns for the effective retention of desired analytes. Hence, an alumina microcolumn sampling stage to effect concentration and isolation prior to analytical measurement is at the core of the investigation. The overall aim is to extend the application of alumina microcolumns, and in particular to provide a new multi-element field sampling device, which gives high sample integrity and preconcentration.

CONTENTS

1 Introduction

1.1 Principles of Emission Spectrometry

In the late 1860's Bunsen and Kirchhoff (1, 2) added salts and their solutions to flames and studied the spectra produced. They observed the characteristic spectral line emissions of a number of elements, and also noted that substances absorb energy most strongly at the same wavelengths at which emission occurs. These results led to Kirchhoff's Law which states "the power of emission is equal to the power of absorption for all bodies which are in temperature equilibrium with their radiations". This law summarises the basis for modern atomic emission and atomic absorption spectrometry.

During the late 1800's, spectra were classified by element, wavelength, line intensity and by series, which were dependent upon line characteristics. Four series, known as Sharp, Principal, Diffuse and Fundamental were described for the alkaline metals. This terminology is retained in modern spectroscopic notation, in that different atomic energy levels are identified by S, P, D and F.

Grotrian developed a graphical method for presenting atomic energy levels and electronic transitions in 1928 (3). The diagrams are still utilised today and permit the representation of spectral terms and transitions as shown in Fig.1.1 for potassium. The vertical axis is an energy axis and the energy levels are indicated as horizontal lines. A spectral emission line results from a transition from a higher energy level to a lower one. The vertical distance representing a transition is a measure of the energy of the transition. When an atom is excited by absorbing light or by collision with excited electrons, ions, or molecules, it normally only remains in this excited state for approximately 10^{-9} s, before it loses all or part of its excitation energy by collisions or emitting a photon.

In emission spectrometry a fine aerosol of the sample solution following nebulisation, is introduced into the flame or plasma, where it is desolvated, vaporised, atomised and ionised. Subsequently, atoms or ions are raised to an excited electronic state. Upon their return to a lower or ground state, the atoms or ions emit radiation which is characteristic. The emitted radiation passes to a detector which isolates the characteristic spectral line of the atom or ion.

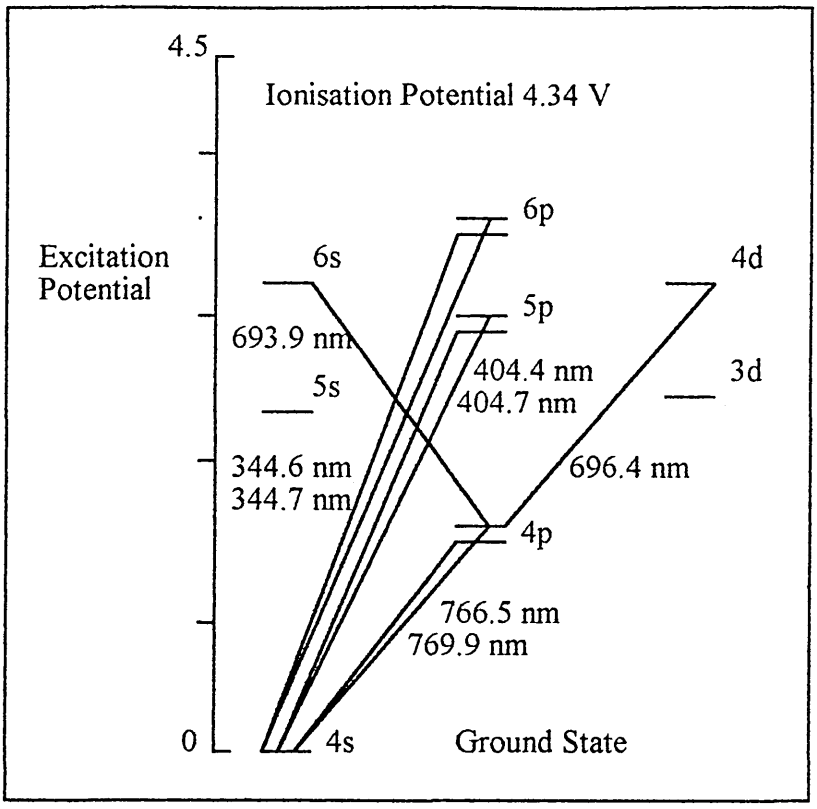


Fig. 1.1 Grotrian Diagram for Potassium

The intensity of a spectral line emission, I_v, is determined by the number of atoms or ions whose identical transitions occur simultaneously. It is given by the expression:

$$I_V = (A_T \, h\nu_0 \, N_0 \, g_u / B(T)) \; e^{-Eu / kT}$$

where A_T is the number of excited atoms undergoing transition, N_o is the number of atoms in the ground state, g_u is the statistical weight of the excited atomic state, B(T) is the partition function, E_u is the energy of the excited state, k is the Boltzmann constant and T is the absolute temperature.

It can be seen from the above equation that the intensity of atomic emission is critically dependent upon temperature. It also follows that when the light path is through an optically thin medium and self-absorption is negligible, a linear relationship between emission intensity and concentration is achieved. However as the concentration of atoms

in the centre of the discharge increases, the possibility of self-absorption increases. Self-absorption occurs when photons emitted by excited atoms are absorbed by atoms in the ground state in the cooler, outer region of the discharge. The self-absorption effect contributes to the characteristic curvature of atomic emission calibration graphs (see Fig. 1.2).

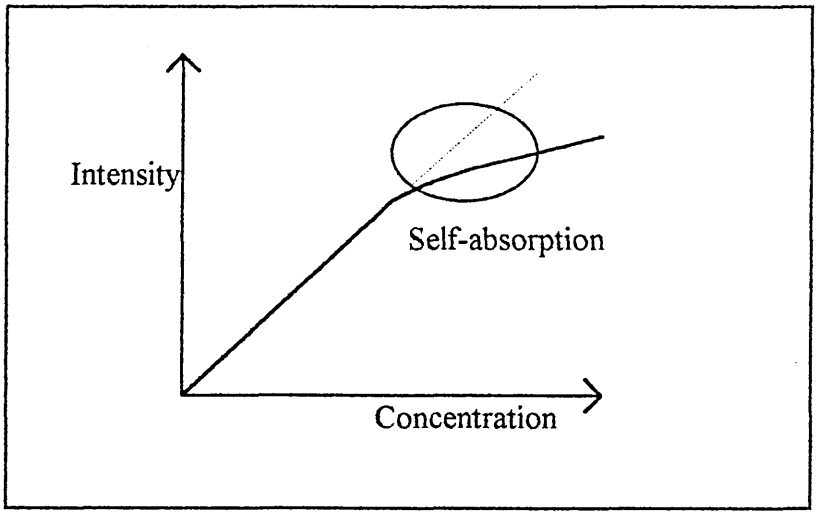


Fig. 1.2 A Characteristic Atomic Emission Calibration Graph

1.2 Excitation Sources for Emission Spectrometry

Excitation sources for analytical atomic emission spectrometry must achieve the following processes:

- the sample must be vaporised
- the sample must be dissociated into its constituent atoms or ions
- electrons in the atoms or ions must be excited to energy levels above the ground state

The energy required for excitation may be implemented by one of several methods, including flames (4), discharge tubes, such as the glow discharge lamp (5) and the hollow cathode lamp (6), electric arcs and sparks (7, 8), and plasmas, including the Direct Current Plasma (DCP) (9, 10), the Microwave Induced Plasma (MIP) (11) and the Inductively Coupled Plasma (ICP) (12). The excitation source used in this thesis is the Inductively Coupled Plasma (ICP), which has been discussed in detail in section 1.3. The ICP was selected as it has been extensively applied to the analysis of solutions, it has

a simultaneous multi-element analysis capability, a wide dynamic range, it can attain low limits of detection and it is relatively free from interferences.

1.3 Inductively Coupled Plasma - Emission Spectrometry

1.3.1 Development of Inductively Coupled Plasma - Emission Spectrometry

In 1961, Reed described the use of the first inductively coupled plasma (ICP), operating at atmospheric pressure. The technique was used for growing crystals of refractory oxides, under high temperature conditions (13). However, it was the work reported later by Greenfield *et al.* in 1964 (14) and Wendt and Fassel in 1965 (15), which established the ICP as a new spectroscopic source. The analytical potential of the technique had been realised.

Greenfield *et al.* used a 2.5kW dielectric-heating generator operating at 36MHz, to produce an argon plasma. This system was proposed to have a high degree of stability, the ability to overcome depressive interference effects, caused by the formation of stable compounds and increased sensitivity of detection. Briefly, the operating principle of this source, involved the heating of a stream of ionised argon gas by induction. The gas was contained in a circular quartz tube, which was surrounded by a coil carrying high frequency alternating electric current. The plasma had to be externally initiated, as cold gas is not ionised and hence not an electrical conductor. Therefore, initiation was achieved by holding a carbon rod in the mouth of the quartz tube. The high frequency field heated the rod, which in turn heated and ionised the argon gas. The carbon rod was removed once the main discharge had begun. The ionised gas plasma emerged at the mouth of the tube as a 'flame'. This was due to the gas stream transporting it down the tube, away from the coil. The discharge was maintained by recycling a portion of the ionised gas, which was accomplished by creating a vortex. The vortex was produced by feeding gas tangentially into the tube. Hence, some of the ionised gas moved back down the tube, in the opposing direction to the main gas flow, due to a partial reduction in pressure created at the centre of the vortex. A secondary stream of argon gas was passed over the quartz tube to cool it. For quantitative analysis

using this system, the sample was introduced as an aerosol into the plasma. The plasma was 1.25 inches long, 0.75 inches in diameter and annular in form, in that it had a hole or low temperature region in its centre. The sample was injected into this region. The tail-flame was produced downstream of the main plasma, was roughly aligned and used as the spectroscopic source.

Wendt and Fassel used a 5 kW, 3.4 MHz generator and a laminar flow of argon gas to produce a plasma. In this considerably different design, re-circulation of the ionised gas was not employed. Hence, this possessed distinct advantages in comparison to the vortex flow configuration. Firstly, a laminar flow had less turbulence than a vortex flow, hence increased stability of the discharge was obtained. Secondly, the laminar coolant flow mixed only slightly with the hot vapours in the core of the discharge. Therefore, the coolant tube remained clean and in use for several months. The addition of aerosols of solutions or powders to tangential flow, caused decreased transmittance of the coolant tube and also devitrification of the quartz. An ultrasonic atomising system was used to produce an aerosol of the sample, which allowed the introduction of virtually any concentration of solution into the ICP.

In subsequent work, Greenfield *et al.* (16) used different injector gases including oxygen, nitrogen and air, and later reported results for the determination of aluminium and phosphorous in a sample of rock. Inductively coupled plasma - emission spectrometry was therefore established as a viable analytical technique, by the end of the 1960's, and numerous publications addressing practical analytical applications of the method were available. In 1969, Dickinson and Fassel (17) presented data, indicating that the ICP system compared favourably with alternative techniques such as flame atomic absorption spectrometry. In fact, striking improvements in detection limits were achieved through effective optimisation of operating conditions.

In the early 1970's, several advances were made in the field. Kirbright *et al.* (18) determined sulphur at 182.04 nm and phosphorus at 214.91 nm, with the use of a nitrogen purged path between the monochromator detector and the plasma. The work was later extended to the determination of iodine, arsenic, selenium and mercury. Scott

et al. (19) described a compact ICP system, and also replaced the elaborate ultrasonic nebulisation method, with pneumatic nebulisation. In 1976, Greenfield *et al.* (20) described an ICP system, coupled to a 30 channel direct reading spectrometer. This system had a simultaneous multi-element capability, automated sample introduction and had been used for routine analysis for a number of years.

However, the most important development for ICP spectrometry, came with the advent of commercially available complete ICP systems. Before the mid 1970's, home made torches and generators attached to single channel monochromators, had been developed and utilised. Unfortunately this failed to take advantage of the most powerful advantage of ICP spectrometry, its simultaneous multi-element capability. Manufacturers of polychromator direct reading spectrometers realised the potential of the technique and several systems were introduced. Improvements were made from increasing familiarity with ICP characteristics. Recently, greater computer sophistication has aided instrument management and improved data handling and presentation. Another important development was the introduction of scanning monochromator and combined simultaneous/sequential ICP systems.

1.3.2 Principles of Inductively Coupled Plasma - Emission Spectrometry

ICP-ES systems are made up of major component parts and these are identified as (see Fig.1.3) :

- the sample introduction system
- the ICP torch
- the high frequency generator
- the transfer optics and spectrometer
- the interface and computer

In basic operation (21), sample is introduced into the high temperature plasma as aerosol mist, *via* pneumatic nebulisation. The ICP source is formed at the mouth of the torch, by the coupling of a flowing stream of ionised argon gas and a powerful radiofrequency field. The analytes in the sample undergo various processes, including

desolvation, decomposition, atomisation, excitation and ionisation. The atomic and ionic radiation emissions characteristic of each analyte are received by the spectrometer and the signals are processed by computer. These principles will be discussed in more detail.

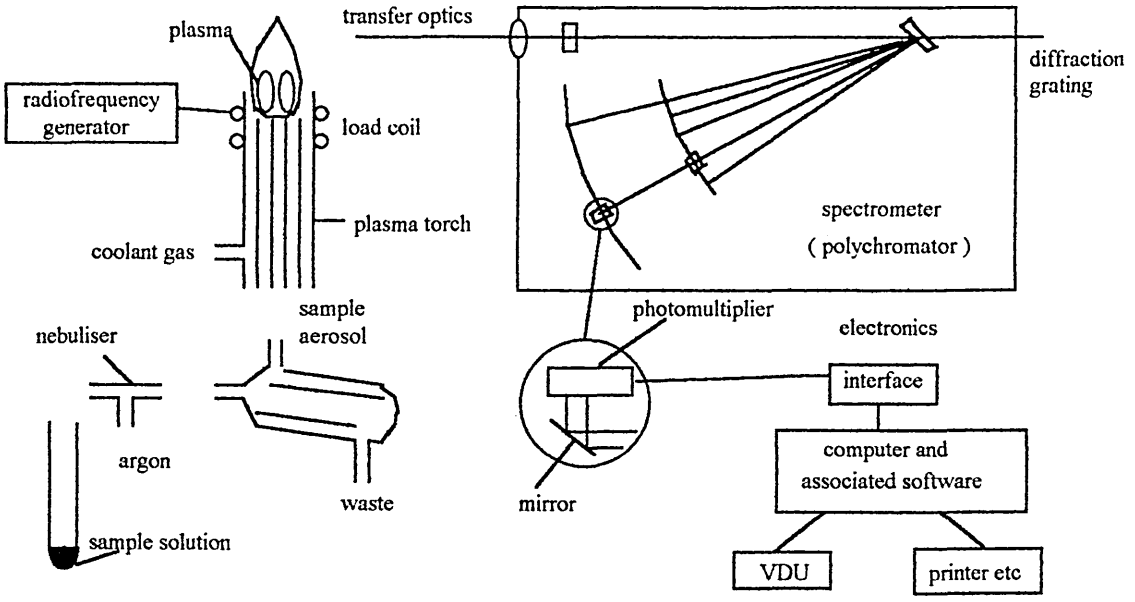


Fig.1.3 Schematic diagram of a simultaneous ICP-ES system

For ICP analysis, the sample must first be introduced into the ICP torch. The usual method is *via* liquid sampling, but solid and gaseous sampling are possible. Sample introduction is achieved *via* the production of a fine aerosol mist of droplets, from the bulk liquid. The pneumatic nebuliser is the most widely used piece of apparatus for sample introduction, and can be cross flow or concentric in configuration, (see section 1.3.3.1). Effective aerosol production requires very high gas velocities, and as a consequence of this, fine capillary tubes. For efficient transport to the plasma, the nebuliser should theoretically generate droplets less than 10 μm in diameter. However, in practice, larger droplets are also generated, and these have to be removed. A critical factor in the precision or reproducibility achieved in ICP analysis, is the nebuliser gas flow velocity, which should remain constant. A device such as a mass flow controller can be employed to stabilise the gas flow velocity. Other devices are also available. In addition to the nebuliser, the other component required for sample introduction is the

spray chamber (see section 1.3.3.2), the purpose of which is to remove large droplets from the aerosol before they reach the plasma. This is usually achieved with a form of impactor bead, which removes large droplets and may aid in creating small droplets. The spray chamber incorporates a drainage system, which removes solution that is not transported to the plasma. It is aligned to ensure that fluctuation in pressure is maintained at a minimum. This is important as slight changes in pressure can affect the emission signal. The transport efficiency of the sample introduction system, that is the proportion of sample which reaches the plasma in relation to that aspirated, is generally less than 1-3 %. In comparison, AAS sample introduction systems have transport efficiencies of 10 % and have shorter signal stabilisation times. Peristaltic pumps are often utilised to regulate the sample flow rate. They are employed to limit the problems associated with viscosity variations in samples and to maintain the pressure in the spray chamber.

Following the introduction of the sample into the ICP system, the next consideration is the sample excitation system. A gas in which atoms are present in an ionised state, is known as a plasma. A large proportion of the atoms in the gas must be ionised for it to be conducting, which is essential for the plasma to be maintained by induction. If an induction coil has a high frequency current flowing in it, a varying magnetic field is created within the coil. Then, if charged particles such as ionised gas flow through this induction coil, the lines of magnetic force will be cut and ohmic or Joule heating is produced. Hence, the interaction between flowing ionised argon gas and an oscillating magnetic field, is known as inductive coupling and creates the ICP discharge. A Tesla spark is used to start the electrical conductivity in the gas, as it flows through the coil. Inductive heating of the flowing gas then sustains the plasma. It is maintained at temperatures between 6000 and 10,000 K. The generator supplies the high frequency current at the induction coil, which is it's' primary function (see section 1.3.3.3). The sample aerosol is transported to the ICP torch, which consists of three accurately aligned concentric quartz tubes (see 1.3.3.4). The outermost tube is encircled by a two turn copper induction coil, which is water cooled. A magnetic field is induced

within this coil, by a radio frequency alternating current and argon gas flows through the torch. The three argon gas flows through the torch are:

- The outermost or coolant gas flow. It flows at a rate between 10-20 l min^{-1}, forms the bulk of the plasma and prevents overheating of the torch.
- The innermost, injector or nebuliser gas flow. It flows at a rate of 1 l min^{-1} and its function is to transport the sample aerosol to the plasma. This gas punctures the flattened base of the plasma, creating a central axial channel through the high temperature discharge.
- The intermediate or auxiliary gas flow. It flows at a rate between 0-1 l min^{-1} and may be used to lift the plasma in relation to the torch. It aids in the prevention of salt build up on the injector tube and is used when organic solvents are nebulised.

The region of the plasma used for spectroscopic observations and determinations is known as the tail-flame. It is the cooler region above the plasma. Usually, a 4 mm vertical window, 12-20 mm above the load coil is used. The radio frequency generators generally operate in the frequency range 27-56 MHz with power input between 1-1.5 kW.

The ICP is a unique method of heating the sample and there are benefits associated with its configuration and very high temperature. These include minimal self-absorption effects. Emission spectrometry functions on the basis that, atoms or ions from the sample are heated by the source, into an energised state. As these atoms or ions revert to a lower energy state, a photon of energy is emitted. It is assumed that the energy emitted is proportional to the concentration of atoms or ions in the sample. However, if some of the emitted photons are absorbed by excited atoms or ions from the sample, energy emitted and concentration will not be proportional. This is known as the self-absorption effect. The ICP is successful in eluding self-absorption effects and linear calibration graphs are produced over a very wide range of concentrations.

The sample, introduced through the base of the plasma, travels along the central channel. The temperature is cooler in this channel in relation to the surrounding plasma, but is sufficient to volatilise and atomise the sample. The temperature profile within the

plasma is shown in Fig.1.4. The profile resembles other high temperature sources in the tail-flame of the plasma only, at a point above the load coil. The technique is therefore reputed not only to have a linear dynamic range over 4-5 orders of magnitude, but has good sensitivity and is relatively free from interferences, (see section 1.3.4). The high temperature of the source provides the relative freedom from chemical interferences. The efficiency of the plasma for exciting atoms and ions, coupled with low background levels, results in good sensitivity.

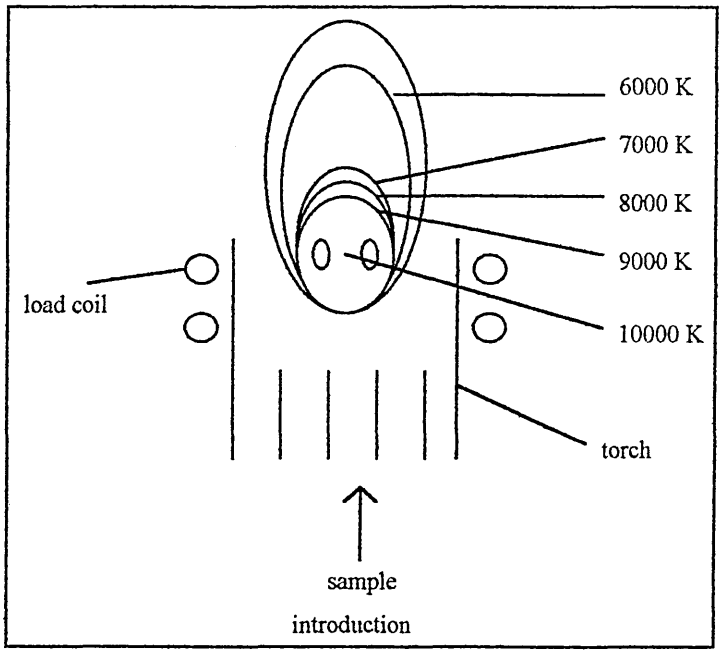


Fig.1.4 Approximate temperatures in the ICP discharge

Following sample excitation, the emission spectrum produced must be quantified and analysed. Hence, an analyte which has been transported to and excited in the plasma, must have any emitted radiation of a selected wavelength(s), converted to an electrical signal which can be measured. This is generally achieved with the use of a diffraction grating, which resolves the radiation into its component wavelengths. The light intensity is then measured utilising a photomultiplier tube, at a specific wavelength for each selected analyte line. Analytes have numerous lines in the spectrum which can be used for analysis.

There are two types of spectrometer available (see section 1.3.3.5):

- The polychromator. This is a simultaneous instrument, as every analyte line is measured in unison.
- The scanning monochromator. This is a sequential instrument, in that each analyte line is measured in succession.

The former is constructed to monitor pre-selected elements and wavelengths, but requires less analysis time, when more than one analyte is to be determined. The latter has unrestricted wavelength selection. However, the spectrometers have similar performance requirements, which can be identified. These include good resolution and stray light rejection. The ability of a spectrometer to separate adjacent spectral lines is known as the resolution of the instrument. High resolution instruments cannot separate two lines which have exactly the same wavelength, (direct spectral overlap), but partial or wing overlap can be reduced or eliminated. Also, some analytes emit intensely, which generates stray light signals from their strong lines. This stray light is recorded on other analyte lines. A good grating reduces stray light, but cannot eliminate it.

At a given wavelength, radiation which reaches the photomultiplier tube consists of that emitted by the analyte and background radiation from additional sources. Background correction is viable in many situations and enables good differentiation between peak and background. Scanning the spectrum on either side of the peak, generally with the use of a motor driven entrance slit, will facilitate off peak background correction. This method will only be successful if it is possible to evaluate the background level underneath the peak. In cases where this is possible, analysis accuracy has been improved significantly, and some interferences have been eliminated. For instance, the shift in background intensity due to recombination radiation, which is produced when free electrons are captured into the bound state of an ion, is eliminated. Spectral interference and correction procedures are detailed in section 1.3.4.

Light which falls on the photomultiplier tube creates a small electrical signal, which in turn charges a microfarad capacitor. The capacitor is charged for a particular time interval, usually 5-15 s, during which the signal is integrated. This process of

accumulating the signal over a period of a few seconds, improves precision. The capacitor is discharged when the analytical cycle is complete, and the analogue signal is converted to a digital output and transferred to the computer. Computer manipulations of the data include, the production of calibration plots and the conversion of intensity measurements to concentrations. Most ICP software systems can fit 1st, 2nd and 3rd order polynomials to calibration plots of intensity against concentration, and some can fit polygonal approximations.

Polychromator systems make less demands on computer software than scanning monochromators. A simultaneous instrument requires a computer that can produce standard calibration plots and can calculate the unknown concentration of analytes in samples from these plots. It must also have the ability to produce inter-element corrections and statistical evaluations. Versatility in data presentation and the capability of storage and access of data are equally important. Precision is improved with alternate analysis of sample and standard. The concentration obtained for the sample is normalised to the mean standard result. In addition to data handling, sequential instruments require computer control of the wavelength drive of the spectrometer. This drive can travel at very high speeds, when scanning the spectral range required, and must be able to precisely locate the selected analytical lines in the spectrum.

1.3.3 Inductively Coupled Plasma Instrumentation

Detailed texts specifically devoted to ICP spectrometry are available (22, 23). Both these references contain compilations of contributions by many authors and give valuable insight into all aspects of ICP-ES.

1.3.3.1 Nebulisers

The function of the nebuliser is to produce a fine aerosol from a liquid sample. The aerosol is transported to the plasma by the nebuliser gas flow. To produce droplets a few μm diameter, a fast stream of gas passes through a small orifice and interacts with the sample liquid flow. ICP nebulisers are smaller, more prone to blockage and have less

critical tolerances than AAS nebulisers. This is due to the lower flow rate required, for adequate residence time of the sample in the plasma, compared to AAS in the flame. The estimated proportion of sample which is taken up and travels to the plasma in preference to waste, is known as the efficiency of the nebuliser, and is only between 1-4 %. For best results, physical parameters which affect nebulisation should be kept as constant as possible. These include density, viscosity and surface tension.

Concentric Nebulisers

The Meinhard nebuliser is the most frequently used of this type and is so successful that other nebuliser types are compared to it. Different tip designs are available.

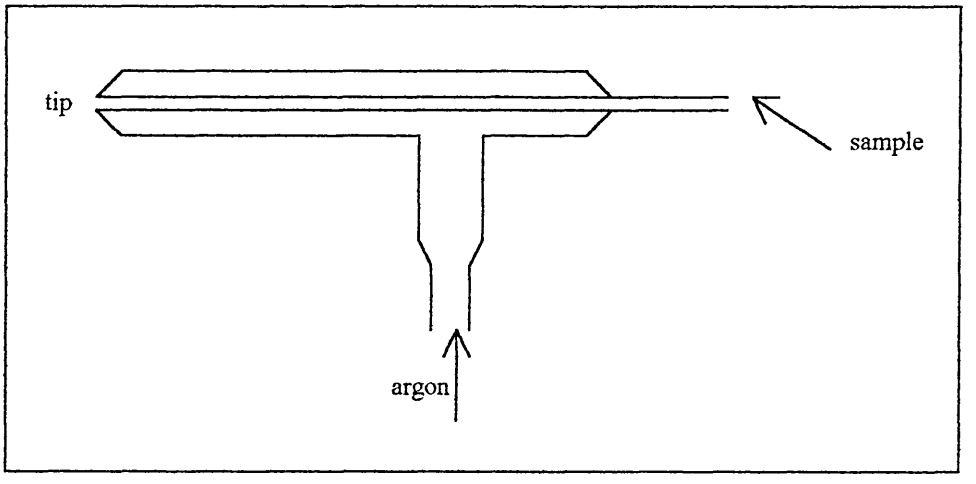


Fig.1.5 A schematic diagram of the Meinhard Nebuliser

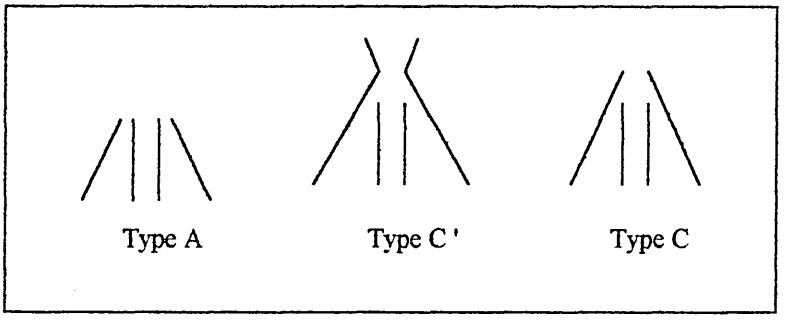


Fig.1.6 Meinhard Nebuliser Tip Designs

With no capillary tubing or hydrostatic pressure, this nebuliser will typically produce a gas flow of 1 l min^{-1}, with a line pressure of 200-300 kPa, and will take up 2-3 ml of water min^{-1}. The Meinhard nebuliser has a central capillary around 0.3 mm in diameter.

Therefore, blockage from samples containing high amounts of suspended solids is possible. However, filtration and centrifuging aid in minimising these blockages. Fibres in sample solutions can also cause problems. The following subject areas must be taken into consideration, when regarding nebulisers:

- salting up of nebulisers

The nebuliser gas flow tends to decrease, when samples of increasing dissolved solids content are introduced into the ICP. As the uptake rate is reduced, different analytes may increase or decrease in sensitivity, due to their position of optimum sensitivity in the plasma. Eventually though, sensitivity decreases. This effect is known as salting up and involves dried solute from the sample, partly occluding the gas orifice. Basically droplets, recirculating in eddy currents, drop onto the nebuliser tip and evaporate to dryness. Hence, solute deposits gradually reduce the gas flow. The type C Meinhard nebuliser is more resistant to salting up. Solutions to this problem include humidifying the nebuliser gas, which inhibits sample evaporation near the gas orifice, and tip-wash, which involves injecting around 0.1 ml of water, into the gas supply line to the nebuliser, between each sample. Humidification is used more frequently with this nebuliser.

- free running and pumped nebulisers

Concentric nebulisers can operate in free running mode. Solutions are drawn up by the low pressure generated, as the nebuliser gas passes through the orifice. The viscosity of the solution and the head effect, the vertical distance through which the liquid is lifted, affect the rate of liquid transfer. The alternative mode is to use a peristaltic pump to transport the solution to the nebuliser. The use of the peristaltic pump has a number of advantages:

- the head effect is eliminated.
- viscosity differences, causing intensity changes, are reduced.
- if a sample is depleted during the course of an analysis, the plasma will not extinguish.
- independent variation of the liquid flow rate from the gas flow rate may be considered.
- clean out time between samples can be decreased by increasing the pump speed.

The main disadvantage is that the peristaltic pump may be conducive to imprecision. For example, this can occur if the pump tubing is tensioned incorrectly, if the tubing is old and worn, or if a poor-quality pump is used. Also, certain applications may involve the use of organic solvents, hence the availability of solvent resistant pump tubing may be a problem.

- nebuliser starvation

Meinhard nebulisers exhibit the characteristic of insignificant variation of analyte signal with liquid flow rate. Hence, sensitivity is not improved by increasing the sample flow rate, higher than the normal uptake rate. Also analyte signal change is insignificant when the sample flow rate is reduced. However, when the rate is reduced to one third of the normal uptake rate, the signal rapidly decreases. Reduction in flow rate is an important consideration if sample volumes are limited.

Cross - flow Nebulisers

Cross-flow nebulisers operate on the principle known as scent-spray. Here, a horizontal jet of gas passes across the top of a vertical narrow tube. This action reduces the pressure and hence draws liquid up the vertical tube. At the top of this tube the liquid is disrupted into fine droplets. A peristaltic pump is usually employed with this nebuliser as it encounters stability problems in the free running mode. Cross-flow nebulisers generally behave like concentric nebulisers. They have the advantage however, of being less prone to salting up. Nebuliser gas humidification can also be used with this system.

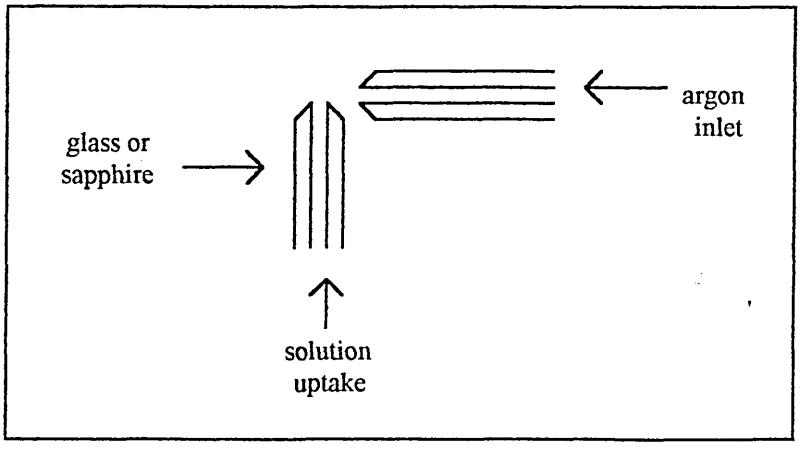


Fig.1.7 Cross-flow Nebuliser Tip Design

Babington - type Nebulisers

The Babington nebuliser operates on the principle that a film of water flows over the surface of a sphere. There is a slot in the sphere, through which air is forced. This action ruptures the film and produces an aerosol. The difference between this nebuliser and those previously described, is that liquid flows over a small aperture, in contrast to passing through it. These nebulisers have a good tolerance for high dissolved solids and suspended solids solutions. Slurries may even be nebulised. A peristaltic pump must be employed for sample introduction though, as they do not operate in free running mode.

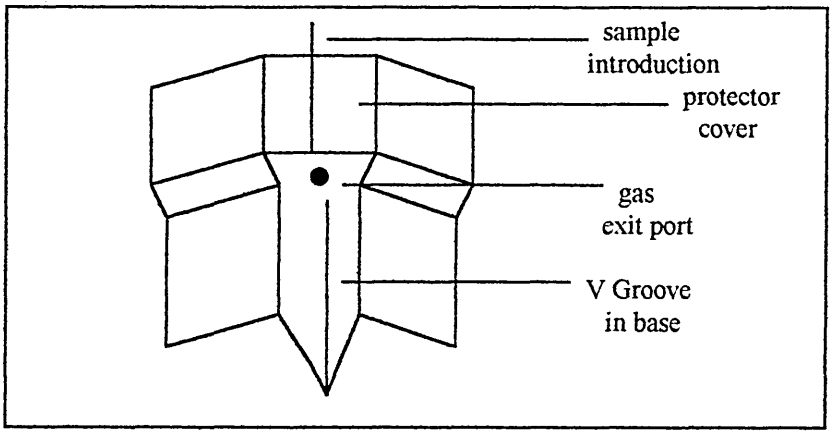


Fig.1.8 A schematic diagram of a Babington - type Nebuliser

Babington type nebulisers compare favourably in terms of precision and sensitivity to concentric and cross-flow nebulisers, for solutions of low to medium concentrations of suspended solids. However, when solutions containing high suspended solids are nebulised, Babington types are superior. The maximum solids level permissible is determined by the tolerance of the torch with respect to blockage. This type of nebuliser experiences extended memory effects, its main disadvantage.

Frit-type Nebulisers

In frit-type nebulisers, solution is pumped onto the face of a fine glass frit, through which the nebuliser gas passes. Sensitivities achieved are not greater than other types of nebulisers, even though this is a highly efficient method of aerosol production. This is because efficient aerosol production is only created at low liquid flow rates. Also, the system is prone to clogging of the frit and has poor clean-out characteristics. The

Hildebrand grid nebuliser is of a similar type and functions on the principle that sample flows over a fine mesh grid, which is positioned in front of the gas stream. Nebulisation takes place from the wetted surface.

Ultrasonic Nebulisers

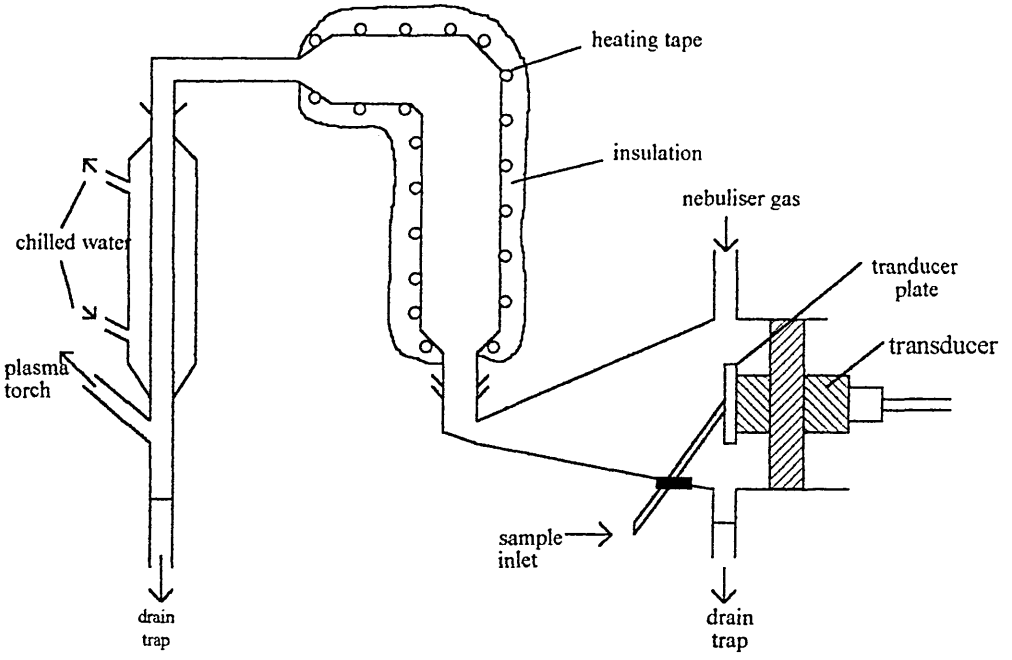


Fig.1.9 A schematic diagram of an Ultrasonic Nebuliser and Desolvator System

Ultrasonic nebulisation is achieved by supplying sample solution to the surface of a transducer, which is operated in the MHz frequency range. This method of nebulisation is highly efficient, as the sample is transported to the plasma at a much greater rate and yet the gas flow rate is not increased. A substantial increase in sensitivity is therefore expected, but is not achieved, due to the larger volume of water reaching the plasma, which quenches it. Desolvation is a solution to this problem. A heated tube is used to evaporate water droplets from the aerosol and a condenser removes the water vapour produced. The sample remaining is then transported to the plasma.

This system has disadvantages, as desolvation not only concentrates the analytes to be determined, but also concentrates the matrix components of the sample. Therefore, background emissions from the matrix may increase, and hence signal to background

ratios will not improve. Thus sensitivity will not improve. Spectral interferences may also become more troublesome. Detection limits are improved by factors of 10-50 for samples containing low concentrations of matrix components, for example fresh waters. In addition this nebuliser is expensive, requiring it's own RF source. Clean-out times are greater than any other type.

The most recent developments in this field have come from the production of highly efficient nebulisation systems. These include direct insertion nebulisers (DIN), micro concentric nebulisers (MCN) and ultrasonic nebulisers which also incorporate a membrane filter (USN+MDX).

1.3.3.2 Spray Chambers

The nebuliser produces an aerosol which contains a widespread distribution of droplet sizes. This is known as the primary distribution. Droplet sizes above 10 μm do not dissociate completely in the plasma and as a consequence of this, quench the ICP due to increased solvent loading. The spray chamber's function is to remove large droplets from the aerosol, which condense and travel to waste. To achieve this, direction of the gas flow is sharply changed, or the aerosol collides with the internal surfaces of the chamber. Hence, the spray chamber has a considerable effect on sample introduction efficiency.

Double pass spray chambers

These are most frequently used and have been optimised to reduce dead spaces. This has ensured greater signal stability and less clean out time.

Single Pass Spray Chambers

These types are available but are only applicable to analytes with low ionisation energies. This is due to larger droplets travelling to the plasma and hence quenching it, which is only of benefit to analytes such as the alkali metals.

Single Pass Spray Chambers with Attachments

These types are the primary alternative to the double pass systems and are frequently used. The design incorporates some type of flow spoiler, to aid in the removal of large droplets.

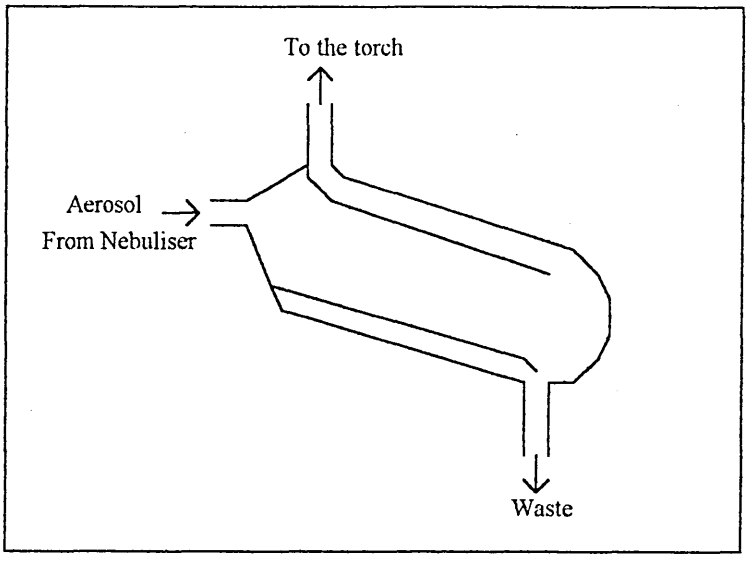


Fig.1.10 Schematic diagram of a Double Pass Spray Chamber

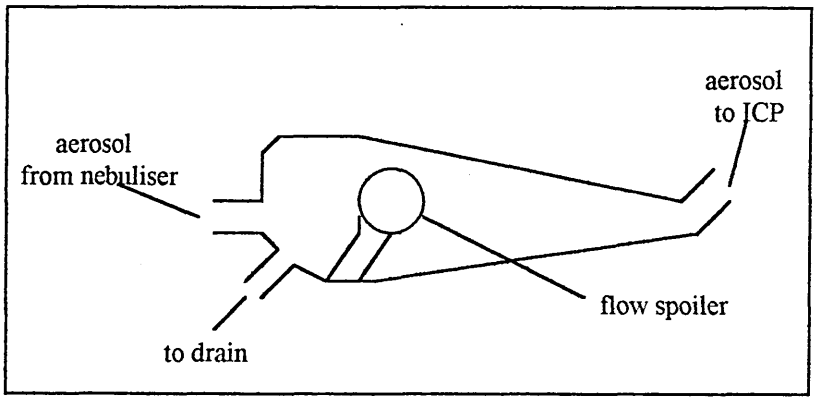


Fig.1.11 A schematic diagram of a Single Pass Spray Chamber with a Flow Spoiler

Spray chambers can be constructed from materials such as glass, PTFE and polyethylene. To push aerosol through the injector tube, a slight positive pressure is required. Dipping the drainage tube into the waste reservoir, accomplishes this. To avoid pressure fluctuations in the spray chamber, removal of waste from the reservoir must be uniform. The most important consideration when regarding sample introduction is memory effect.

The total time required for analysis is affected by the time taken for the sample introduction system to clean out, in between samples. Clean out times are influenced by:

- uptake tubing
- nebuliser
- spray chamber
- analyte

1.3.3.3 Generators

The function of the generator is to provide a high frequency current in the induction or load coil. This creates an oscillating magnetic field which maintains the plasma. The load coil is a copper tube which can be copper only or silver coated. It is usually water cooled, but gas cooled systems are available. The coil temperature is a factor which affects emission intensity and hence a built-in water circulating system is usually provided, which contains a pump, cooler and reservoir. Two classes of generator are available and in widespread use.

Crystal Controlled Generator

This generator utilises a piezoelectric crystal to provide an output at constant frequency. The final circuit is tuned by motor driven capacitors, to tolerate impedance changes in the coil. Maximum efficiency of the generator is thus ensured.

Free Running Generator

In this generator, the impedance of the final circuit is frequency dependent, and hence the frequency adjusts to changes in the coil. This implies that the generator has only a nominal frequency.

Generators generally operate at the industrial standard frequencies of 27.12 and 40.68 MHz. The reason for this is that legally, radio frequency generators must be shielded and it is simpler at the above frequencies. However, frequencies between 1 and 148 MHz have been used to operate ICP's. Usually an increase in signal to background ratio is observed with increase in frequency. Emission line intensities decrease, along with the background continuum.

The forward or incident power generators normally operate at between 0.9 and 1.2 kW. Higher powers, between 2-2.5 kW, are required for organic solvents only. Improvements to the signal to background ratio are not found with an increase in power. Emission line intensities increase, but there is a greater increase in spectral background. Initiation of the plasma involves the adjustment of gas flows, powering up and impedance matching the generator if necessary, and seeding the torch with electrons. It is usually an automatic sequence, and initiation is finally achieved with a Tesla coil spark.

1.3.3.4 Torches

The Greenfield Torch

Greenfield *et al.* (14) designed the first torch to be specifically used for ICP spectrometry. The three concentric tube design, solved the problem of injecting sample into the plasma. This plasma has a doughnut shape when observed from above. The Greenfield torch was 29 mm in diameter and required high power and high gas flows, 12-38 l min^{-1} of Ar and 20-70 l min^{-1} of N_2. The plasma was robust, could operate with existing AAS nebulisers, tolerate torches with poor concentricity and permitted the injection of air. However it had high running costs.

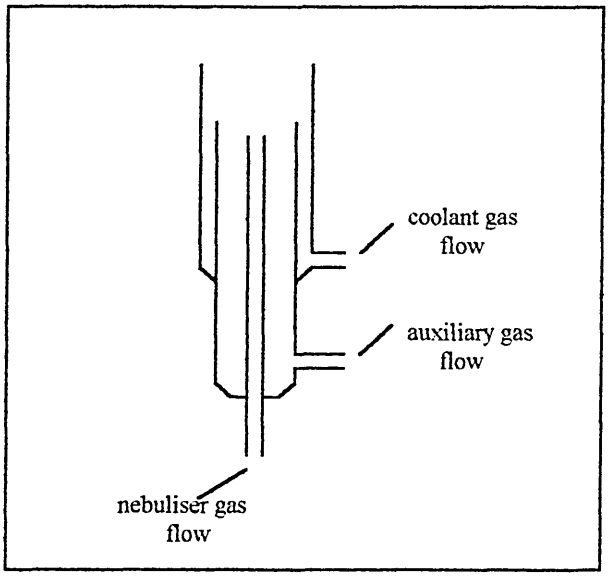


Fig.1.12 A schematic diagram of the Greenfield Torch

The Fassel Torch

Wendt and Fassel designed a smaller torch using three concentric tubes (15). No doughnut shape was formed, and sample travelled around the outside of the plasma. This torch has since been redesigned to allow doughnut formation and is used almost exclusively in all ICP systems. It requires lower gas flows than the Greenfield torch, typically 10-18 l min^{-1} and operates at a power of 0.9-1.2 kW. It is intolerant of air injection however.

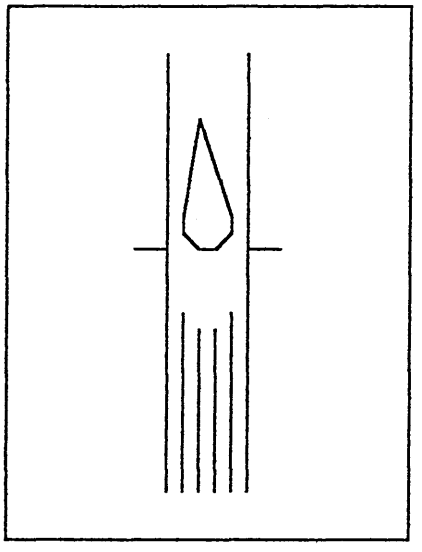


Fig.1.13 A schematic diagram of the Fassel Torch

Essential characteristics pertaining to torches are:

- The ratio of the external diameter of the auxiliary tube, to the internal diameter of the coolant tube, known as the configuration ratio, is < 0.9. This ensures plasma stability and ease of initiation.

- The coolant tube is longer than the other tubes. This reduces plasma background in the OH spectrum region. Air entrainment at the edges of the plasma is prevented by this configuration, significantly reducing OH background.

- The diameter of the injector tube is kept relatively wide at around 1.8 mm. This prevents blockage but renders plasma penetration harder.

Fixed, fully demountable or partly demountable Fassel torches are available:

- fixed torches

Fixed torches are constructed with impressive accuracy, enabling the ICP to be run at economic coolant gas flow rates. They exhibit long-term consistency and are easily removed and replaced. However, they are relatively high in cost.

- fully demountable

Fully demountable torches are difficult to reassemble for accurate alignment, and hence optimisation is necessary. However, coolant and injector tubes can be inexpensively replaced when needed.

- partly demountable

The advantage with partly demountable torches is that the injector tube can be replaced with a material other than quartz, such as alumina, permitting the determination of Si in HF solutions for example.

1.3.3.5 Spectrometers

Inductively Coupled Plasma-Emission Spectrometry is a technique with a multi-element analysis capability. This can be achieved in a simultaneous manner where every analyte is measured in unison, or sequentially where each analyte is measured in succession. Certain characteristics are required of any ICP spectrometer, which are discussed as follows:

- Wavelength Range

The highest wavelength generally measured by the spectrometer is Rb 780.02 nm, although there is a Cs line at 852.12 nm. The latter wavelength is difficult to attain and spectrometers that are capable of this experience poor sensitivity, due to a decrease in photomultiplier tube performance above 800 nm. The lower wavelength limit is around 140 nm, although below 200 nm sensitivity decreases. Hence for an air path spectrometer 140-800 nm is the usual wavelength range. ' Vacuum and nitrogen-purged systems are available which provide greater sensitivity in the region below 200 nm. Several analytes have their most sensitive line and/or the line most free from spectral

interferences in the vacuum UV region. The primary wavelengths for Cl, F and O remain unattainable.

- Resolution

This is determined by the spectrometer's ability to separate an analyte line, from adjacent lines of matrix components in the sample. A poorly resolving instrument may be adequate for simple matrices such as water, but complex matrices such as geological samples, will require a high resolution spectrometer. Resolution can be increased using, higher dispersion diffraction gratings, higher spectral orders, narrower slits and longer focal lengths.

- Light Throughput

A spectrometer with high light gathering powers is preferable for ICP systems, due to the relatively low light levels emitted from the source. This is improved using, large gratings, shorter focal lengths, wide slit widths and lower dispersion gratings.

- Stability

It is necessary for a fixed wavelength spectrometer, to remain exactly on the required wavelength, and a variable wavelength spectrometer, to locate the required wavelengths reproducibly. A number of measures can be taken to assist this, including insulating the spectrometer.

- Stray Light

High concentrations of intense emitters in the sample, such as the alkaline earth elements, produce a relatively high intensity of light, which enters the spectrometer. A shift in analyte background is observed, as scattering causes light other than that emitted by the analyte, to reach the detector at the isolated analytical line. To aid in stray light prevention, the internal parts of the spectrometer are blackened and the area around the grating is masked.

The two types of spectrometer available will now be discussed in detail.

Simultaneous Spectrometers (Polychromators)

This system has the advantages of high sample throughput, superlative stability and greatest speed of analysis, in that data acquisition time is identical, whether one or fifty

analytes are being measured. The disadvantages include expense, for example, the instrument requires a photomultiplier for every analyte required, and inflexibility, for instance, if a different analyte is required, other than those requested at the time of instrument construction, it will be unattainable.

Problems can be alleviated in a variety of ways. A difficult analyte can have more than one line included on the spectrometer. A moveable primary slit can be included. This will allow analytes, with wavelengths in close proximity of fitted lines, to be measured, as the spectrum can be moved. Also, a monochromator may be included, which is adjusted manually to the wavelength required. The output is measured by the polychromator, as though it was a fitted line. This is know as the n+1 channel.

Pashen - Runge Spectrometer

Most polychromators are of this type. The optical parts, the primary slit, diffraction grating and secondary slits, are located on a theoretical circle, known as the Rowland circle. The diameter of the circle is equal to the radius of curvature of the grating. All points on the circle are therefore in focus.

- The lens

The function of the silica biconvex lens is to focus the plasma image, onto or near the primary slit. It also seals the spectrometer against leakages of air, in vacuum and purged systems. It is also possible to transfer light to the spectrometer, utilising an optical fibre as the alternative to a lens. This enables the position of the spectrometer to be more flexible, and light can be transferred to several spectrometers. The efficiency of light transfer in optical fibres is greatly reduced below 230 nm, and hence the lens is still required for the vacuum UV region.

- Primary slit

All spectrometers have the primary slit parallel to the long axis of the plasma, which is the optimum configuration. To ascertain that a precise region of the plasma is measured, masking is used to decrease the height of the slit. The slit is usually 20 μm in width and can be moved short distances in the plane of the spectrometer, about a mean position. This movement changes the angle of incidence on the grating, moving the spectrum

across the secondary slits. This enables a wavelength scan to be produced i.e. the spectrum is scanned for a short distance about a fitted line. Hence, if background correction is required, the background could be observed using this procedure. Alignment could also be checked.

- Diffraction grating

The function of the diffraction grating is to disperse the light entering the spectrometer into its constituent wavelengths. They can be of two types, known as ruled or holographic. Holographic gratings have better stray light rejection characteristics, are easier to make and have better resolution. They are used in first order, as their ability to reflect is lower than in ruled gratings. Hence, they are unusable in higher orders. A ruled grating can be blazed at a suitable angle, hence achieving efficiency in higher orders. A wide wavelength range can then be covered. Resolution improves with increasing order, but is relatively poor in first order. Filters are situated in secondary optics to separate over lapping orders. This system appears to produce stray light levels similar to holographic gratings.

- Secondary slit assembly

A mask which contains slits is supported in the slit frame. These slits are located in a position which corresponds to an analyte wavelength required. There are two types of mask. The first is cut by an etching process, which is easy to align, but further addition of lines is then impossible. The second utilises adjustable slits which are separate from the mask. This system is very difficult to align, but line additions and changes are possible. Concave mirrors are generally used to focus an individual line, onto a photomultiplier tube. Hence, the light which passes through the slit, is taken out of the plane of the spectrometer to a tube, positioned above or below it. Cross talk between channels is therefore minimised, as scatter produced behind the slit frame is reduced. Optical fibres and light guides can also be utilised to focus a line. This application not only minimises scatter, but also aids when two closely spaced wavelengths are required. For instance, it may be impossible to fit these lines due to a lack of space, with the close

proximity required by 2 mirrors or tubes. The maximum number of lines currently possible is approximately 60.

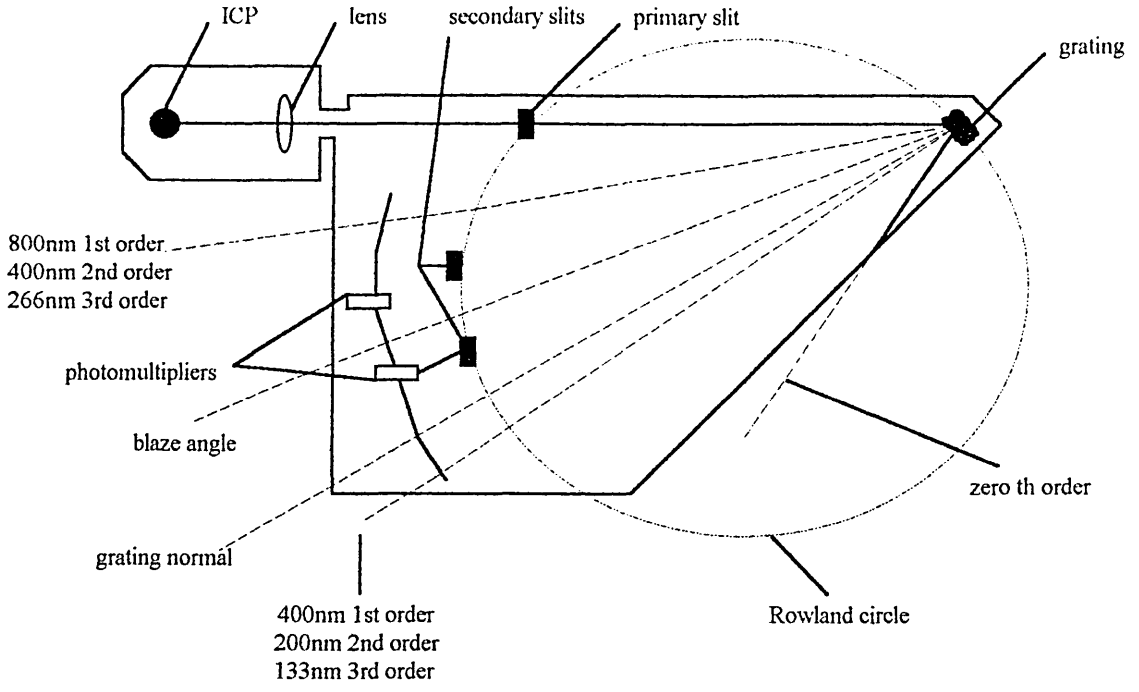


Fig.1.14 A schematic diagram of the optical system of the Paschen - Runge Spectrometer

- Photomultiplier tubes

The most efficient light measuring detector is a photomultiplier tube. They have low dark current, which is the thermal emission from the cathode with no light input. This is significant, when a considerable amount of the signal measured is dark current. This occurs at low wavelengths. A virtually linear response is produced over the whole of it's operating range. Photomultiplier tubes are chosen for specific wavelengths in simultaneous instruments, ensuring no compromise on performance. The only disadvantage is that no spatial resolution of the light it receives is produced. Photodiode arrays can provide this information, which may lead to simultaneous background correction for example. However, they have poorer sensitivity and smaller linear ranges in comparison with photomultiplier tubes. Vidicon tubes are also available, but have similar problems with sensitivity.

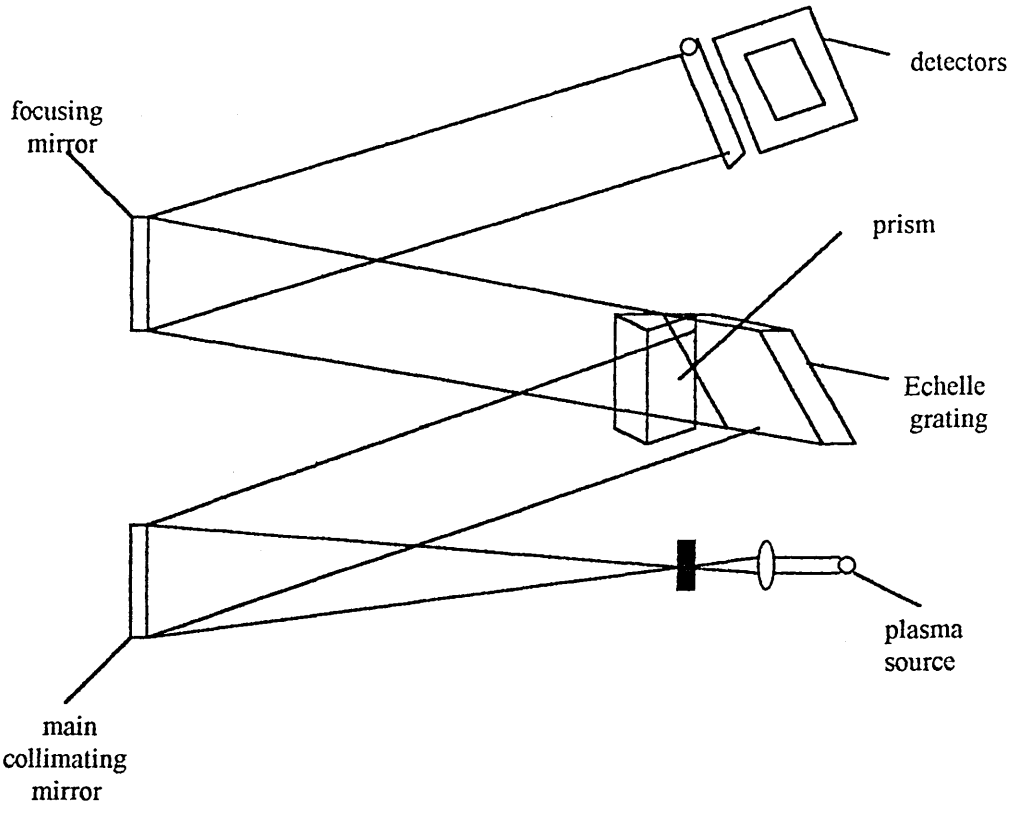


Fig.1.15 A schematic diagram of the optical system of the Echelle Simultaneous Spectrometer

These spectrometers contain Echelle gratings, which have widely spaced grooves that form right angle steps. The narrow side of the groove profile reflects the light almost normally, as the grating is illuminated at a high angle of incidence. Only very high order spectra, between n = 28 to 118, are produced with this system, over a narrow angle. A moderately limited band width, with very high resolution is covered by each spectrum. Also, maximum advantage of the light energy is taken, as all of the reflection is close to the blaze angle. Order sorting is required, as the spectra all overlap, and is achieved using a prism. This implies that cross dispersion takes place, producing a rectangular spectrum. Hence spectral wavelengths are dots opposed to lines. Light dispersion into it's component wavelengths is generally better with this system. A rectangular cassette containing holes is used to isolate the required wavelength. This is equivalent to the secondary slit frame in the Paschen-Runge assembly. The line program required is easily

changed as cassettes can be exchanged. A maximum number of twenty photomultiplier tubes are positioned directly behind the cassette.

Sequential Spectrometers (Monochromators)

These systems measure the required analytes in pre-defined succession. They have the advantage of the ability to acquire any wavelength within their range. Hence, it is possible to select the optimum line for every analyte, in any matrix. They have the primary disadvantage of speed, in that for every analyte n, n x data acquisition time is required. This is due to slewing from line to line. Polychromators have n = 1. Precision is an important parameter to consider with sequential instruments. It is difficult to determine, but it is assumed that the longer the time necessary for analysis, the greater the possibility of deterioration in precision due to drift.

Czerny-Turner Spectrometers

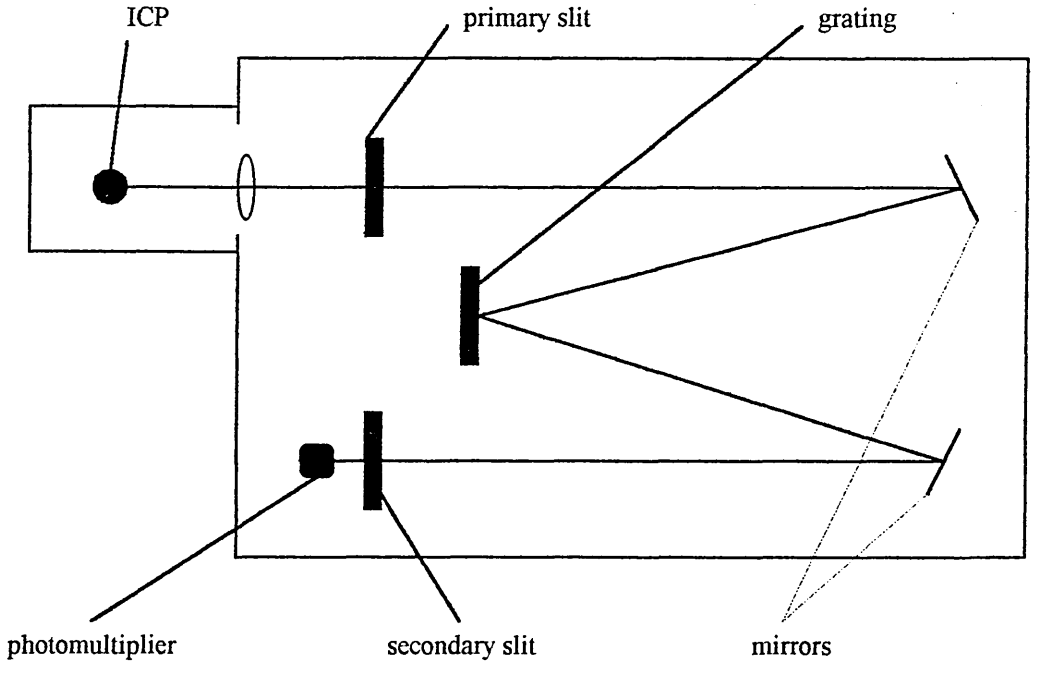


Fig.1.16 A schematic diagram of the optical system of the Czerny-Turner Scanning Monochromator

This is the favoured system, and has primary optic considerations similar to that of a polychromator. A concave mirror focuses the light onto a plane diffraction grating, which is rotated by a stepper motor. Hence, the spectrum is moved across the secondary

slit. A single photomultiplier tube is chosen for its broadest spectral response. However, performance decreases slightly with this detector, at the ends of the wavelength range. As the instrument slews from line to line, an automatic gain control can change the high voltage applied to the tube. This will be required if large variations in spectral line intensities are to be measured. The operation of the stepper motor is fairly precise. However, the half-width of a line emitted from the ICP is around 0.02 nm and hence slewing exactly to the peak of a line is difficult.

A scanning procedure is generally used to exactly locate the position of a line. The following operations are commonly used:

- reference line location

This is a fixed position in the spectrum which may be a selected Ar line from the plasma. Step numbers can be calculated from this reference, and wavelength drift may be monitored.

- drive calibration

There is not an absolute relationship between the number of steps moved by the stepper motor from the reference position, and the wavelength detected. This is due mainly to mechanical deficiencies in the drive action. Hence, a mathematical function is required, which calibrates fixed positions or determines the apparent position of each line measured.

- peak location

The mathematical correction is still insufficient to ensure direct peak measurement. This can be due to changes in temperature or vacuum. Therefore, for every line measured, a scan of a small window around the chosen wavelength is produced. An algorithm is employed to decide if the peak has been located and its position. Hence, the position of maximum intensity is determined by fitting a curve to chosen points on the peak. This algorithm ensures that false peaks are not located, by incorporating an intensity cut-off point. Peaks located below this intensity are regarded as background.

Erbert-Fastie Spectrometer

This is a simple form of the Czerny-Turner spectrometer, and is generally utilised in a double monochromator configuration. The purpose of this arrangement is to give better stray light characteristics. Wavelength slewing is achieved by driving the gratings of both spectrometers, using the procedure described above. A refractor plate is positioned in front of the secondary slit in the second monochromator, which is moved rapidly to acquire the exact location of the line. This technique has a speed advantage, as the slewing and scanning operations can be separated into two different movements, which are implemented simultaneously. Hence, relatively large steps can be applied on the grating drive due to its broad range, while short distances are moved by the refractor place, ensuring greater precision from the smaller steps.

Paschen-Runge spectrometer

The spectrometer utilised is identical to the simultaneous instrument. However, the grating is fixed and scanning is achieved by primary and secondary slit movement. The secondary slit frame is substituted with an arrangement of 2 mm pre-cut slits, which are positioned at fixed intervals. Two photomultiplier tubes are located in a carriage, which is driven around the frame, until the chosen tube is behind the required slit. This is a long, imprecise operation, as the light received by the tube is around a couple of nm from the line required. The exact wavelength is acquired with fine tuning. Hence, the primary slit is moved a pre-determined short distance, a maximum of 2 mm, utilising a large number of motor steps, which is highly precise. Both movements occur simultaneously which improves speed. A difference to the simultaneous instrument is that order-sorting filters are placed in front of the primary slit. This instrument has better precision than peak search systems.

Echelle spectrometer

This has a similar configuration to the simultaneous spectrometer. However, an aperture plate, containing 350 pre-set apertures replaces the cassette. In sequence, the photomultiplier is driven to required apertures, using x-y coordinates, which have been stored. The technique is rapid and precise, due to the small distances moved. The

difference between this system and all other monochromator designs, is that it can only access 300 pre-programmed wavelengths. This however, should be sufficient.

Combined simultaneous/sequential spectrometers

These systems are the ultimate in speed and flexibility, although they are relatively expensive. Combinations of the polychromator and monochromator designs detailed are used. They can function solely as a simultaneous, or a sequential instrument, or as a combination.

1.3.4 Inductively Coupled Plasma Interferences

It should be noted that ICP-ES is relatively free from interferences, and that usually matrix matching of samples and standards reduces most interferences to levels which enable accurate analysis to be performed. However the interferences observed in ICP-ES can be divided into three groups. These are spectral overlap, stray light and matrix effects. Spectral and stray light interferences are connected to the spectrometer. Matrix effects are associated with sample introduction and excitation. The interferences will be discussed in detail, although it should be noted that the causes of interferences are often complex. Compilations of ICP spectral lines, which provide valuable data and information concerning interferences are available (24, 25).

Spectral Overlaps

- Direct Spectral Overlap

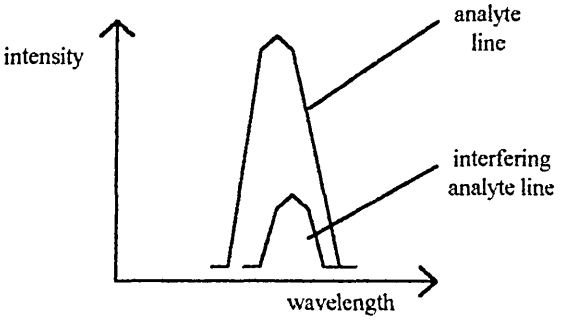


Fig.1.17 Direct Spectral Overlap

The spectral line of another analyte is located beneath the analyte line. The solutions to this type of interference involve changing the spectral line measured for the analyte, or assessing the interference and subtracting this value from the intensity obtained.

- Partial or Wing Overlap

An interfering analyte line partially overlaps the analyte line. Improving the resolution of the spectrometer may eliminate or significantly reduce this type of interference.

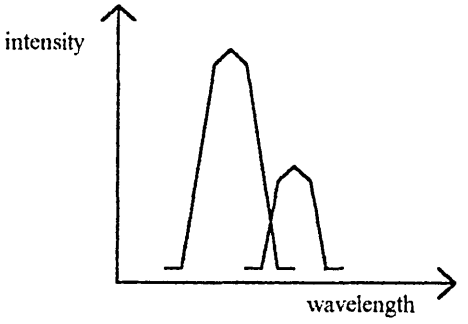


Fig.1.18 Wing or Partial Overlap

- Background Continuum

A background continuum is located beneath the analyte line, which is added to both the background intensity and the analyte peak. The background intensity must be measured at a position on either side of the peak. The interference can then be subtracted from the intensity obtained.

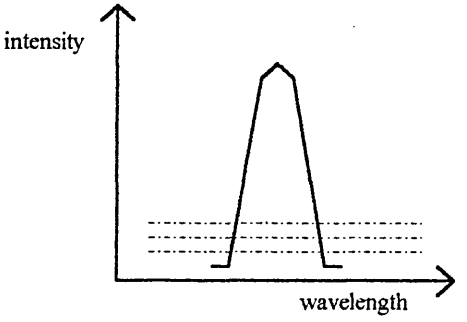


Fig.1.19 Continuum or Background Overlap. The diagram indicates three levels of interference which correspond to an increase in concentration of the interfering analyte.

- Lorenzian Line Broadening

The analyte line is located on the wing of an interfering analyte line, which is an intense emitter. A polynomial mathematical correction procedure is required to eliminate this type of interference.

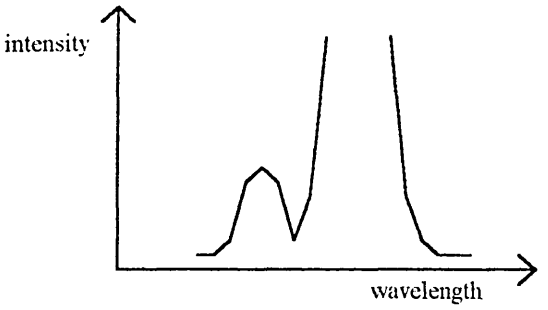


Fig.1.20 Lorenzian Line Broadening

Spectral interferences can generally be avoided by selecting an alternative line for the analyte, which is free from the particular interference. Those that can not be evaded in this way, may be corrected with the application of a mathematical correction procedure.

Stray Light Interferences

- Stray Light Interference

This interference is similar to the continuum spectral overlap interference. The background is raised significantly, due to the presence of an intense emitter in the sample. The optical quality of the spectrometer requires improvement to reduce this interference, or the background intensity should be measured at a position on either side of the peak and subtracted from the intensity obtained.

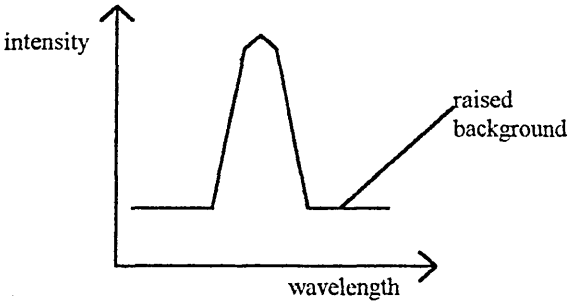


Fig.1.21 Stray Light Interference

- Background Continuum Interference

This interference is caused by recombination radiation. This type of radiation is emitted, if free electrons in the plasma are captured by an ion. The background is raised

significantly and therefore background correction, as described above, is required to reduce this interference.

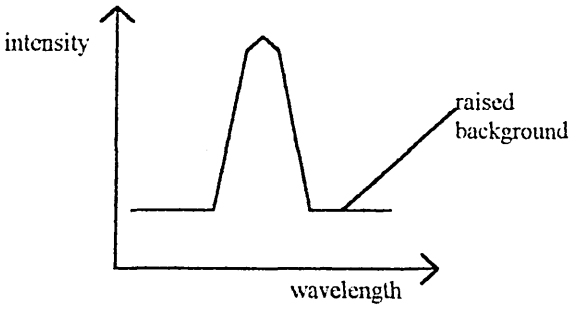


Fig.1.22 Electron - Ion Recombination Background Continuum Interference

Matrix Effects

- Sample Introduction Changes

Changes in sample composition, such as the dissolved solids content or the concentration of acid present in solution, is a source of the interferences known as matrix effects. The efficiency of the nebuliser is altered with a change in sample composition, and hence the sensitivity. For example, matrix effects vary with acid concentration and type. This interference is alleviated by matrix matching the standards and sample solutions.

- Molecular Bands

This type of interference arises, due to the occurrence of molecular bands high in the plasma, such as NO and OH. There is a depression of analyte signal and an increase in background, hence reduced sensitivity. The solution to this is to select an alternative line for the analyte.

- Excitation Changes

This type of interference is due to great fluctuations in the proportion of interfering analytes present in each sample. A reduction in sensitivity is observed, in that the analyte signal decreases and the background intensity increases. Interactive matrix matching eliminates this interference. This involves determining the concentration of the interfering analytes present in the sample, and then calculating the dilution factor required to adjust the concentrations to set reference levels. The adjustment required is effected and the sample is re-analysed.

1.3.5 Comparison of Inductively Coupled Plasma-Emission Spectrometry with Alternative Spectrometric Techniques

The alternative instrumental techniques currently available for multi-element analysis are atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), direct current plasma spectrometry (DCPS), microwave induced plasma spectrometry (MIP), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-emission spectrometry (ICP-ES). Inductively coupled plasma-emission spectrometry has been selected as the preferred detection technique in this thesis due to a number of distinct advantages. These include that it is an effective source of atomic emission, it has a wide dynamic range, typically over 4-5 orders of magnitude and detection limits are low for most elements, falling in the range 1-100 $\mu g\ l^{-1}$. Many wavelengths of varied sensitivity are available for the determination of any one element, indicating that ICP-ES is suitable for ultratrace to major component analysis. It is also a highly precise technique with a simultaneous multi-element capability and has been applied extensively to the analysis of solutions. The ICP-ES technique is compared in greater detail below to AAS and ICP-MS, the main techniques for solution analysis. X-ray fluorescence is mostly used for solid sampling and is superior to ICP-ES for major element analysis, DCP-ES suffers from greater chemical and ionisation interferences, whereas MIP's lend themselves more easily to sample introduction by vaporisation or as detectors for chromatographic effluent, such as gas chromatography (GC-MIP), and are thus not considered further.

Flame Atomic Absorption Spectrometry

ICP-ES has the following advantages compared to AAS:

- successful measurement of a more extensive range of analytes.
- lower detection limits for the refractory analytes, such as Al, Mo, Zr the lanthanides and analytes not normally attempted by AAS, for instance B, P and S.
- a wider dynamic range.
- being less prone to interferences.
- multi-element capability.
- greater cost-effectiveness with increasing numbers of analytes to be determined.

ICP-ES has the following disadvantages compared to AAS:

- detection limits for Cd, Pb, Cs and Rb are inferior.
- inferior single element determinations, due to poor cost-effectiveness.
- more expensive instrumentation and running costs.

Inductively Coupled Plasma - Mass Spectrometry

ICP-ES has the following advantages compared to ICP-MS:

- higher levels of dissolved solids in sample solutions can be tolerated.
- "major" levels of analytes present in samples can be determined.
- instrument precision is better.
- the instrumentation is less expensive.

ICP-ES has the following disadvantages compared to ICP-MS:

- the technique is not able to detect every analyte.
- detection limits are 1-2 orders of magnitude poorer.
- it is more prone to spectral interferences.
- it is not able to measure isotope ratios.

1.4 Flow Injection Analysis

1.4.1 Introduction

Flow Injection Analysis (FIA) was introduced as a new concept for continuous flow analysis, in 1975 by Ruzicka and Hansen (26). Conventional continuous flow analysers were based on the principle of air-segmented streams, which were introduced by Skeggs in 1957 (27). This system ensured samples were not contaminated by the previous sample. Samples were aspirated in succession into a tube, through which they travelled intermittently with air bubbles, delivered by a separate pump. At predetermined points, reagents could be added to the continuous flow, to induce chemical reactions. Hence, processed samples flowed through the detector, following de-gassing, which monitored the signal continually.

1.4.2 Principles of Flow Injection Analysis

Flow injection analysis is the technique by which a discrete sample volume is injected into a non-segmented, continuous carrier stream (28). The sample injected forms a zone, which travels towards a detector. The detector continually monitors the signal as it changes, due to the zone passing through the flow cell. A single line FIA manifold is depicted in Fig.1.23. A pump, P, is used to transport the carrier stream, CS, through thin tubing. The injection port, S, is utilised to introduce a fixed volume of sample into the moving carrier stream. The reaction coil, C, ensures the sample zone disperses and reacts with the constituents of the carrier stream. Hence, a species is formed which can be detected and recorded on its passage through the flow cell, FC. Fig.1.24 depicts a typical detector response, generated by FIA. The height of the peak, H, is directly related to the concentration of the analyte.

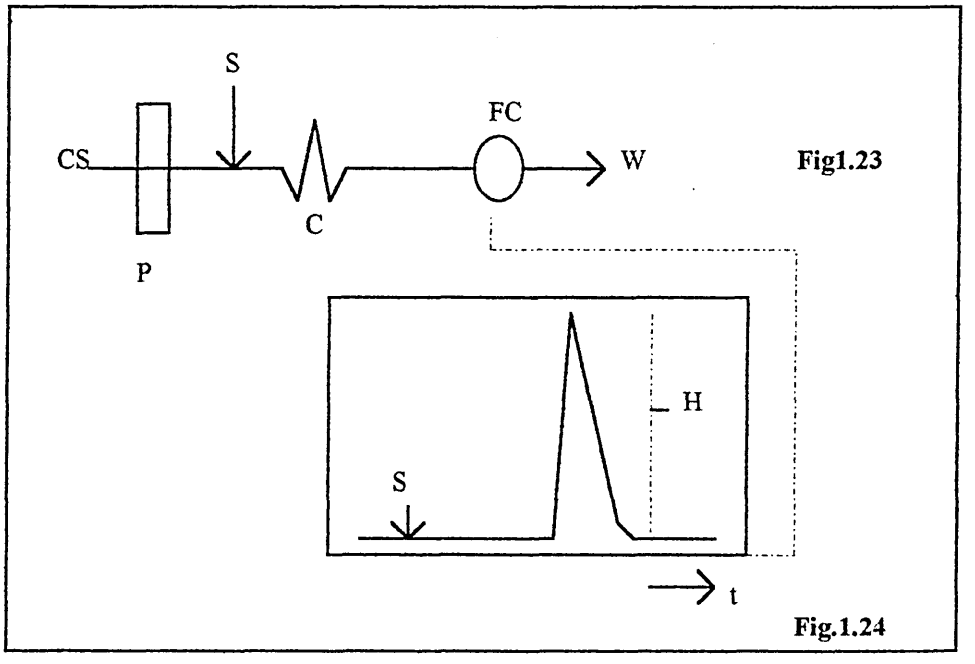


Fig1.23

Fig.1.24

Fig.1.23 A schematic diagram of a single line FIA manifold. CS - carrier stream, S - sample injection, FC - flow through cell, C - mixing coil, P - pump and W - waste.
Fig.1.24 A typical detector response. S - sample injection, H - peak height and t - time.

Flow injection methods can perform a variety of diverse tasks, and reproducible measurements are attained, by controlling the dispersion of the sample in the carrier

stream, from injection to detection. Dispersion (D) is measured by relating the maximum concentration of analyte determined in the sample zone (C^{max}), to the original analyte concentration in the sample, without dispersion (C^0).

$$D = C^0 / C^{max}$$

Sample dispersion is controlled by the manipulation of key experimental parameters, such as flow rate and sample volume, and FI systems can be categorised according to the degree of dispersion.

Large Dispersion (D > 10). This is required for on-line sample dilutions and is achieved by incorporating a mixing chamber into the carrier stream.

Medium Dispersion (D = 3 - 10). This is used in FI applications where a chemical reaction or a standard addition procedure is necessary. Significant mixing of the sample is required and is attained with the use of a reaction coil, for example.

Limited Dispersion (D = 1 - 3). This is utilised in systems that require direct sample introduction, therefore, key parameters are fixed to inhibit dispersion.

Reduced Dispersion (D < 1). This applies to experiments involving on-line analyte preconcentration. Increased sensitivity is achieved in these applications. This is the value of D for the experiments carried out in this thesis.

FIA has advantages such as: high precision, high sampling rates, the ability to perform on-line sample processes such as dilutions, standard additions, solvent extraction, chemical reactions and ion exchange, economical use of reagents, simplicity and flexibility (29). There are many review articles available on the subject of flow injection analysis, which encompass various topic areas. These include, present and future developments, trends and applications of the technique (30-38), specific applications, such as water analysis (39-41), agricultural and environmental analysis (42), and pharmaceutical analysis (43), sample handling and pre-treatment (44), dispersion

phenomena (45), developments in ICP-ES (46-47) and ICP-MS (48-49), and FI on-line preconcentration techniques (50-52).

1.5 Flow Injection Techniques in Combination with Inductively Coupled Plasma-Emission Spectrometry

The development of FIA methodology in combination with ICP spectrometry arose to surmount specific limitations of the ICP technique. Hence, FIA has been utilised to enhance sensitivity and minimise physical and spectral interferences found by conventional ICP.

Initially, FI was used as a direct sample introduction technique, minimising problems associated with the conventional nebulisation of samples containing high dissolved solid contents or high viscosity. Hence, samples such as blood serum (53) could be analysed, due to the injection of microlitre sample volumes interspersed with carrier, which effectively flushed the system and prevented nebuliser/injector tip blockage. Hence, a limited dispersion FI system was employed.

A standard addition procedure, originally proposed by Tyson for flame atomic absorption spectrometry (54), was employed by Greenfield, for the determination of Ca in Portland cement by FI-ICP-ES (55). The sample was used as the carrier stream and 25 µl aliquots of standard solution were injected into this. A medium dispersion FI manifold was produced, with the incorporation of a 100 cm length of tubing between the point of injection and detection, which permitted a degree of mixing.

On-line sample preconcentration and matrix removal can be achieved with the use of reduced dispersion FI manifolds. Olsen *et al.* utilised microcolumns packed with Chelex-100, to effect separation and enrichment of trace analytes from seawater by FI-AAS (56). Similar on-line pre-treatments have been employed using FI in conjunction with ICP-ES (57), considerably improving its analytical capability. Other possibilities for on-line preconcentration include solvent extraction (58) and hydride generation (59).

In summary, the combination of FI-based methodology and ICP spectrometry has considerable versatility and efficacious advantages, when compared to the conventional

ICP technique. It can be utilised to perform sample enrichments and overcome matrix effects and spectral interferences.

1.6 Developments of On-line Microcolumn Preconcentration with Flow Injection - Atomic Spectrometry

Atomic spectrometric methods of analysis, including atomic absorption spectrometry (AAS), inductively coupled plasma-emission spectrometry (ICP-ES) and inductively coupled plasma-mass spectrometry (ICP-MS), are prone to matrix interferences. The use of ion-exchange for enrichment and/or matrix removal prior to spectrometric detection is on the increase. Microcolumns of exchange material provide a relatively cheap, robust and reproducible method of pre-treatment, when incorporated on-line using flow injection (FI). Therefore a review of on-line microcolumn preconcentration procedures combined with atomic spectrometric detection is provided in this section. Many reagents have been developed, including anion, cation and chelation exchange resins. The most common chelating resin is Chelex-100, which contains iminodiacetic acid functional groups, but several others exist including 8-quinolinol. Cation exchange resins include AG 50W and Amberlite 120, both of which contain sulphonic acid functional groups, and anion exchange resins such as Dowex 1 and Amberlite IRA 400, contain quaternary ammonium functional groups. A novel method of ion exchange is possible with the use of activated alumina, which is amphoteric and can thus function as both an anion and cation exchanger. Review articles are available concerning on-line microcolumn preconcentration/separation (60-62). Specific applications of this technique to waters and seawater are also invaluable (63-64).

1.6.1 Iminodiacetic Acid Based Resins

The original study in which a microcolumn was incorporated on-line, in a flow injection system, for the preconcentration and separation of trace analytes from a complex matrix, prior to AAS detection, was described by Olsen *et al.* in 1983 (56). The

microcolumn contained the chelating resin Chelex-100, which has iminodiacetic acid functional groups, and the complex matrix was polluted seawater.

Initially a single line flow injection manifold was utilised, as a method of direct sample introduction, similar to Fig.1.25. A calibration range for the analytes Cu, Cd, Pb and Zn was established, with the injection of 150 µl aliquots of a series of standards, into a continuous non-segmented carrier stream of 5 x 10^{-4} M H_2SO_4. The AAS recorded the absorbance continuously. This technique was employed to investigate the effect of the seawater matrix. A succession of Pb standards were prepared, with and without the addition of 31.3 g l^{-1} NaCl, a simulation of the seawater matrix, and injected into the carrier stream. The limit of detection (LOD) obtained for both was 32 µg l^{-1}, hence the NaCl produced no effect. The LOD's calculated for Cu, Cd and Zn were 5, 9 and 10 µg l^{-1} respectively.

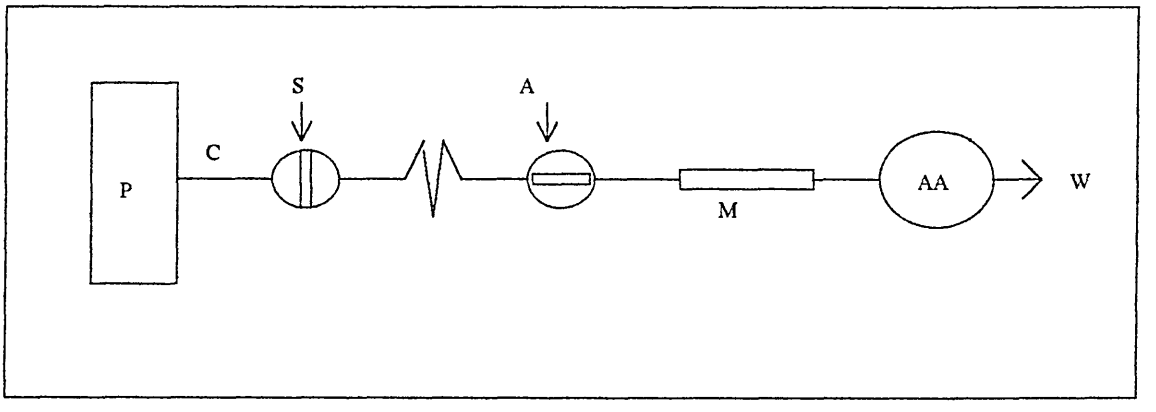


Fig.1.25 A schematic diagram of a single line FIA-AAS manifold for on-line preconcentration using a microcolumn of Chelex-100. C is the carrier solution, ammonium acetate. S is a valve and the point of sample injection (1 ml). Elution is effected by the addition of 180 µl of 2M HNO_3 from valve A. M = microcolumn, W = waste. Reproduced from Reference 56.

The FI manifold was modified, and a microcolumn of Chelex-100 incorporated into the system, to achieve on-line preconcentration. This is shown schematically in Fig.1.25. The carrier solution, 0.05 M ammonium acetate, mixed with the 1 ml sample volume, during the passage from injection point to the microcolumn. The trace analytes were retained on the column, which could be subsequently eluted, with the introduction of 180 µl of 2 M HNO_3. Calibration was achieved with the injection of a series of

standards, in the range 20-500 $\mu g\ l^{-1}$, which were preconcentrated and then eluted. Two peaks were observed during each cycle, the first during the enrichment period. This was attributed to non-selective absorption of light, emitted by sodium atoms from the sample matrix, an interference which could be eliminated with background correction. The influence of pH on recovery was investigated. The carrier stream was adjusted to pH 7, 9 and 10. The recovery increased with increasing pH, the optimum being 10, as incomplete deposition occurred for pH 7 and 9. However, problems were encountered with this configuration. The Chelex-100 suffered extreme volume changes when transformed from the NH_4^+ to the H^+ form. Hence, tighter and tighter packing occurred downstream, due to the uni-directional flow, causing blockage. Also, the centre of the sample zone was insufficiently mixed with the carrier solution, inducing incomplete deposition for the seawater samples, which had been acidified for preservation. A dual-line system was adopted. This arrangement permitted, continuous addition of ammonium acetate to the aqueous carrier stream and passage through a mixing coil, which ensured the stabilisation of pH along the whole length of the injected sample zone, and, the flow to change direction from the preconcentration step to the elution step, which alleviated the downstream blockage problem. Another feature of this system is, that the sample passes through the microcolumn and then to waste. Hence, the sample does not enter the AAS and background correction is no longer necessary. The LOD's obtained by this technique were 1 $\mu g\ l^{-1}$ for Cd and Zn and 10 $\mu g\ l^{-1}$ for Pb. Results produced by this technique were compared to results obtained by potentiometric stripping analysis (PSA). The enrichment capability of the microcolumn was studied. Sample volumes between 4-5 ml yielded incomplete deposition, but volumes up to 2 ml gave complete deposition and hence produced good recoveries.

Due to the large number of samples requiring analysis, the FI manifold was additionally modified. An integrated microconduit provided improved automation, yielding a design that was less labour intensive. It is noted that methods for determining trace analytes in natural waters and seawater are flawed. A substantial proportion of the analyte may be present in bound form (e.g. a colloidal form), insoluble in acid or in the

form of a strong complex which is not dissociated. Chelex-100 adsorbs the free or labile form of the analyte only; bound forms are inaccessible. Hence the results produced for seawater by Olsen *et al.* (56) are not necessarily a measure of the total analyte content present in the sample.

Hartenstein *et al.* utilised a microcolumn of Chelex-100 to increase the sensitivity for multi-element measurements by ICP-ES (65). The FI manifold permitted continuous aspiration of water to the plasma, effectively washing the nebuliser and stabilising the plasma, with counter-current pumping of sample and eluent preventing tight packing of the resin. A parallel, dual column system was in operation, competently doubling the sampling frequency to 30 h^{-1}. Sample loading times ranged from 40-240 s, which at a flow rate of 9.5 ml min^{-1}, was equivalent to 6-36 ml. Samples merged with the buffer stream (0.5 M ammonium acetate). Inductively coupled plasma operating parameters were initially optimised for the FI method. The compromised optimal conditions found for conventional ICP-ES were consistent with those found for the FI-ICP-ES method, with respect to observation height and incident power. Factors influencing the performance of the column were then investigated. The pH of the sample was increased from 5 to 9. The analytical sensitivity for the analytes Ba, Be, Cd, Co, Cu, Mn and Ni increased with increasing pH. However, Al, Fe and Pb showed maximum sensitivity at $pH < 8$. This was probably due to the formation of hydroxides of these analytes at high pH, which were not retained by the column. A compromise of pH 9 was chosen to ensure good deposition for every analyte. The influence of sample flow rate was studied. Increased signals were observed for the analytes as the flow rate was increased from 4 to 9.5 ml min^{-1}. However, the signals decreased when the rate was raised to 11 ml min^{-1}. The mean retention efficiencies calculated for 9.5 and 11 ml min^{-1} were 55 and 45 % respectively, indicating that a possible kinetic effect was responsible for the signal decrease, as the sample volume had remained constant. The kinetic effect relates retention efficiency to the time the sample is in contact with Chelex-100. The on-line microcolumn preconcentration FI-ICP-ES system, yielded reproducible results with a 6 % RSD at the 10 $\mu g\ l^{-1}$ level, for every analyte except Al. Signal enhancements between

10-30 fold were achieved for every analyte except Al, improving detection limits on average by 1-2 orders of magnitude, in comparison with conventional ICP-ES. The technique also provides, on-line sample treatment, elimination of chemical or spectral interferences from the matrix, elimination of matrix introduction into the nebuliser, ensuring no blockages, and possible speciation of trace analytes. Finally, it was suggested that the technique is capable of distinguishing between labile and inert forms of trace analytes in different types of water sample.

Hartenstein *et al.* (66) improved their system to obtain 100 % recovery of the trace analytes Ba, Be, Cd, Ca, Co, Cu, Pb, Mg, Mn, Ni and Zn, utilising the FI-ICP-ES method for the determination of trace analytes in tap and rain water. A single Chelex-100 microcolumn was incorporated into the FI manifold and standards were matrix matched by adding appropriate levels of Ca, Mg, K and Na. To achieve 100 % recovery, several parameters were studied. The sample flow rate was adjusted to 8, 9.5 and 11.5 ml min^{-1}, producing mean recoveries of 70, 55 and 45 % respectively. Lower flow rates may have yielded improved recoveries, however, 8 ml min^{-1} was chosen as optimum, as one of the objectives was to achieve maximum preconcentration in the minimum period of time. Microcolumn volume was optimised by increasing the length of the column. Volumes of 0.2, 0.3, 0.4 and 0.5 ml were compared. The volume 0.2 ml produced a lower peak area than 0.3-0.5 ml. The chosen volume was 0.3 ml, as this column required less time for elution, implying greater sampling frequency could be achieved with this column. The internal diameter (i.d.) of the 0.3 ml volume microcolumn was next optimised. It was observed that the smaller the diameter of the column, the greater the peak area. However, blockage of the column occurred, due to the tight packing problem of the resin, when the diameter studied was 1.65 mm. Hence, 1.85 mm i.d. was selected as optimum. The recovery obtained for the optimised Chelex-100 microcolumn, using a sample flow rate of 8 ml min^{-1}, for a 5 min sampling period, was 100 %. The enrichment capability of the microcolumn was investigated. Factors of 10-15 fold min^{-1} were observed. Also, although the elution volume was 0.2-0.5 ml, elution required 30-50 s to complete, which is equivalent to 0.5-0.8 ml. Hence, dispersion of the eluted

sample plug had occurred. The elution tubing volume was minimised with respect to length and i.d. Finally, it was shown that the majority of the analytes were more easily retained on Chelex-100 than the alkaline earth metals. This was expected from their respective selectivity coefficients. However, the exception was Pb. The assumption was that the optimum pH for deposition of Pb was < 8, this study was carried out at pH 9.2. Further investigations concluded that the presence of significant proportions of the alkaline earth elements would not affect column performance, which is essential for the analysis of natural waters. Results were presented for the analytes Ba, Cd, Co, Cu, Mn, Ni and Zn in tap water by the microcolumn enrichment technique with ICP-ES detection. The analytes Cu, Mn and Zn were also determined by conventional ICP-ES but the concentrations of the remaining analytes were beyond the detection capability of the technique. Tap water spiked with known concentrations of the mentioned analytes was also analysed. The recoveries obtained for the spiked samples were between 95-100 %. However, the Mn concentration obtained by FI-ICP-ES was only 10 % of the value produced by ICP-ES. This was reputed to be due to the possibility that only labile species of Mn were retained by the Chelex-100. Similar results were found for the rain water samples. Recoveries of 90-110 % were calculated for the remaining analytes. However, the Mn recovery was only 25 %, indicating that a proportion of the spiked Mn was chemically converted by the matrix to a form which was not retained by Chelex-100. Hence, it should be noted that on-line microcolumn preconcentration with Chelex-100 and ICP-ES detection may only quantify labile species of the analyte, which may be a useful tool in speciation studies.

Liu *et al.* utilised a microcolumn of Chelex-100 in a fully automated FI-AAS system, which produced a high sampling frequency with highly reproducible results (67). In this procedure, complexing agents such as cysteine and ethylenediaminetetraacetic acid (EDTA) were used for elution. This was possible, as their affinity for the trace analytes was greater than that of Chelex-100. Hence, the extreme volume changes encountered with the use of nitric acid, were eliminated, the resin did not pack tight and blockage was prevented. Microcolumn dimensions, resin particle size and sample and

elution flow rate were optimised to produce maximum sensitivity. Utilising ammonium acetate, buffered at pH 5.2 as the carrier stream, the effect of sample flow rate on peak height was studied. Microcolumns of different dimensions, ranging from 50-150 mm in length and 1.5-3 mm i.d., packed with Chelex-100 of different particle sizes (p.s.), for example 50-100 or 100-200 mesh were used. Retention efficiencies of 100 % were achieved for a 3 mm i.d., 50 mm column containing 100-200 mesh resin and a 3 mm i.d., 150 mm column, containing 50-100 mesh resin, up to sample flow rates of 15 ml min^{-1}. The former column produced a larger peak height, due to a smaller dispersion of the elution plug. The optimum elution flow rate was 6 ml min^{-1}, with the peak area decreasing at higher flow rates. Eluent concentration was also optimised. Complete elution of Cu was achieved with 0.01 M cysteine, but incomplete elution was observed for Cd, Pb and Zn. EDTA (0.025 M) completely eluted Cd and Pb, but incomplete elution was found for Mn, Cu and Zn. The presumption was that the reaction kinetics were too slow, therefore, a 30 s stop period was incorporated into the elution cycle, which yielded complete elution for Mn, Cu and Zn. The analytes could be sequentially eluted using these procedures, for example, Cu could be eluted first with 0.02 M cysteine, then Mn could be eluted with 0.02 M EDTA, using the stopped flow configuration. Results for Cd, Cu and Mn were presented. Detection limits of 0.09 μg l^{-1} for Cd and Cu and 0.08 μg l^{-1} for Mn, with 60-80 fold preconcentration, were achieved using a 10 ml sample volume. Precision for concentrations above 2.5 μg l^{-1} was between 2-4 % RSD. However, when the technique was applied to the determination of Cu in river water, poor recovery was obtained. This was assumed to be due to the possibility that the sample matrix converted the added Cu to a form inaccessible to the Chelex-100.

Milosavljevic *et al.* used a FI-AAS system, incorporating a Chelex-100 microcolumn, for the indirect determination of ethylenediaminetetraacetic acid (EDTA) (68). The column was saturated with Cu(II) solution, prior to the injection of a standard or sample containing EDTA. Cu(II) ions were displaced in proportion to the concentration of EDTA, which were then detected by AAS. The carrier solution and

sample volume were investigated to achieve maximum sensitivity. NaCl and acetate buffer required long wash out periods for the excess Cu(II) regeneration solution. Ammonia buffer (0.05 M pH 9.3) indicated rapid wash out times and hence was chosen as the carrier solution. A sample volume of 200 µl was selected as optimum, because the sensitivity did not increase significantly at higher volumes. It was observed that the Chelex-100 microcolumn required the injection of regeneration solution (Cu(II) solution) following each injection of sample or standard solution, otherwise a decrease in sensitivity ensued. This technique could achieve a detection limit of 0.1 mg l^{-1} for EDTA and indicated good reproducibility, with a RSD of 1.4 % at the 0.5 mg l^{-1} level. A recovery of 96 % was observed, which implied EDTA displaced 96 % of the Cu(II) ions expected. A variety of common inorganic anions, which form weak complexes with Cu(II), for example Cl^-, Br^-, CO_3^{2-}, PO_4^{3-}, NO_3^- and SO_4^{2-}, were studied as possible interferences on the AAS signal. Only Na_2CO_3 increased the AAS signal, when present in solution at a level > 5 %. A similar study was carried out for organic ligands, which form strong complexes with Cu(II). Glycylglycine (10^{-4} M) increased the absorbance, effectively displacing Cu(II) from Chelex-100. This technique could possibly be applied to the study of metallic ion pollutants in the environment.

Garcia *et al.* compared the use of four resins, Chelex-100, Dowex 50W-X2, Amberlite IRA-400 and the synthetic resin Kelex adsorbed on Amberlite XAD-7, for the on-line preconcentration and determination of Al in dialysis concentrates, by AAS and ICP-ES (69). The influence of pH on retention efficiency was studied. The optimum pH for Chelex was 5-6, Dowex 1-2, Kelex 6-7 and Amberlite 7. Buffered to the required pH, the influence of eluent type, (NaOH, KOH, HCl or HNO_3) and eluent concentration, on absorbance was investigated. Chelex required 2.5 M NaOH (100 µl) as eluent for optimum recovery, hence the drastic volume changes associated with nitric acid eluent were eliminated. Dowex required 2 M KOH and Amberlite 1M NaOH. Kelex was rejected from further study as the exchange rate for the resin was too slow. The effect of the high salt matrix on retention capability was studied. The addition of sodium chloride and sodium acetate had no effect on the retention capability of Chelex. The Al signal

increased with increasing concentration of NaCl, up to 3 $\mu g\ l^{-1}$ for the resin Amberlite. Therefore 3 $\mu g\ l^{-1}$ NaCl was added to samples and standards prior to analysis. Also, acetate concentrations > 40 $\mu g\ l^{-1}$ decreased the Al signal. The Al signal for Dowex was progressively inhibited above concentrations of 20 $\mu g\ l^{-1}$ acetate and 15 $\mu g\ l^{-1}$ NaCl. The addition of Ca, Mg, K and Na had no effect on the retention capability of Amberlite. Both Ca and Mg bind weakly to Chelex, but were effectively eluted with the carrier solution (CH_3COONa-CH_3COOH, pH 5.5). Dowex was rejected from further study, as Ca and Mg, significantly reduced the recovery of Al. Hence, both Chelex and Amberlite can be used for the analysis of dialysis concentrates, except, in the case of Amberlite, when the acetate concentration in the sample exceeds 40 $\mu g\ l^{-1}$. The detection limits found for Amberlite and Chelex were 0.02, 0.003 $mg\ l^{-1}$ and 0.015, 0.003 $mg\ l^{-1}$ respectively by AAS, ICP-ES. Reproducibility and agreement for reference dialysis concentrates were good.

Temprano *et al.* utilised a microcolumn of Chelex-100 in a FI-AAS system for the determination of Co in digested glass samples (70). The pH range for optimum retention of Co on the resin was 4.5-10. A pH of 7 was selected to prevent potential matrix interferences of the Co signal. For example, a major element in glass samples is Al, which has optimum retention on Chelex between pH 4.5-6.5. A variety of eluents at different concentrations were investigated, for the elution of Co from the resin, including NaOH, HNO_3, HCl and H_2SO_4. Basic solutions did not elute Co. A 200 µl volume of 5 M HNO_3 was selected as optimum. The effect of flow rate on recovery remained unchanged between 2-4 $ml\ min^{-1}$. A flow rate of 2.5 $ml\ min^{-1}$ was chosen for further studies. The effect of ionic strength on the Co signal indicated that additions of NaCl up to concentrations of 0.5M, had no effect on recovery of Co. The enrichment capability of two microcolumns, both 3 mm i.d. either 5 or 10 cm in length, was evaluated. The peak area calculated was similar for both, hence the 10 cm column was chosen. The recovery obtained for a 1 ml sample volume was 102 ± 5 %. The detection limit was 20 $\mu g\ l^{-1}$. A 4 fold preconcentration was achieved and an RSD of 1.5 % was produced at the 0.5 $mg\ l^{-1}$ level. The volume changes associated with this resin were encountered in

this investigation and it was recommended that the column be renewed following 50 injections. Finally, the major constituents of glass were investigated to determine if they had any effect on the recovery of Co. The Co:Fe ratio present in glass samples can be up to 1:500. However at ratios above Co:Fe 1:100 the recovery of Co was effected. Hence 0.5 % sodium citrate was added to all standards and samples, effectively masking the Fe interference. The interference from Si was considerable, therefore the digestion process was modified to ensure almost complete removal of this interfering element. The results obtained for two glass samples by microcolumn preconcentration and FI-AAS detection agreed well with conventional ICP-ES.

Comber *et al.* developed an on-line digestion system, combined with microcolumn preconcentration using Chelex-100 and FI-AAS detection, for the determination of Cu complexes in natural waters (71). Three ligands, (glycine, nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA)) were utilised to demonstrate the effect of the on-line digestion system. Over 90 % of the complexed Cu was recovered in the presence of any of the three ligands, when on-line UV photolysis was utilised. When UV photolysis was not utilised, the recovery of Cu was reduced to 85, 45 and 2 % in the presence of glycine, NTA and EDTA respectively. Hence, the speciation of Cu can be studied using this procedure. The technique was applied to an Aquacheck sample. The result obtained, 71 $\mu g\ l^{-1}$, was similar to the certified value 69 $\mu g\ l^{-1}$.

Treit *et al.* incorporated a microcolumn of Dowex 50W-X8 into a FI system with AAS detection, for the determination of free Cu in solution (72). Dowex has the same functional groups as Chelex-100 (iminodiacetic acid). This technique was applied to the ethylenediaminetetraacetic acid (EDTA) titration of 2×10^{-5}M Cu^{2+}. In this approach, the sample solution containing Cu^{2+} ions is passed through the Dowex microcolumn until complete breakthrough of the free Cu has occurred. Hence until equilibrium between the resin and the sample solution has been achieved. The sorbed Cu is subsequently eluted from the resin and measured by AAS. The effect of eluent concentration and pH on the Cu signal were investigated. An inert precious metal

nebuliser was not available, hence concentrated acids could not be used for elution, therefore, EDTA was selected as the eluent. Optimum sensitivity was achieved with 0.02 M EDTA at pH 3.5. EDTA did not exhibit the same behaviour, when applied to the elution of Ni from the Dowex resin. This was assumed to be due to a slower complexation rate, and the high selectivity of the technique. Investigations indicated that a sample volume of 41 ml was required to completely fill the available sites on 2 mm column, hence, 7.5 min was required for analysis, at the selected flow rate of 5.5 ml min^{-1}. This system could be applied to the determination of free analytes in natural and waste waters and biological samples.

Tabani and Kratochvil (73) provided a system design strategy for micro computer controlled data acquisition/processing, of an ion exchange AAS system for ion speciation. Robots were used for sample preparation and handling in this on-line speciation FI-AAS technique. A microcolumn packed with Dowex 50W-X8 was incorporated into the system. The resin retained the labile species of the analytes Ni and Cu, whilst the bound species were not retained.

Hewavitharana *et al.* (74), used a similar approach to Treit *et al.* (72) to determine free Ca in the presence of complexed or bound Ca, in urine samples. In this method, 0.75 M $NaNO_3$ was added to each sample and standard solution, to achieve similar retention behaviour on Dowex 50W-X8, before elution with 2 M HNO_3 and detection by FI-AAS. The time required to fill all available sites, and hence reach equilibrium, was investigated for the concentrations 0.5-5 mg l^{-1} Ca, at a constant flow rate of 4.5 ml min^{-1}. The time required to fill all available sites did not significantly change with increasing Ca concentration. However, the time required did significantly decrease from 12 to < 1min when the $NaNO_3$ solution was increased from 0.1-0.75 M. Hence 0.75 M $NaNO_3$ was selected as optimum concentration. The effect of pH in the range 5-7 did not change the Ca signal observed. The resin was shown to selectively retain free Ca in the presence of Ca-citrate and Ca-phosphate complexes, under present experimental conditions. The technique was applied to the determination of free Ca in urine samples, the results of which were consistent with the free Ca levels expected.

Hewavitharana *et al.* developed this technique further (74), to determine free Ca and Mg in solutions containing complexed forms of these analytes (75). The time required for the equilibration of the Dowex 50W-X8 microcolumn was examined, using a 2.5 x 10^{-5} M Ca^{2+} or Mg^{2+} solution in 0.1 M KNO_3 at pH 5.2 ± 1. Less than 3 min were required, at a flow rate of 5 ml min^{-1}. The resin indicated high selectivity for free Ca and Mg only, in the presence of Ca or Mg acceptor ligands, such as citrate or phosphate.

Kumamaru *et al.* used a suction-flow on-line microcolumn preconcentration technique for sensitivity enhancements with ICP-ES (76). The resin Muromac A-1, which has iminodiacetic acid functional groups similar to Chelex-100, was used to enrich Cd by a factor of 25 fold. The procedure was applied to the determination of Cd in certified biological reference materials and waste water samples. A 5 ml volume of sample or standard solution was added to a teflon suction cup. The solution was sucked into the FI system and merged with buffer, 0.1 M sodium citrate at pH 5, before passing through the microcolumn. The eluent 1M HCl was also sucked into the system, from the cup, to elute Cd from the microcolumn. The nebuliser flow rate of 4.7 ml min^{-1} was utilised to achieve optimum sensitivity. Microcolumn dimensions, i.d. and length, were optimised. A 1.6 mm i.d., 10 cm column produced excellent sensitivity. The effect of eluent volume on signal intensity was also investigated. Maximum sensitivity was realised with 0.25 ml of 1M HCl. The detection limit obtained for Cd with this system was 0.05 μ gl^{-1}. The RSD for 0.1 mg l^{-1} Cd was 2.2 % and the sample throughput was 25 h^{-1}. The application of this procedure to the determination of Cd in the National Bureau of Standards reference material Bovine Liver, and the certified reference material Pepperbush, issued by the National Institute for Environmental Studies, showed good agreement. The results obtained for waste water samples were similar to those produced by graphite furnace AAS.

Hirata *et al.* utilised a microcolumn of Muromac A-1 to increase sensitivity for Al, Cr(III), Fe(III), Ti and V, by on-line FI-ICP-ES (77). These analytes form hydroxides and precipitate at alkaline pH, even in the presence of buffer solution, hence

it is necessary to preconcentrate them at acidic pH. Initially compromise optimal conditions were investigated for the ICP-ES. A 16 mm observation height and 1.3-1.4 kW incident power were selected for the 5 analytes. The sensitivity increased with increasing pH, between 2.5 and 5, hence a pH between 3 and 4 was selected. A decrease in sensitivity was observed at higher pH, which was presumed to be due to the formation of hydroxides of the analytes, which were not retained by the resin. However, the Cr and Ti signals did increase above pH 8, possibly due to the retention of a proportion of the hydroxides formed by these analytes. The analyte signals increased as the sample flow rate increased from 3-9 ml min^{-1}, therefore 6 ml min^{-1} was selected. The Muromac resin, buffered with 0.5 M ammonium acetate at pH 3.8, improved the enrichment of Cr by a factor of 3, when compared to Chelex-100 under the same conditions. This may have been due to differences in surface area of the resins, implying Muromac had more available sites for retention. It was also shown that smaller i.d. microcolumns improved sensitivity, therefore a 2 mm i.d. column was chosen. Signal enhancements between 34-113 fold were observed for peak height for this system. Al was enhanced by a factor of 34, which was low compared to the remaining analytes. It was found that Al chelated by the resin, was only partially eluted with 2 M HNO_3, even 6M HNO_3 could not completely recover the chelated Al. Cr however, was enriched 113 fold, which was considered to be due to Cr weakly chelating with Muromac and therefore was easily eluted. The detection capability of this technique was 1 $\mu g\ l^{-1}$ for Cr, Ti, V and Fe and 10 $\mu g\ l^{-1}$ for Al, with RSD's within 5 %. Interference effects on the Cr determination, from other inorganic ions were investigated. Although Mg present in solution was not completely retained by the resin under these conditions, chelated Mg eluted from the microcolumn increased the Cr signal, as did Mn. Al reduced the Cr signal, possibly due to competition for available sites. This technique could be applied to clinical and environmental samples.

Hirata *et al.* utilised an automated on-line preconcentration FI-AAS system, containing a microcolumn of Muromac A-1, to improve sensitivity for the analytes Cd, Zn, Cu, Mn, Pb, Fe and Cr (78). The system had a sample throughput of 13 h^{-1},

detection limits in the range 0.14-2.1 $\mu g\ l^{-1}$, and, for a 20 ml sample volume, enrichment factors between 90 and 180 fold. To prevent dispersion of the eluent plug, the tubing length, from the point of eluent injection to the microcolumn, was optimised at 25 cm and Ar segmentation improved precision. Smaller i.d. microcolumns improved analyte signal, however, 4 mm i.d. was selected, to prevent the pressure in the FI system becoming too high and leakages developing. A 7 cm column permitted adequate analyte retention. The particle size and quantity of Muromac A-1 were optimised, with 50-100 mesh and 50 mg selected. The optimum sample and elution flow rates were 5 and 4.85 ml min^{-1} respectively. The effect of pH on analyte signal was studied. The analytes Cu, Zn, Pb and Fe(II) indicated optimum recovery in the pH range 1-5, Cd and Mn in the pH range 2-6 and Fe(III) and Cr(III) at pH 1. The enrichment capability was investigated for sample volumes between 5-20 ml. Optimum preconcentration factors were achieved with 20 ml volumes. The analytes Cd, Mn and Pb indicated greater enhancements than Cu, however, when the eluent concentration was increased from 2 M HNO_3 to 7M, the Cu enrichment improved. This suggested that Cu was retained more strongly by the resin, compared to Cd, Mn and Pb. This procedure was applied to the determination of Cd and Cu in the certified reference materials Tomato Leaves, issued by the National Bureau of Standards, and Pepperbush, Pond Sediment and Mussel, issued by the National Institute for Environmental Studies. Initially, the effect of potential interferences from matrix elements was examined. A reduction in the recovery of Cd was observed in the presence of Al and Ti, however at pH 5, 97 % was recovered. It was therefore necessary to matrix match the standard solutions, to obtain reliable results for Cd in the mentioned materials. A reduction in the recovery of Cu was observed over the entire pH range required for Cu retention. Hence, a standard addition procedure was adopted for the analysis of the above samples. The results attained agreed favourably.

Caroli *et al.* incorporated a microcolumn of iminodiacetic acid modified ethylcellulose (IDAEC) into a FI system, with ICP-ES detection, for the determination of Cd, Co, Cu and Pb in water, seawater and urine samples (79). The performance of the IDAEC resin was compared to Chelex-100 and (CPPI), carboxymethylated

polyethyleneimine-polymethylenepolyphenylene isocyanate, with respect to enrichment factor, analytical throughput and recovery. The sample flow rate was investigated and selected at 2.5 ml min^{-1}. Above this flow rate, the pressure on the system became too great. A 20 mm i.d., 50 mm length microcolumn was also selected to ensure the pressure on the system was not problematic. The effect of eluent (2 M HNO_3) volume, on peak height was studied. Volumes exceeding 100 µl yielded a reduction in peak height, which was presumed to be due to dispersion of the eluent plug. The parameters investigated above were utilised for CPPI and Chelex-100. Under optimal conditions, the recovery of the 4 analytes from each resin, was studied and compared to the batch-wise process of analysis. The batch operation produced superior recoveries, but was also laborious and time-consuming. The performance of the resins was similar, except IDAEC retained a greater proportion of Cd and Pb, which was assumed to be due to the fibrous nature of the resin, in that, it was easier to pack, had more available sites and improved exchange kinetics. Also, the enrichment factors produced were between 45-60, 38-47 and 23-49 for IDAEC, CPPI and Chelex-100 respectively and the detection limits calculated for the 4 analytes, in 3 different matrices, were equivalent or superior for IDAEC when compared to the other resins. Hence IDAEC is the most efficient resin. The technique was applied to samples RM 4121 and 5424 which were issued by the World Meteorological Organisation, which indicated that the procedure was practicable.

Heithmar *et al.* utilised a macroporous iminodiacetate resin (IDA), to preconcentrate the analytes Ti, V, Mn, Fe, Co, Ni, Cu, Cd and Pb from synthetic matrices and waste waters, by FI-ICP-MS (80). The samples were digested in a microwave oven, prior to analysis, to remove natural organic chelating ligands. The analytes were retained by passage through the IDA microcolumn. Matrix elements, such as Ca and Mg were removed from the column with a pre-wash of 2 M ammonium acetate. The trace analytes were subsequently eluted with 1M HNO_3. The internal standards, Y and Bi, were introduced and mixed with the eluent, downstream from the microcolumn, before ICP-MS detection and determination. The effect of the

concentration of the buffer solution, on the retention of the analytes was investigated. Ammonium acetate concentrations from 0.03-0.25 M indicated incomplete deposition of the analytes. Above 0.25 M however, complete deposition was observed. The chosen concentration of buffer was 2 M, which ensured variations in sample pH, were effectively buffered to pH 5.2 ± 0.2. The preconcentration efficiency was studied, and the result for every analyte was between 120-150 %. Investigations indicated that the NH_4^+ ion, eluted from the microcolumn with the trace analytes, was providing pronounced signal enhancements. The detection limits obtained for this technique are given in Table 1.1.

Analyte	Isotope	Detection Limit µg/l
Ti	48	0.04
Ti	49	0.02
V	51	0.006
Mn	55	0.006
Fe	54	1
Fe	57	0.3
Co	59	0.0004
Ni	60	0.01
Ni	62	0.02
Cu	63	0.004
Cu	65	0.007
Cd	111	0.006
Pb	208	0.005

Table1.1 Detection limits obtained for on-line microcolumn preconcentration with ICP-MS detection. The microcolumn contained the reagent IDA. Reproduced from Reference 80.

Two complementary approaches were suggested to improve these detection limits. The analytes V, Cu, Cd, Pb and Ti indicated, that the major contribution to the blank signal was produced from the analytes themselves. Hence, the detection limits could be improved by significant reagent purification. The remaining analytes produced blank signals that were predominantly from other sources, such as molecular ions, and an increase in the sample size could therefore improve detection limits. The reproducibility and the linear range of the technique were favourable. The analyte Zn was abandoned at this stage due to elevated blank signals. It was also observed that the analytes V, Cu, Ti

and Co were not completely eluted in the first elution.

The study was completed with the analysis of simple synthetic matrices. The degree of residual interference from molecular ions of the alkali, alkaline earth elements and chloride, was examined as a function of pre-elution wash out time. Only Ca at 2000 mg l^{-1} produced a residual spectral interference, at wash out times greater than 1 min. This was the apparent 1.8 μg l^{-1} ^{48}Ti signal, produced from 0.03 % ^{48}Ca remaining on the microcolumn. The samples were also analysed by direct nebulisation, utilising FI without microcolumn preconcentration. Every isotope except ^{54}Fe, was subjected to a molecular ion interference, produced from the matrix elements. The recoveries obtained from a 10 μg l^{-1} spiked synthetic solution, were between 85-115 % for the IDA enrichment technique, except ^{55}Mn, 81 % and ^{48}Ti, -34 %, in the presence of high Ca. The recoveries obtained for the direct procedure were poor for most of the analytes. Hence, the developed preconcentration procedure was highly beneficial. Finally, the on-line enrichment technique was applied to the analysis of waste waters, with and without microwave digestion. The results indicated that digestion of the samples was required to obtain good recoveries for every analyte, from the sample matrix.

Ebdon *et al.* incorporated a iminodiacetate (IDA) microcolumn into a FI-ICP-MS system to preconcentrate the trace analytes V, Mn, Cu, Zn, Cd and Pb in biological materials (81). The analytes were separated from interfering polyatomic species, produced by matrix elements. Recoveries of 100 % were attained for the analytes Mn, Cu, Cd and Pb, 90 % for V and 85 % for Zn, from the certified materials 1566 Oyster Tissue and Tort-1 Lobster Hepatopancreas, issued by the National Institute of Standards and Technology. Precision of replicate analysis was 3-4 % and detection limits between 0.6-9.9 μg l^{-1} were achieved. The samples were digested in a microwave oven and had a final acid concentration of 5 %. Therefore, the concentration of buffer required to ensure complete deposition of the analytes onto the IDA resin, and complete elution of the alkali and alkaline earth elements was investigated. A concentration of 1.5 M ammonium acetate at pH 5.3 was selected. The samples were analysed directly and with microcolumn preconcentration. The interferences $^{32}SO_2^+$ and $^{32}S_2^+$ on the analyte isotope ^{64}Zn and $^{35}ClO^+$ on the analyte isotope ^{51}V, were completely eliminated with

the microcolumn procedure. This technique was applied to the analysis of Cr. Only 50 % of this analyte was chelated. Following extensive experimentation, this was increased to 60 %, but precision was poor. It was suggested that Cr had formed complexes with the buffer solution which were not retained by the resin. The technique was applied to the analysis of the above certified reference materials. Reasonable agreement was obtained with the certified values for most of the analytes. The concentrations obtained for Cu and Zn in Tort-1 were low and this was presumed to be due to the number of ions in the digest exceeding the capacity of the column. The sample was diluted and the analysis repeated. The results obtained were far superior, suggesting that the concentration of analytes in the original sample had exceeded the capacity of the microcolumn. Hence, for samples of high concentration, dilution of the sample or longer columns, containing more resin are required for analysis.

Prakash *et al.* utilised an automated preconcentration unit, in the comparison of two ion-exchangers by FI-ICP-ES (82). The chelaters EDTrA-cellulose, which contains iminodiacetate functional groups and HSO_3oxine-cellulose, containing 8-hydroxyquinoline functional groups, were packed into microcolumns and incorporated on-line, for the determination of the analytes Al, Be, Cd, Co, Cr, Cu, Ga, In, Mn, Ni, Pb, V and Zn. Initially the exchangers were compared using column chromatography, with subsequent determination by ICP-ES. The effect of pH on the retention of the analytes was investigated, with and without the presence of Ca^{2+} (0.1 M). Quantitative recovery was attained for the analytes Cd, Co, Cu, Ni, Pb, V and Zn, with the HSO_3oxine column and Cd, Co, Cu, In, Mn, Ni, Pb, V and Zn, with the EDTrA column, at pH 5.5. These analytes were enriched up to factors of 40 fold and detection limits between 2-200 $\mu g\ l^{-1}$ were attained. The chelaters performed efficiently on-line, increasing sample throughput from 2-5 h^{-1} to 10-30 h^{-1} and lowering the detection limits achieved.

Schramel *et al.* utilised a PC controlled on-line preconcentration system (TRACECON, Knapp GmbH, Graz, Austria), for the determination of the analytes Cu, Fe, Zn, Cr, Ni, Mn and V, by FI-ICP-ES (83). A microcolumn of EDTrA-cellulose was incorporated into the system, for the enrichment and determination of the analytes in

biological and environmental certified reference materials. Detection limits in the range 0.05-1 $\mu g\ l^{-1}$ were achieved for 5 ml sample volumes. The effect of pH on the retention of the analytes was investigated. The retention of Cr, Fe and Mn was pH dependent, therefore pH 4 was selected as a compromise. The effect of eluent flow rate (3 or 6 ml min^{-1}) on elution of the analytes was studied. Elution was accelerated at 6 ml min^{-1} however, the analyte peak area was smaller. The elution flow rate selected was 3 ml min^{-1}. Increasing the sample flow rate from 2-6 ml min^{-1}, indicated that incomplete retention was occurring above 4 ml min^{-1}. Hence 4 ml min^{-1} was chosen as the sample flow rate. This technique was applied to the analysis of a variety of certified reference materials. Close agreement with certified values were attained, except for Cr. This was possibly due to speciation of this analyte. Hence, Cr(III) was retained by the EDTrA microcolumn, but Cr(VI) (anionic Cr) was not.

Israel *et al.* utilised the TRACECON automatic ion-exchange device, for the determination of the analytes Zn, Cd, Pb, Ni, Fe, Co, Mn, V and Cu, in pure alkali metal salts, by FI-ICP-ES (84). A microcolumn of EDTrA-cellulose was incorporated into the FI system, to perform analyte enrichment and matrix elimination. Detection limits in the range 0.0021-0.12 mg kg^{-1} were attained. Recoveries between 80-90 % were achieved for the analytes La, Zn, Co, Mn, Cd, Pb, Ni, Cu and Fe, at pH 5. A low recovery was obtained for V of 60-70 %. Al and Cr could not be recovered reproducibly at this pH and hence were excluded from further study. The results obtained for ultrapure KNO_3, by this procedure, a standard additions method and semi-quantitative ICP-MS, agreed closely with specified values. The exceptions were Co, which was at a concentration that precluded determination by FI-ICP-ES and Cu and Fe, which indicated lower concentrations than expected by ICP-MS, possibly due to analyte suppression by the matrix. The analysis of analytical reagent grade KNO_3 and KOAc, by this procedure and a standard addition method indicated reasonable agreement.

Ebdon *et al.* compared the use of two resins, in the determination of the alkaline earth and the first row transition elements, by on-line microcolumn preconcentration and FI-ICP-MS detection (85). A commercially available resin, (Metpac CC-1) and a

synthesized resin, (Xylenol Orange coated onto Dowex 1 X8) were packed into microcolumns and incorporated into the FI system, to effect matrix separation and preconcentration, in the analysis of brine samples and the certified reference material NASS-3. The residual NaCl present in the eluent, following the injection of a 30 % m/v brine sample and subsequent wash out period, was determined by AAS. It was found to be 0.3 %, a level the ICP-MS could tolerate as a FI eluent plug. Internal standards were added to the eluent, to improve calibration. Quantitative recovery of the alkaline earth elements was obtained at pH 11 with the Xylenol Orange column. However, incomplete retention of the first row transition elements was found at this pH. This procedure was therefore utilised to determine Mg, Sr and Ba in brine samples. Ca could not be determined, due to the polyatomic interferences Ar^+, ArH_2^+ and CO_2^+ at m/z 40, 42 and 44 respectively. The Metpac column indicated quantitative recovery for the analytes Mg, Sr, Mn, Cu, Co, Ni, V, Cr and Zn. Hence, this resin was utilised for the analysis of the certified material NASS-3. The results obtained were in reasonable agreement with the certified values. Clearly the resins behave differently, although they essentially have the same functional group, (iminodiacetic acid). It was assumed that the environment of the functional group was different, inducing dissimilar results. The Xylenol Orange column was efficient at retaining the alkaline earth elements, however the Metpac column was recommended, if the first row transition elements were required for analysis.

Bloxham *et al.* determined Mn, Co, Cu, Zn and Pb in seawater samples with FI and ICP-MS detection. An iminodiacetate based resin (Metpac CC-1) was utilised for analyte enrichment and matrix removal (86). Initially a number of key experimental parameters were optimised using AAS and AES, to ensure complete retention of the analytes and the elimination of the seawater matrix. These were buffer concentration (ammonium acetate) and pH, sample concentration and pH, and eluent (nitric acid) strength. At buffer concentrations < 0.01 M, significant retention of Na^+ was observed due to non-selective ion exchange. At concentrations between 0.01-1 M, Cu showed quantitative retention. A buffer concentration of 0.01 M was selected to minimise reagent contamination. The optimum pH of the buffer for quantitative retention of Cu

was 5.3. Undiluted seawater was utilised because Na^+ were not retained using the buffer conditions selected. The effect of sample pH on the Cu signal was investigated between pH 3 and 8. Complete retention of Cu was achieved at pH 8 only, hence this pH was selected for seawater analysis. An increase in eluent concentration from 0.5 to 2 M, produced sharper peaks. Therefore 2 M HNO_3 was selected for subsequent experiments. The buffer contained trace analyte impurities, which seriously degraded the detection limits obtained using ICP-MS detection. Hence, the buffer was purified off-line with the use of column chromatography. Three certified reference materials were then utilised to validated the proposed method (NASS-3, CASS-2 and SLEW-1). A standard addition technique was utilised. Good agreement with the certified values was achieved for Mn, Co, Cu, Zn and Pb, except Co in NASS-3. Good recoveries (94-105 %) were achieved for the analytes, except Co in NASS-3 (137 %) and CASS-2 (131 %). This was assumed to be due to reagent contamination.

1.6.2 Salicyclic Acid Based Resins

Fang *et al.* utilised an efficient FI-AAS system with on-line microcolumn preconcentration, for the determination of Cu, Zn, Pb and Cd in seawater (87). The FI system was optimised, to produce a high sampling frequency, 60 h^{-1}, detection limits between 0.03-0.5 $\mu g\ l^{-1}$ and good reproducibility, 1.2-3.2 %. Three chelating resins were compared under these conditions, Chelex-100, an 8-quinolinol based resin immobilised on controlled pore glass and a phenol-formaldehyde based resin with salicyclic acid functional groups, resin 122. Initially, the swelling property of Chelex-100 was studied. The buffer concentration and sampling period required to achieve the smallest volume changes, were imposed. The FI system was optimised to obtain the most efficient configuration. A dual column system, loaded simultaneously and eluted sequentially, increased sample throughput. The sample and eluent were pumped directly through the microcolumns at certain flow rates for specified periods of time, in place of loop injections. Also, the sample matrix did not enter the nebuliser and the eluent was not used as a carrier. Under the optimal FI configuration, the three resins were

compared with respect to concentration efficiency, reproducibility and freedom from interferences. The same flow rate, column dimensions, pH of buffer and concentration of eluent were utilised in each instance. The 8-quinolinol provided the highest concentration efficiencies. This was presumed to be due to faster exchange kinetics, resulting from the surface bound functional groups. However, the recoveries obtained for the analytes, from the seawater matrix were poor. This was due to interference from Mg. Chelex-100 and resin 122 exhibited freedom from matrix interferences and produced similar recoveries for the trace analytes. The exception was Cd, which could not be satisfactorily recovered with resin 122. It was suggested that 8-quinolinol could be applied to the analysis of relatively simple matrices, such as tap and rain water, to achieve maximum sensitivity. Chelex-100 could be applied to samples with a relatively high content of alkaline earth elements, when a wide range of trace analytes were required. Resin 122 could be applied in similar circumstances, if Cd analysis was not required. It did not undergo drastic volume changes, therefore it easier to handle than Chelex.

Fang *et al.* incorporated a microcolumn of resin 122 into a FI-AAS system, for the enrichment and determination of Ni, Cu, Pb and Cd in water samples (88). It was observed that each analyte had a different optimum elution flow rate. This was due to the relative stability of the analyte complexes formed with the resin. An elution flow rate was selected as a compromise, lower than the optimum nebuliser rate, 5 ml min^{-1}, to attain good sensitivity. The effect of the i.d. of the microcolumn, for fixed column lengths, on the sensitivity of the system was investigated. For 35 mm columns, 2.2-3. 5mm i.d. indicated superior sensitivity. Potential interferences from matrix elements on the analyte signals were studied. At pH 5.5 Ca and Mg, present in water samples at relatively high concentrations, were partially adsorbed by the resin. On elution, the Cu signal was enhanced by 10 and 46 % respectively, by these elements. This interference was removed by rinsing the microcolumn with 1 M ammonium acetate prior to elution. However a 20 % loss in sensitivity was observed. As a compromise 0.1 M ammonium acetate was used to rinse the column, which did not completely remove the interfering

elements, but noted no loss in sensitivity. Under these conditions, the recovery of Cd, and to a lesser extent Ni, from sewage and seawater was poor. This was partially alleviated with the use of a longer microcolumns containing more resin. The competition for available sites was less severe, hence Ni recovery was increased from 40-75 %. The recovery of Cd remained poor, 25 %, except in tap water, which is a relatively pure water matrix. Satisfactory recoveries of the remaining analytes were obtained from the three water types.

Milosavljevic *et al.* utilised a microcolumn of resin 122 to perform on-line speciation, with FI-AAS (89). A mixture containing free and ethylenediaminetetraacetic acid (EDTA) complexed Cu was injected into the carrier stream. Free Cu(II) ions were retained by the resin, and complexed Cu, $[CuEDTA]^{2-}$, passed through the microcolumn and was detected by AAS. The Cu(II) ions were subsequently eluted with 2 M HNO_3 and detected. Calibration was achieved with the injection of one component of the mixture only. The analysis of mixtures, containing established concentrations of each component, was then verified. The recoveries obtained were favourable. The procedure was repeated for the resins Chelex-100 and 8-quinolinol. Resin 122 retained around 1 % of the $[CuEDTA]^{2-}$, 8-quinolinol retained 30 %. Hence resin 122 was selected for this technique, as the competition for Cu ions between this resin and EDTA was less pronounced. This competition effect could be exploited, by using various resins with different chelating abilities, for sequential analysis of mixtures containing analyte complexes of different stabilities.

Milosavljevic *et al.* determined Cr(III) and Cr(VI) by FI-AAS, utilising microcolumn preconcentration with resin 122 (90). In this technique, cationic Cr(III) was selectively retained and preconcentrated by resin 122, in the presence of anionic Cr(VI), which passed, without retention, through the microcolumn and was detected. The Cr(III) was subsequently eluted by 2 M HNO_3 and determined by AAS. Calibration was achieved by injecting one component of the mixture only. Detection limits of 85 and 16 $\mu g\ l^{-1}$ were attained for Cr(VI) and Cr(III) respectively, with a 1 ml sample loop. Sample manipulation was simplified with the on-line addition of buffer, (0.05 M

ammonia solution at pH 9.2) and utilising a mixing coil, in preference to conventional volumetric addition of buffer to samples and standards off-line. The results obtained were essentially similar for the resin 8-quinolinol.

1.6.3 Oxine Based Chelating Reagents

Malamas *et al.* developed an on-line trace analyte enrichment and matrix isolation system with FI-AAS, by incorporating a microcolumn of 8-quinolinol, azo-immobilised on controlled pore glass (CPG) (91). The analytes Cu, Co, Cd, Ni, Pb and Zn were successfully recovered from the chelating reagent. Initially, a variety of buffer solutions, such as acetate, borate and phosphate, adjusted to different pH values were investigated, to determine their effect on retention of the analytes. Each analyte had a pH range in which 100 % recovery could be achieved. The pH range varied with the type of buffer and concentration of the analyte. At low pH however, a large proportion of the analytes were not retained. This appeared to be due to hydrogen ions displacing the analyte ions, converting the reagent to its neutral form, and hence hindering retention. The analytes which formed the least stable complexes with the reagent, were more easily displaced by the hydrogen ions. The sample volume was increased in proportion to the concentration of the solution. For example, the volume was increased to 200 ml for Ni, in order to detect quantities such as 2 $\mu g\ l^{-1}$. It was observed that retention of the analytes remained unchanged when the flow rate was increased from 4-14 ml min^{-1}. Acidic eluents of varying concentrations were investigated to ensure complete elution. All the analytes were completely eluted with 0.4 ml of 1 M HNO_3, except Fe. It was suggested, that if the reagent in the microcolumn became saturated with a mixture of analyte ions, continued sampling would permit analytes which form strong complexes with the reagent, to displace those which form weak complexes. This was investigated. The selectivity of the reagent is Cu > Cd > Ca. A 10 fold excess of Cu significantly reduced the recovery of Cd, but a 1000 fold excess of Ca had no effect on Cd recovery. This was beneficial as many natural waters contain relatively high concentrations of Ca. The determination of Cu in tap water was investigated by this technique and graphite furnace

AAS. The results obtained were similar, but the FI-AAS procedure was more precise. The reagent was compared to Chelex-100, the 8-quinolinol was presumed to be easier to handle, due to the fact it did not experience swelling problems. It was not known how the reagent would perform when applied to samples containing strong soluble complexes, colloids or particles.

Marshall and Mottola utilised a microcolumn of 8-quinolinol immobilised on silica, to preconcentrate and determine Cu in water samples issued by the Environmental Protection Agency (EPA), by FI-AAS (92). The extraction behaviour of the reagent was established with the use of a batch procedure. Extraction / pH profiles indicated that the analytes Cu, Fe, Ni and Co were selectively extracted at pH 5, in the presence of Ca. Hence, the technique could be applied to the analysis of samples which contain relatively high concentrations of the alkaline earth elements. The particle size of the sorbent was fixed at 150-200 μm, to ensure the pressure in the system did not become too great. The effect of microcolumn dimensions on the capacity of the sorbent was investigated. Two microcolumns, 1.43 mm i.d., 100 mm in length and 2.6 mm i.d., 30 mm in length, containing the same quantity of sorbent were studied. The capacity of the former column was slightly larger than the latter. The technique produced a 35 fold enrichment of Cu, for a 10 ml sample volume and a detection limit for this analyte of 1.5 $\mu g\ l^{-1}$. The microcolumn enrichment technique with AAS detection was applied to the determination of Cu in EPA samples. Very good agreement with the certified values was achieved.

Fang *et al.* summarised fundamental and practical considerations, in the design of on-line microcolumn preconcentration flow injection atomic spectrometric systems (93). Utilising the recommended proposals, a procedure for the on-line preconcentration and determination of Co in water samples was developed. A microcolumn containing 8-quinolinol immobilised on controlled pore glass was incorporated into a FI-AAS system for analysis. The primary consideration is that the technique is reliable and efficient. An efficient system has high enrichment factors and high sampling frequency. These are achieved by ensuring maximum retention and elution efficiencies. Good recovery of the analytes from real samples, ensures accurate results. Secondary considerations include

selecting volume based loading of the sample or time based. Time based sampling indicated higher concentration efficiencies, however, the flow rate had to be checked regularly to ensure changes, such as partial blockages had not occurred. Single column or dual column operation had to be considered. Single column sampling is simple, but dual column operation is more efficient. Washing the column between analysis was considered. Omission of this procedure proved more efficient, although loss of analytes was observed. The loss was reproducible however. Finally the sample flow rate and column dimensions were optimised, to produce maximum retention, elution and recovery of the analytes from real samples. Utilising a dual microcolumn system, with columns of 3 mm i.d. and 45 mm in length, a sample flow rate of 9.5 ml min^{-1}, and a time based sampling operation, without intermediate column washing, Co was determined in tap, sea and waste water. A preconcentration factor of 48 was achieved at a sampling frequency of 60 h^{-1}. Good recoveries and a detection limit of 0.2 $\mu g\ l^{-1}$ were attained.

Bysouth *et al.* utilised microcolumns containing various immobilised reagents to preconcentrate Pb by FI-AAS (94). A enrichment factor of 40 was achieved, for a 12 ml sample volume and a detection limit of 1.4 $\mu g\ l^{-1}$ for this analyte. The effect of pH on the enrichment capability of the reagent 8-quinolinol was investigated, utilising various buffer solutions. At pH > 7 effective enrichment was observed. The optimum pH range was different to that indicated previously for Pb (91). It was presumed to be due to the higher flow rates used in this procedure. To ensure chelation rather than precipitation occurred, a pH of 8 was chosen. The buffer solutions borax/boric acid and borax/citric acid were studied. The analyte Fe competes with Pb for active sites on the chelating reagent. If Fe could be suppressed by buffer solution, no interference of the Pb signal would be observed. However, the citrate buffer competed with the reagent for both Fe and Pb, hence the borate buffer was selected. The effect of the eluent concentration on the Pb signal was studied. Hydrochloric acid (1 M) indicated maximum sensitivity. Potential interfering elements of the Pb signal were studied. The elements Ca, Cu, Fe and Mg indicated significant interference. It was presumed that these elements were chelated by the reagent and hence competed for active sites. Therefore, if the element

was more strongly chelated by the reagent or was present in sufficiently high concentration, the adsorption of Pb was affected. A variety of reagents 8-quinolinol, 2-methyl-8-quinolinol, 4-(2-pyridylazo)resorcinol and pyrocatechol violet, immobilised on silica gel, borosilicate glass and silica gel were utilised to preconcentrate a 100 $\mu g\ l^{-1}$ Pb standard. The signals obtained were similar for every material. This suggested that the hydroxyl groups on silica gel and borosilicate glass, bind Pb similarly to the functional groups of the immobilised reagents. The results obtained for Pb in water samples by this technique and by a standard addition procedure were different, indicating that the reagents were not selective for Pb.

Beauchemin *et al.* used on-line preconcentration with ICP-MS detection to determine Mn, Co, Ni, Cu and U in the certified river water SLRS-1 and Mn, Mo, Cd and U in the open ocean reference water NASS-2 (95). A microcolumn of 8-hydroxyquinoline was incorporated into a FI system, achieving detection limits in the range 0.03-0.3 $\mu g\ l^{-1}$. It was observed that buffer solution, 0.1 M ammonium acetate, was required to completely retain analytes in the on-line system. The analyte Cu was eluted 30 s later than the analytes Mn, Co and Ni. This was expected as Cu forms more stable complexes with the chelating reagent. Buffer solution was permitted to wash through the microcolumn for 1 min following the elution process to revert the chelating reagent to the form required for deposition and to ensure analytes, which had not been retained by the reagent, had been transported to waste. Analyte sensitivity and detection limits were not improved by the same factor for each analyte. This was attributed to, the level of reagent contamination limiting the enrichment factor, or the removal of an interfering species by this technique, significantly improving the enrichment, when compared to direct analysis. The reference material SLRS-1 was analysed using this technique. A standard addition procedure was adopted. Good agreement with the certified values were obtained for every analyte except Ni.. This was proved to be due to an isobaric interference from $^{44}Ca^{16}O$ on ^{60}Ni, produced from the retention of a proportion of the Ca present in the sample, by the reagent. A standard addition procedure and isotope dilution was used in the analysis of NASS-2. Good agreement

was attained for the analytes, Mo, Cd, U and Mn. Signal enhancements for the analytes Ni and Cu, presumably from the reagents used, produced results higher than expected. The results for Pb were poor. Further investigation of the technique is to be conducted.

Fang and Welz designed a high efficiency, low sample consumption, on-line preconcentration system, with FI-AAS, for the determination of Cu, Cd and Pb in seawater samples (96). A microcolumn of quinolin-8-ol immobilised on controlled pore glass was utilised to achieve a sampling frequency of 120 h^{-1} and enrichment factors of 25-30 fold for a 1.6 ml volume of sample. The design of the system was initially studied to improve previously determined limitations of the technique. These included high sample consumption, low sample throughput and susceptibility to interferences, when compared to AAS and graphite furnace AAS. To increase sampling frequency to 120 h^{-1}, the sample loading period could only be 20 s and elution period 10 s. The sample and elution flow rates were reduced to facilitate low sample and reagent consumption, and to reduce susceptibility to interferences. A single column configuration was easier to manipulate and conical shaped microcolumns with a short tubing length, 5 cm, from the column to the AAS, improved dispersion. The analytes Cu and Pb were successfully recovered from seawater (95 %) by the on-line microcolumn enrichment technique with AAS detection. However recovery of Cd was poor (70 %).

Beinrohr *et al.* utilised a microcolumn of quinolin-8-ol, chemically bound to a spherical cellulose sorbent, (Ostorb Oxin), to enrich Cu from various soluble inorganic salts, ammonia and sodium hydroxide with AAS detection (97). The microcolumn was connected to the nebuliser of the AAS and the sample and eluent were sucked through it, utilising the negative pressure of the nebuliser. The accuracy of the results was established, by comparison with anodic-stripping voltammetry and electrothermal AAS. Employing this simple procedure, complete elution of the analytes Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Pd and Zn was achieved with dilute solutions of mineral acids. In further studies 2 M HCl was selected as the eluent. The effect of pH on the recovery of the analytes was investigated. Each analyte had a pH range in which maximum recovery was achieved. The analyte Cu indicated complete recovery over the pH range 2-12 and

was selected for further investigation. The recovery of the analytes was investigated from a 0.1 and 1 M NaOH matrix. Only Pb, Pd and Zn indicated poor recovery from the 1 M matrix. Two microcolumns were studied, A and B, with dimensions of 50 mm and 2 mm i.d. A had a dead volume of 300 µl and B, 160 µl. Column A experienced lower sensitivity, incomplete deposition for low Cu concentrations and lower capacity when compared to B. Hence B was chosen for further studies. It was observed that using different sample volumes, 0.1-10 min sampling times, the dynamic range possible with this technique covered 4 orders of magnitude. A detection limit of 0.3 µg l^{-1} was achieved for the 10 min sampling period. The influence of the matrices $Ca(NO_3)_2$, NaOH, NaCl, $(NH_4)_2SO_4$, $MgSO_4$ and aqueous NH_3 on the recovery of Cu was studied. No effect was observed for concentrations of these matrices up to 1 M. However, higher concentrations of the matrices, (2-3 M) reduced the recovery of Cu slightly to 90-95 %, and owing to the simple design of the system, nebuliser and burner blockages occurred for long sampling periods. At concentrations less than 10 µg $l^{-1}$of Cu, the recovery was poor. The results obtained by this method for Cu in each matrix were between 0.014 and 0.038 µg g^{-1}. These results obtained were compared to anodic stripping voltammetry and graphite furnace AAS and the agreement was good.

Bysouth *et al.* used various masking agents to improve the selectivity of 8-hydroxyquinoline immobilised on silica gel, for Pb (98). The reagent was packed into a microcolumn and incorporated on-line in a FI-AAS system to enrich Pb in tap water samples. Initially, 50 µg l^{-1} Pb solutions were prepared containing 10 mg l^{-1} of Cu, Fe or Al. Different buffer systems at pH 8 were used in the preconcentration step. These included 0.05 M borax containing 1 % m/v sodium fluoride, sodium cyanide, triethanolamine, acetylacetone or thiourea. The effect of the potential interfering elements on the Pb signal, for each buffer system, was investigated. Triethanolamine, fluoride and thiourea reduced the interference on the Pb signal, from these elements. Cyanide reduced the interference from Cu only. A buffer system of 0.2 M boric acid, 2 % triethanolamine, 2 % thiourea and 2 % acetylacetone was used to enrich Pb from solutions containing different concentrations of interfering ions. In all cases, the extent

of the interference on the Pb signal was reduced with buffer solution containing the masking agents. Recoveries obtained for spiked tap water samples were between 94-108 % and a detection limit of 6.8 $\mu g\ l^{-1}$ was achieved. Good agreement was achieved for samples and standards provided by National Rivers Authority Environmental Laboratory, for this technique and electrothermal AAS.

Okamoto *et al.* determined Cd in certified biological reference materials by suction-flow on-line preconcentration with ICP-ES detection (99). A microcolumn of porous active carbon impregnated with 8-quinolinol, was incorporated into the system, the design of which is previously described (76). A detection limit for Cd of 0.25 $\mu g\ l^{-1}$, a sampling frequency of 35 h^{-1} and precision of 1.1 % RSD was achieved. The ICP-ES conditions were optimised for Cd determination. These included incident power, carrier gas flow rate and observation height. For a fixed concentration of Cd in solution (500 ng), the effect of column dimensions on the Cd intensity was studied. A 2 mm i.d. column produced the highest intensity. A column length of at least 5 cm was required to achieve complete deposition. A column greater than 20 cm produced back pressure, which the system was incapable of tolerating. A 10 cm column was therefore selected. The sample, buffer and elution flow rates were investigated. Maximum intensity for Cd was attained for flow rates between 1.5-4.5 ml min^{-1}. To ensure maximum sample throughput, 4.5 ml min^{-1} was chosen. The effect of eluent concentration on the Cd intensity was studied. Maximum intensity was achieved for concentrations of HCl between 0.5-1 M. The selected concentration was 0.5 M. The column required reloading with 8-quinolinol, following 80 determinations. The effect of sample pH on the recovery of Cd was investigated. Optimum recovery was attained for samples of pH 2-7. The pH of the citrate buffer solution was required to be between 8.5-10.5, to ensure complete deposition of samples in the above pH range. The enrichment capability of the microcolumn was investigated. Sample volumes between 1-20 ml could be enriched by the reagent. The species Na, Ca, Sr, V, NH_4^+, Se, Cl^-, NO_3 and SO_4^{2-} indicated no interference on the Cd intensity. The technique was used to determine Cd in Oyster Tissue, issued by the National Bureau of Standards and Pepperbush, issued by

the National Institute of Environmental Studies. The results obtained were in good agreement with certified values.

Purohit and Devi synthesized and characterised two resins, oxine/formaldehyde/resorcinol and oxine/formaldehyde/hydroquinone (100). Conditions were optimised for the preconcentration of Cu by batch extraction, column chromatography and on-line FI-AAS with these resins. Greatest Cu enhancement was achieved in the pH range 2-3.5. The effect of different buffer systems, (Tris, phosphate and acetate) on the Cu signal were investigated. The signal was less affected by pH, utilising the phosphate buffer. For a fixed sample flow rate of 2 ml min^{-1} and i.d. of 2 mm, the effect of column length was studied. A column length of 2 cm column ensured complete retention of Cu. Increasing the carrier flow rate under these conditions decreased the Cu peak height. The effect of eluent volume and concentration, on the elution of Cu was investigated. A volume of 50 µl of 0.5 M HCl ensured complete elution. The detection limit achieved with this system was 5 µg l^{-1}.

Purohit and Devi extended their studies (100), by synthesizing and characterising a series of chelating resins involving 8-hydroxyquinoline and resorcinol-hydroquinone (101). The resins were used for the preconcentration of Cd and Zn by batch extraction with FI-AAS detection. Column chromatographic separations were also achieved. The effect of pH on analyte retention was investigated. The optimum pH for retention was 3 for Zn and 6 for Cd. The microcolumn length was optimised for a fixed column diameter of 2 mm i.d. A length of 2 cm ensured complete retention. A variety of acids, at different concentrations and injected volumes, were investigated. A volume of 50 µl of 1 M HNO_3 ensured complete elution. The carrier flow rate was varied from 0.5-5 ml min^{-1}. Complete retention of the analytes was observed for flow rates up to 3 ml min^{-1}. The detection limit achieved for Cd and Zn utilising this procedure was 1 µg l^{-1} and 95 % recoveries were attained.

Mohammad *et al.* utilised a microcolumn of 8-hydroxyquinoline, immobilised on controlled pore glass beads, in a FI-AAS system, to preconcentrate and determine Al in water samples (102). An enrichment factor of 76 was achieved and the detection limit

was 3 μg l^{-1}. Initially, the effect of pH on Cu retention was investigated. The objective was to demonstrate the pH at which Cu precipitates in solution. The pK_a value for Cu is 5.4-5.8. At pH > 4, the absorbance measured for Cu decreased indicating Cu precipitation for both the FI technique and electrothermal AAS. Therefore, the effect of various buffers at different pH values, on the retention of Al was investigated. The buffer selected would be a complexing agent for Al which was soluble in water. It would also form complexes of sufficient stability to maintain Al in solution at high pH, but not compete with the reagent for Al. Acetate, citrate, malonate, oxalate, picolinate and tartrate buffers were studied. Al was not retained at low pH. At pH 10 Al was retained by the reagent from every buffer system. Malonate at a concentration of 0.1 M, indicated greatest retention of Al between pH 9.2-10. Utilising this procedure, the effect of potential interfering species, Na, Ca, F, Mg, Fe and Cu, on the Al recovery was studied. The recovery was not significantly affected by these species, at concentrations similar to those present in natural water and seawater samples. The technique was applied to the determination of Al in river water samples and the certified reference water SLRS-1. Close agreement was attained by FI-AAS, electrothermal AAS and ICP-ES. The recovery of Al from seawater samples by this method was good (98-102 %).

Porta *et al.* utilised a microcolumn of Amberlite XAD-2, to preconcentrate and determine the analytes Cd, Cu, Fe, Mn, Ni and Zn, in the River Po and Antarctic seawater samples, by FI-ICP-ES (103). The procedure was based on the pre-complexation of the analytes with quinolin-8-ol, and subsequent retention and enrichment of the analyte complexes on the XAD-2 column. Acid elution was used to effectuate determination. Initially, recoveries obtained for the analytes, from standard solutions, river and seawater samples, were poor. However, acidification of the samples prior to analysis, increased the recoveries obtained for the analytes, from these matrices, to 85-108 %. Detection limits obtained were in the range 4-60 ng l^{-1}. This procedure was applied to the analysis of river and seawater samples. The results produced for river water were in close agreement to those obtained by graphite furnace AAS, except for Cd. The levels determined in seawater were between 16 ng l^{-1} to 0.4 μg l^{-1}.

Purohit and Devi extended their investigations (100, 101) by synthesizing and characterising chelating resins containing quinolin-8-ol and, resorcinol or hydroquinone monomers, cross-linked through furfuraldehyde, formaldehyde or benzaldehyde (104). The resins were packed into microcolumns and incorporated on-line in a FI-AAS, to enrich and determine Pb. Utilising acetate buffer, the effect of pH on the retention of Pb was investigated. The resin quinolin-8-ol/hydroquinone/furfuraldehyde indicated greatest retention at pH 3, the remaining resins at pH 5. For a 2 mm i.d. microcolumn, the effect of column length (2-8 cm), on the retention of Pb was studied. Complete retention was observed for a length of 2-3 cm. The effect of eluent concentration and volume on the elution of Pb was considered. Complete elution was ensured with 50 µl of 1 M HNO_3. A detection limit of 10 µg l^{-1} was achieved.

Huang and Jiang determined the trace analytes Mn, Co, Ni, Cu, Cd and Pb in certified reference waters, utilising a microcolumn of SO_3-oxine CM-cellulose in a FI-ICP-MS system (105). The TRACECON (Knapp GmbH, Graz, Austria) preconcentration unit was used for analyte enrichment/matrix separation. Detection limits at the ng l^{-1} level were achieved. The ICP-MS operating conditions were optimised for the elution flow rate. The effect of pH on the retention of the analytes was investigated. Complete recovery of Cu was attained between pH 1-7, Mn, Co and Ni between pH 5-8 and Pb at pH 4-7. Only a maximum of 60 % of the analyte Cd could be recovered between pH 5-8. A pH of 5-7 was selected as optimum, as the matrix elements Ca and Mg were quantitatively recovered between pH 8-10. The capacity of the microcolumn was 30 µ mol g^{-1} and a replacement column was necessary following 50-70 determinations. The effect of various acids at different concentrations on elution of the analytes was studied. Complete elution was achieved with a 1 M HNO_3/ 1 M HCl mixture. The effect of potential interfering matrix elements, Na, Mg, Ca and Cl, on the analyte responses was investigated. As little as 20 g l^{-1} Cl^-, reduced the Mn and Pb recovery to 70-80 %. This was possibly due to the formation of $PbCl_3^-$ and $MnCl_5^-$ complexes, which were not retained by the reagent. Close agreement with the certified values was achieved, for the river water reference material SLRS-2, utilising this

technique. A standards addition procedure was adopted and applied to the determination of the open ocean reference water NASS-3. Significantly higher concentrations were attained for ^{60}Ni and ^{59}Co than expected. This was presumed to be due to isobaric interference from $^{44}Ca^{16}O$ and $^{42}Ca^{16}O^{1}H$ respectively. A higher concentration for ^{65}Cu was also produced, which was assumed to be caused by $^{40}Ar^{25}Mg$.

McLaren *et al.* used on-line preconcentration and FI-ICP-MS, to enrich and quantify the trace analytes Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb in seawater reference materials (106). A commercially available chelation system, Dionex "IC/ICP", containing the material MetPac CC-1, which has iminodiacetic acid functional groups, immobilised on a styrene-divinylbenzene polymeric support and a microcolumn of 8-hydroxyquinoline (I-8-HOQ), immobilised on silica gel were used for preconcentration. Detection limits between 1.6-55 ng l^{-1} were attained for the former column, and 0.3-47 ng l^{-1} for the latter. The optimum pH for retention of the analytes was 5.5 for the MetPac column and 8 for the I-8-HOQ. Intensity/time profiles of standard solutions, with and without the microcolumn in the FI system, indicated that every analyte was eluted simultaneously from the MetPac column. The analyte Cu eluted later than the remaining analytes from the I-8-HOQ column. This was due to the very strong complex formed with this analyte and the reagent. High background signals were observed for ^{57}Fe and ^{55}Mn, which were due to the isobaric interferences $^{40}Ar^{16}OH$ and $^{40}Ar^{14}NH$ respectively. Similar intensity/time profiles of seawater samples, indicated the severe problems encountered with the direct analysis of saline samples. Most of the analytes experienced an isobaric interference from a polyatomic species. On-line preconcentration and separation significantly reduced the interferences on the analyte signals. It was suspected that the I-8-HOQ microcolumn was contaminated with Co and Fe, which were released on elution, producing results higher than expected for these analytes. A guard column was placed on-line to reduce contamination from reagents such as the buffer solution. The technique was applied to the seawater reference materials CASS-2 and NASS-3. The MetPac column indicated good agreement with the analytes Cu, Ni and Pb. A slightly higher result than expected was achieved for the

analytes Cd, Mn and Zn, which was presumed to be due to contamination from the reagents used. The agreement for Co and Fe was generally poor, due to a high blank value and an isobaric interference respectively. Therefore, the analytes Co and Fe cannot be accurately determined by this technique. In general, the performance of the I-8-HOQ microcolumn was superior to the MetPac column, except for Fe and Co.

Mohammad *et al.* extended their studies (102), developing an on-line preconcentration system for the determination of Al, Ga and In by AAS (107). A microcolumn of quinolin-8-ol, immobilised on controlled pore glass beads, was incorporated in to a FI system, to facilitate enrichment and matrix separation. A detection limit of 3 $\mu g\ l^{-1}$ for each analyte was achieved. In the previous report (102), a complexing agent was selected, which prevented the precipitation of aluminium hydroxide or the formation of aluminate, but did not inhibit the formation of aluminium chelates with the I-8-Q column. Hence, malonate at a concentration of 0.1 M and pH 10 was chosen as the buffer solution. Similar investigations were applied to the analytes Ga and In. The effect of different buffers, acetate, citrate, malonate, oxalate, picolinate, tartrate and NH_4Cl, at various pH values, on the retention of the analytes were studied. Malonate gave greatest retention for Ga between pH 8-10. Acetate and citrate produced poor retention for Ga. Acetate was unable to maintain Ga in solution and citrate formed such strong complexes with Ga, that the I-8-Q could not compete for the analyte. With the exception of acetate and citrate, every buffer produced effective retention of In between pH 8-10. Hence, to retain all 3 analytes from water samples, the buffer malonate at a concentration of 0.1 M and pH 10 was utilised. At concentrations expected in natural waters and seawater, the elements Na, Ca, F, Mg, Fe and Cu had no effect on the recovery of Al. However, if the concentration of Fe was increased from 10, to 20 and 40 $mg\ l^{-1}$, the recovery of Al was reduced to 74 and 54 % respectively. This appeared to be due to the precipitation of Fe and subsequent coprecipitation of Al. The same effect was observed Ga. However, the principal interference for Ga is Al. The addition of F^- reduced the interference, but it was more effective to reduce the sample pH to 8 or below. The analyte Al also interferes with the recovery of In. The

interference was reduced as detailed above. The effect of Fe on the recovery of In was severe. The use of picolinate and tartrate or NH_4Cl and F^- extended the tolerable Fe concentration to 1 mg l^{-1}. The recovery of Al from river water, seawater and the reference material SLRS-1 was effective. The low concentration of Ga and In in seawater precluded their determination by the optimised enrichment technique with AAS detection, however recovery of these analytes from a seawater matrix was successful.

Peng *et al.* used on-line microcolumn preconcentration with desolvation, for the determination of Al, Cu, Cd, Fe and Mn in human serum, by FI-ICP-ES (108). A desolvation device was connected to the microcolumn, which was packed with 8-hydroxyquinoline-5-sulphonic acid, immobilised on active carbon-silica gel. Thus, following preconcentration and subsequent elution, the eluent travelled to the desolvation device, and hence, dry aerosol was introduced to the ICP-ES for analysis. Detection limits of 0.3-5.1 μg l^{-1} were achieved. The effect of desolvation temperature on the analyte signals was investigated. The signals increased as the temperature increased from 70-120 ^oC. The temperature 120 ^oC was selected. The effect of various buffers, at different pH on the retention of the analytes was studied. At pH > 5 effective retention was attained. Acetate buffer at pH 5.6 was chosen. Increasing the sample volume from 0.5-2.5 ml increased the intensity obtained for the analytes. A compromised volume of 1.2 ml was selected to achieve a sampling frequency of 12 h^{-1}. The effect of eluent concentration, in the range 0.01-4 M, on the elution of the analytes was investigated. Complete elution was achieved with 2 M HCl. The effect of interfering species, Na, Ca, Mg, NH_4^+, Cr and Ni, at concentrations between 0.5-1 g l^{-1} in solution, on the analyte signals was studied. No interferences were observed. It was found that the order of stability, with respect to the formation of analytes complexes with the reagent was Fe > Al > Ni > Mn, Cd, Cu. The alkali and alkaline earth elements were not retained under these conditions. This technique and graphite furnace AAS were applied to the determination of the analytes in human serum. Close agreement between the two procedures was attained.

Schramel *et al.* utilised the TRACECON (Knapp GmbH, Graz, Austria) preconcentration apparatus, to determine the analytes Zn, Cu, Ni, V, Cr, Fe, Mn, Co, Pb, Cd and Al in certified biological samples, by FI-ICP-ES (109). A microcolumn of 8-hydroxyquinoline covalently bonded to cellulose flakes, was incorporated into the system and used to achieve detection limits between 0.1-11.3 $\mu g\ l^{-1}$. The effect of sample pH on the retention of the analytes was studied. A pH of 6.5, achieved with acetate buffer (0.1 M) gave maximum retention of each analyte. The sample flow rate was increased from 2-10 ml min^{-1}, however the retention efficiency of the microcolumn remained unchanged. As the eluent flow rate was increased from 3-6 ml min^{-1}, the analyte peak area decreased. A rate of 3 ml min^{-1} was therefore selected for both sample and eluent flow rate. The analytes Mn and V eluted from the column slightly faster than the remaining analytes. This was assumed to be due to these analytes forming the least stable complexes with the reagent and hence, were easier to displace from the column. The effect of different eluents, at various concentrations, on the elution of the analytes was investigated. Either 0.5 M HNO_3 or 1 M HCl were sufficient for complete elution of each analyte. A mixture of these acids (1 M), was selected as optimum. The effect of matrix elements, Mg, Ca, Fe, Na and Cl, on the recovery of the analytes was studied. The presence of Ca and Mg at concentrations up to 500 mg l^{-1} and Fe up to 50 mg l^{-1} had no effect on the recovery of the analytes, with the exception of Cr. The addition of the complexing agents tartrate (1 %) or citrate (0.1 %) inhibited the hydrolysis of Fe and Al, however Cr recovery was still affected. If the citrate concentration was increased to 0.5 %, the retention of Ni, Mn, V and Cr was affected. The reagent was unable to retain the citrate complexes formed with these analytes. The technique was applied to the analysis of the certified reference material 1577 Bovine Liver. The results obtained for Zn and Mn were significantly lower than the reported values. This sample contains a relatively high Cu content, 193 $\mu g\ g^{-1}$. It was observed that above 10 mg l^{-1} Cu in solution, the retention of the analytes Mn, Zn and Ni was affected. Dilution of this sample enabled close agreement with the certified values to be achieved. A selection of standard reference materials were analysed. Close agreement with the certified results

and good recoveries from these matrices were achieved for every analyte, except Fe and Cr. It was suspected that these analytes were present as species which were not retained by the microcolumn.

1.6.4 Miscellaneous Column Packing Materials

Bengtsson *et al.* synthesized and characterised the chelating ion exchanger, N,N,N'-tri-(2-pyridyl-methyl)ethylenediamine (TriPEN), which was immobilised on controlled pore glass (110). The exchanger was packed into a microcolumn and incorporated on-line in a FI-AAS system, to achieve sensitivity enhancements for the analytes, Ag, Cd, Co, Cu, Mn, Ni, Pb and Zn. The analytes Pb, Mn, Al, Ca and Mg were not quantitatively retained using this procedure, however, the presumption was, that superior recoveries for these analytes could be achieved with changes in experimental parameters.

Bysouth *et al.* designed a FI preconcentration system, for the determination of Pb by AAS (111). An interface was contrived which permitted the valves and pump in this configuration, to be controlled by an autosampler. Hence, precise timing of preconcentration and elution steps was implemented. The detection limit was improved by a factor of 50 by this technique, when compared to direct sample introduction.

Plantz *et al.* determined V, Cr, Ni, Co, Cu, Mo, Pt, Hg and Bi in the certified reference materials CASS-1 (seawater) and 2670 (urine), issued by the National Bureau of Standards, by FI-ICP-MS (112). The reagent bis(carboxymethyl) dithiocarbamate was synthesized and utilised to form neutral complexes of the analytes, which were subsequently adsorbed onto the non-polar Amberlite XAD-4 resin. The resin was packed into a microcolumn and incorporated on-line in the FI system, to effect analyte enrichment and matrix removal. The analytes were eluted from the resin with 0.1 M NH_4OH. Detection limits in the range 8-80 ng l^{-1} were achieved for a 0.5 ml sample volume, and at least 97 % of the analytes were recovered from these matrices.

Wang and Barnes evaluated two chelating resins for on-line preconcentration with FI-ICP-ES (113). The resins poly(dithiocarbamate) (PDTC) and

carboxymethylated poly(ethylenimine)-poly(methylenepolyphenylene) isocyanate (CPPI) were packed into microcolumns and incorporated into the FI system. Thirty-five analytes were investigated. The resin PDTC quantitatively recovered the analytes Al, Ba, Ca, Cd, Cr, Cu, Fe, La, Mg, Mn, Ni, Sc, Sr, Ti, V, Y and Zn at pH 8.6. The analytes Ag, Ba, Ca, Cd, Co, Cu, Dy, La, Mg, Mn, Sc, Sr, Ti, U, V, Y, Zn and Zr were quantitatively recovered from the CPPI resin at pH 5-6. The PDTC resin was applied to the determination of Cu and Zn in water samples and the certified reference material 1643a, issued by the National Bureau of Standards. Good accuracy, recovery and precision were observed.

Shah and Devi synthesized and characterised a series of poly(hydroxamic acid) resins, which were used for the enrichment and determination of Cr(III) by FI-AAS (114). A detection limit of 0.1 m gl^{-1} and 90-95 % recovery of the analyte was achieved. The technique was applied to the analysis of seawater samples.

Elmahadi and Greenway cultured and harvested the alga Selenestrum capricornutum, which was subsequently covalently immobilised on CPG. The I-Alga was packed into a microcolumn and incorporated on-line in a FI-AAS system, for the preconcentration and determination of Cu, Pb, Zn, Co, Hg and Cd (115). Detection limits between 0.05-30 $\mu g\ l^{-1}$ were achieved for a sampling frequency of 20 samples h^{-1}. Cobalt exhibited low recovery, 85 %, and Co and Hg were susceptible to depressive interference effects, in the presence of high concentrations of other analytes.

Mentasti *et al.* compared two procedures for the on-line preconcentration and determination of the analytes Cd, Cu, Fe, Mn, Ni and Zn in Antarctic seawater samples, by FI-ICP-ES (116). The resin Amberlite XAD-2 was packed into a microcolumn, placed in the FI manifold and utilised for enrichment. The reagent 8-hydroxyquinoline (8-oxine) was used to form neutral complexes with the analytes, which were adsorbed by the resin in the preconcentration step. The analytes were subsequently eluted into the ICP-ES with 2 M HCl / 0.1 M HNO_3. Alternatively, the resin was loaded with 1-(2-thiazolylazo)-2-naphthol (TAN), packed into a microcolumn, incorporated on-line and used for enrichment. The detection limits attained were in the range 4-60 ng l^{-1} for the

8-oxine procedure, with recoveries between 78-94 % and 2-40 ng l^{-1} for the TAN loaded column, with recoveries of 92-105 %. The results obtained by both methods for collected seawater samples, were compared to those produced by anodic and cathodic stripping voltammetry.

Esmadi *et al.* utilised on-line precipitation for the enrichment and determination of Cd, Zn and Cu by FI-AAS (117). A microcolumn of Pyrex glass beads was incorporated into the FI manifold. The analytes and a precipitating anion, (CO_3^{2-} for Cd and Zn, S^{2-} for Cu), were mixed on-line, and the subsequent precipitate was retained in the microcolumn. The precipitate was dissolved with a suitable reagent before determination, (H_3PO_4 for Cd, HCl for Zn and NaCN for Cu). Detection limits in the range 6-40 µg l^{-1} were attained and complete recovery of the analytes was observed. A sampling frequency of 16 h^{-1} was achieved. The species BrO_3^-, MnO_4^-, Br^-, SCN^-, Ba, Sn and SO_4^{2-} had no effect on analyte recovery, however the presence of $C_2O_4^{2-}$, Pb, F^- and CN^- resulted in poor analyte recovery. This was assumed to be due to either, competition for the precipitating anion or the partial dissolution of the precipitate, by the interfering species.

Ljunggren *et al.* utilised a microcolumn of desferrioxamine to preconcentrate and determine Al in an on-line FI-AAS (118). The lactate buffer was used to ensure Al was maintained in solution and the column was heated to 50 ^oC to facilitate retention. Al was recovered quantitatively from a lactate-acetate buffer and a detection limit of 0.2 µg l^{-1} was attained. The buffer 1 mM citrate / 0.1 M Tris, reduced the recovery of Al to 30 %. This was presumed to be due to competition between citrate and the resin, for the analyte. The technique was applied to the analysis of dialysis solutions and the results were compared to those obtained by graphite furnace AAS. The low concentration of Al in these solutions (1-4 µg l^{-1}) precluded its determination by graphite furnace AAS.

Naghmush *et al.* utilised microcolumns of loaded Amberlite XAD-2 resin, to enrich and quantify Cu in natural waters, by FI-AAS (119). Pyrocatechol Violet (PV), 4-(2-pyridylazo)resorcinol (PAR) or Eriochrome Blue Black R (EBBR) loaded XAD-2 were used for preconcentration, PV indicating the highest stability constant with Cu.

The retention of Cu on XAD-2-PV was affected by the presence of > 50 mg l^{-1} Ca, however, the interference observed by the presence of Fe, was eliminated by the addition of F^-. The recovery of Cu from this resin was > 90 %, for Cu concentration in solution of up to 20 μg l^{-1}. This was far superior to the recovery of Cu obtained by the commercially available Spheron Oxine 1000 resin (54 %). A detection limit was attained of 0.06 μg l^{-1}. This technique was applied to the determination of Cu in collected natural waters. The results obtained were in close agreement with those produced by electrothermal AAS.

Olbrych-Sleszynska *et al.* compared the use of two modified resins, for the preconcentration and determination of Ni by FI-AAS (120). Amberlite XAD-2 and the anion exchanger Amberlyst A-26 were modified with Eriochrome Blue Black R (EBBR). The resins were packed into a microcolumn and incorporated on-line in the FI system. The analytes Cr, Fe, Co, Cu, Zn, Ga, In, Pb, Bi, Mn and Cd could be retained by one or both of the resins, in various proportions. The analyte Ni was 100 % retained by both resins, however, XAD-2-EBBR was more selective for Ni, and was therefore chosen for further study. The analyte Fe(III) reduced the recovery of Ni, if present in solution at concentrations above 5 mg l^{-1}. Ni was detected in solution at 0.1 μg l^{-1}. A stability trial indicated, that Ni could be > 95 % recovered from this resin after 12 months.

Porta *et al.* utilised a microcolumn of Amberlite XAD-2 resin, functionalised with 1-(2-thiazolylazo)-2-naphthol (TAN), to enrich and quantify the analytes Cd, Cu, Fe, Mn, Ni and Zn, in Antarctic seawater and River Po samples, by on-line FI-ICP-ES (121). A cartridge of Chelex-100 was used to purify reagents on-line. The analytes were completely recovered from the above matrices. Detection limits in the range 2-40 ng l^{-1} were achieved. This procedure was applied to the analysis of river and seawater samples. The results obtained for river water, were in close agreement with those obtained by graphite furnace AAS and the procedure detailed in reference (103), except for Cd. Both preconcentration procedures indicated good agreement for seawater samples.

Salacinski *et al.* determined Al in beverages and water samples, by on-line microcolumn preconcentration and FI-AAS detection (122). A commercially available strong cation exchanger, was packed into the microcolumn to facilitate enrichment. A pH < 4 was selected to ensure Al was maintained in solution, as ($[Al(H_2O)_6]^{3+}$). Quantitative results were obtained for this technique, for Al concentrations in solution as low as 75 $\mu g\ l^{-1}$. The results attained for tea, coffee, tap and reservoir waters, indicated similar Al concentrations, as those previously reported.

Elmahadi and Greenway used on-line microcolumn preconcentration and FI-AAS detection, to determine the analytes Cu, Zn, Cd, Pb, Co and Hg (123). The microcolumn contained cysteine, covalently immobilised on controlled pore glass, using the bi-functional reagent glutaraldehyde. Detection limits in the range 0.1-30 $\mu g\ l^{-1}$ were achieved utilising a sampling frequency of 20 h^{-1}. The analytes Cu, Hg, Zn and Pb indicated greatest sensitivity in phosphate buffer, the remaining analytes in Tris buffer. Complete elution was attained using 0.1 M thiourea in 0.1 M HNO_3. Recovery of the analytes was good, except for Co. This was due to incomplete retention of this analyte. No significant interferences were observed, except for Co. This analyte has the lowest affinity for cysteine, therefore the remaining analytes displaced Co.

Maquieira *et al.* utilised a microcolumn of the yeast Saccharomyces cerevisiae, to enrich and determine the analytes Cd, Cu, Fe, Pb and Zn, by FI-AAS (124). The yeast was covalently immobilised on controlled pore glass. Enrichment factors between 125-2000 fold, and detection limits in the range 0.1-8 $\mu g\ l^{-1}$ were achieved. The analytes yielded maximum retention within the pH range 6-7.5. Different strengths and acid mixtures were required to completely elute these analytes. The elution characteristics indicated, that the analytes were bound to this reagent with differing strengths:- Fe > Pb, Cd > Cu, Zn. No significant interferences were observed, when matrix ions (Ca, Mg) were present in the range 1-4 $mg\ l^{-1}$. Recoveries between 89-98 %, and RSD's between 1.1-2.6 % were found. The technique was applied to sample 144 (sewage sludge), issued by the Community Bureau of References. The results obtained for Cd and Cu by a standard addition procedure, were in good agreement with the certified values.

Maquieira *et al.* utilised a microcolumn of Cyanobacteria (Spirulina platensis) covalently immobilised on controlled pore glass, for the on-line enrichment of Cu, Zn, Cd, Pb and Fe by FI-AAS (125). Detection limits in the range 0.2-10 μg l^{-1} were achieved. The analytes Cu, Zn and Cd were weakly bound below pH 7 and strongly bound above it, while Pb and Fe were bound strongly at pH 6 and 7, respectively. It was therefore assumed that different sites were used for binding (biosorption and ion exchange sites). Different strengths and acid mixtures were required to completely elute these analytes. The elution characteristics indicated, that the analytes were bound to this reagent with differing strengths:- Fe > Cu > Cd, Pb > Zn. No significant interferences were observed on the remaining analytes, when Cu, Zn, Cd, Mg and Pb were present at up to 8 mg l^{-1}. Quantitative recoveries were obtained for the analytes (95-102 %), except for Pb (85 %). The technique was applied to sample 144 (sewage sludge), issued by the Community Bureau of References. The results obtained for Cd and Cu by a standard addition procedure, were in good agreement with the certified values.

Nagmush *et al.* investigated a number of cellulose sorbents for on-line microcolumn preconcentration of Cr(III) and Cr(VI) with FI-AAS detection (126). The column packing reagents Cellex CM, Cellex P, Varian KS and Chelex-100 were investigated for the enrichment of Cr(III). Cellex P was found to be the most effective reagent. The reagents Varian AT 660 and Cellex T were studied for the preconcentration of Cr(VI). Cellex T was found to be superior. The effects of common cations present in natural waters (Na, K, Ca, Mg, Mn, Cu, Al and Fe) on the recovery of Cr(III) was studied. A significant increase in the Cr signal was observed in the presence of 5 mg l^{-1} Fe(III). This was due to the simultaneous retention and elution of Fe with Cr(III). A change in analytical wavelength from 357.9 to 425.4 nm eliminated the Fe interference up to concentrations of 20 mg l^{-1}. The presence of SO_4^{2-} at the 10 mg l^{-1} level significantly decreased the Cr(VI) signal, due to competition for active sites. Increasing the length of the column from 5 to 75 mm eliminated this interference. No interference effects were observed for 150 mg l^{-1} Cl^- and 50 mg l^{-1} NO_3^-. Simultaneous preconcentration of Cr(III) and Cr(VI) was achieved with the use of a dual column FI

system. The technique was applied to the speciation of Cr in tap, well and river waters. Moderate agreement with the total Cr determined by electrothermal AAS was obtained. Detection limits of 0.78 and 1.4 $\mu g\ l^{-1}$ for Cr(III) and Cr(VI) respectively were obtained using this procedure.

Yang *et al.* utilised a microcolumn of carboxymethylated poly(ethylenimine)-poly(methylenepolyphenylene) isocyanate (CPPI), to enrich and determine Cd, Cu, Pb and Zn in rain and tap waters, by FI-ICP-ES (127). Enrichment factors of 35-55 fold were achieved, with a sampling frequency of 20 h^{-1} and a precision (RSD) of 3-5 %. Detection limits between 0.05-0.6 $\mu g\ l^{-1}$ were attained. The effect of sample flow rate was investigated between 2.25 and 6 ml min^{-1}. Maximum sensitivity was achieved at a flow rate of 3 ml min^{-1}. The elution flow rate was studied between 1.2-4 ml min^{-1}. The optimum eluent flow rate was 1.5 ml min^{-1}. An eluent (HNO_3) concentration of 2 M ensured complete elution, but did not destroy the resin. The smallest possible eluent volume to ensure complete elution was 120 µl. A linear relationship was observed between sampling time and analyte signal between 1.5-5 min. Satisfactory agreement was obtained for Cu and Zn in rain and tap water samples, by this technique and graphite furnace AAS. The recovery of the analytes from rain water, utilising a standard addition procedure, was performed for validity of measurement. Recoveries between 89-102 % were achieved.

Nagmush *et al.* investigated a variety of different sorbents for the on-line speciation of Pb in natural waters, with FI-AAS detection. A microcolumn of the cellulose sorbent Cellex P was incorporated into the FI system and utilised for the enrichment of Pb species (128). A detection limit of 0.17 $\mu g\ l^{-1}$ was achieved for inorganic Pb, and the precision of this technique at the 10 $\mu g\ l^{-1}$ level was 5.9 %. The sorbents investigated were Cellex P, Cellex CM, Chelex-100, Spheron-Oxine 1000, Amberlite XAD-2, Dowex 50W and Varion KS. Cellex P was found to quantitatively retain inorganic Pb, dimethyl lead, trimethyl lead, diethyl lead, triethyl lead and tetraethyl lead species. The tetraethyl lead species were eluted from the column with ethanol, the inorganic lead and the remaining organolead species were eluted with 1 M HNO_3. The

method was applied to the speciation of Pb in tap and river waters. The results obtained indicated that the lead level in these samples was below the permissible level for drinking water (50 $\mu g\ l^{-1}$), and that the tetraethyl lead in these samples was below the detection capability of this method. The samples were spiked with Pb at the 20 $\mu g\ l^{-1}$ level and the recoveries obtained were between 81-105 %.

Yebra-Biurrun *et al.* determined Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in natural waters with AAS, following on-line microcolumn preconcentration (129). A microcolumn filled with the chelating resin poly(aminophosphonic acid) (PAPhA) was utilised for the enrichment procedure. Detection limits between 0.4 (Zn) and 5 (Co) $\mu g\ l^{-1}$ were achieved for a sampling rate of 48 h^{-1}. The precision (RSD) ranged between 1.1 to 3.3 %. The effect of potentially interfering ions on the analyte signals was studied. No interference was observed for Al^{3+}, B^{3+}, Ca^{2+}, Mg^{2+}, Si(VI), Cl^-, SO_4^{2-} and NO_3^- when present in solution at concentrations encountered in natural waters. The method was applied to the certified reference material (CRM) IAEA/W-4. The results obtained were in good agreement with the certified values, and 98-105 % recoveries were obtained for a spiked CRM sample. The procedure was then applied to the determination of trace analytes in selected tap water samples.

1.6.5 Anion Exchangers

Kamson and Townshend compared two anion exchangers for their ability to remove interferences on the determination of Ca, by on-line FI-AAS (130). The resins Amberlite IRA-400 and De-Acidite FF were packed into microcolumns and incorporated into the FI system. Hence, the anionic species was retained by the resin, on passage of a sample through a column. The Ca was not retained and was subsequently determined by AAS. Initially, the effect of the potential interfering species, sulphate, phosphate and silicate, on the Ca signal was investigated, by conventional aspiration. It was observed that all three species significantly reduced the analyte signal, when present in solution. Therefore, the microcolumn technique was applied to the determination of Ca. Both anion exchangers completely removed the anionic interferences from the species sulphate

and phosphate, due to their retention by the resin. The silicate interference was not removed. However, the addition of HF, converted the silicate to hexafluorosilicate, which was completely retained by both resins, eliminating the interference observed by this species. The effect of the potential cationic interferences, Al, Fe, La, Ba and Na was studied. Al indicated significant interference on the Ca signal. In an attempt to remove this interference, the conversion of Al to hexafluoroaluminate was studied. This was unsuccessful.

Haj-Hussein *et al.* utilised a microcolumn of cupric sulphide, for the indirect determination of CN^-, by on-line FI-AAS (131). The passage of a sample, buffered with KOH and containing CN^-, through the column, produced a chemical reaction. A proportion of the cupric sulphide was dissolved, forming cuprocyanide complexes. The eluent from the column therefore contained Cu, which was subsequently determined by AAS, indirectly determining CN^-. A detection limit of 1 m gl^{-1} was attained and a sampling frequency of 40-50 h^{-1}. Potential anionic interferences were studied. Acetate, sulphate, borate, oxalate, phosphate, thiocyanate, bromide, chloride, iodide, nitrate, nitrite, fluoride and carbonate had no effect on the analyte signal. Only citrate showed significant interference, indicating the high selectivity of the technique.

Garcia *et al.* determined Al in dialysis fluids and tap water samples, by on-line microcolumn preconcentration with FI-AAS and FI-ICP-ES detection (132). The resin Amberlite IRA-400 was utilised for the enrichment of Al and matrix separation. The detection limit obtained by FI-AAS was 20 μg l^{-1} and by FI-ICP-ES was 3 μg l^{-1}. Sodium chloride enhanced the Al signal significantly up to concentrations of 3000 mg l^{-1} therefore, the concentration of NaCl in every sample and standard solution was maintained at 3500 mg l^{-1}. The presence of Na, K, Ca, Mg, Zn, Cu, Cr(VI), acetate, carbonate, sulphate and hydrogen carbonate, had no effect on Al recovery. The presence of Fe(III), Cr(III), fluoride, phosphate and ethylenediaminetetraacetic acid (EDTA) however, significantly reduced the Al recovery. This was due to either the retention of Fe and Cr by the resin, which subsequently trapped Al, as it could not be eluted with 1 M NaOH or, the formation of Al complexes with F^-, PO_4^{3-} and EDTA which were not

retained by the resin. The technique was applied to the analysis of human serum, however Al was not determined. The serum was spiked with known concentrations of Al, nevertheless Al was not determined. It was suspected that Al was present in this sample, in the protein transferrin and could not be retained by the resin. The analysis of dialysis samples and tap water was investigated by FI-ICP-ES and graphite furnace AAS. The results obtained indicated reasonable agreement.

Patel *et al.* developed an on-line speciation technique, for the preconcentration and determination of V(V) in the presence of V(IV), by FI-AAS (133). A microcolumn of silica bonded Bond Elut, a strong anion exchanger, was incorporated into the FI system, to effectuate enrichment of V(V). Vanadium (IV) was not retained by the resin and was therefore detected by AAS. The V(V) was subsequently eluted with 1 M NaOH and determined. Vanadium (V) was quantitatively recovered at the 50 $\mu g\ l^{-1}$ level. The recovery of V(V) was significantly reduced by the presence of Cl^-, at concentrations in solution > 0.5 M.

Qi *et al.* utilised a microcolumn of 8531 fibre, which contains phosphine oxide functional groups, to enrich and determine Au in ores and metallurgical samples, by on-line FI-AAS (134). Acidic Au(III) was selectively retained by the fibre, and 5 $g\ l^{-1}$ thiourea was used to elute the anions for subsequent determination. A detection limit of 0.2 $\mu g\ l^{-1}$ and a sampling frequency of 40-60 h^{-1} were achieved, utilising an efficient, automatic FI manifold. The effect of potential interfering species on the analyte signal was investigated. No significant deterioration of the analyte signal was observed, in the presence of more than 40 species. Close agreement with the certified reference materials Au and Ag ores, was obtained. The technique was applied to the analysis of ores and metallurgical samples, attaining satisfactory results.

Shabani and Masuda determined Re in seawater samples, utilising on-line microcolumn preconcentration and FI-ICP-MS detection (135). The anion exchanger Dowex 1-X8 was used for enrichment. A detection limit of 0.1 $ng\ l^{-1}$ was achieved. Seawater samples were analysed by this technique and by a similar isotope dilution

technique. The results obtained were in reasonable agreement and were equivalent to previously reported values for Re in seawater.

Gomez and McLeod evaluated the use of two anion exchangers, for the enrichment and determination of Au in refinery effluents, by on-line FI-ICP-ES (136). Amberlyst A-26 and sulphydryl cotton fibre (SCF), were packed into microcolumns and incorporated into the FI system to facilitate preconcentration. Ammonia solution and potassium cyanide respectively, were used for the subsequent elution and determination of Au. The presence of Cl^- assisted in the retention of Au, for both exchangers. This was presumed to be due to the stabilisation of the Au(III) as a chloro complex in solution. It was observed that the presence of F^- and PO_4^{3-} significantly reduced the recovery of Au from the Amberlyst exchanger and Br^- and I^- had the same effect from the SCF exchanger. A detection limit of 1.7 $\mu g\ l^{-1}$ was attained for Amberlyst and 0.8 $\mu g\ l^{-1}$ for SCF. The recovery of Au from two refinery effluents was acceptable and levels of 12 and 25 $\mu g\ l^{-1}$ were found for both exchangers.

The same workers also utilised a microcolumn of sulphydryl cotton to enrich and determine Au in natural waters by FI-ICP-MS (137). A detection limit of 0.19 $ng\ l^{-1}$ was achieved, and the RSD at the 5 $ng\ l^{-1}$ level was 3.6 %. Simple aqueous Au standards were prepared and Au standards in colloidal form. This was achieved with the addition of humic acid to the standards. The key experimental parameters investigated and optimised in a previous study (136) were utilised in this investigation. Although 250 µl of 0.01 M KCN is an effective eluent, repeat injections of eluent indicated residual background contamination. This was assumed to be due to reversible adsorption of Au on tubing, components of the sample introduction system and the sampling cones of the MS. The memory effect was minimised with the use of 0.01 M HCl as carrier. Quantitative retention of colloidal gold (94 -104 %) was achieved with this procedure. It is believed that ionic Au is retained by chemical complexation and mechanical trapping and/or electrostatic interactions may be responsible for the removal of colloidal Au. Hence, sulfhydryl cotton fibre may have the capacity to quantitatively retain both ionic and colloidal Au. The technique was applied to the determination of Au in mineral,

stream and lake waters. Relatively high levels were found in the lakes and streams. Au was not determined in the mineral waters but spike recovery data was acceptable (90-99 %).

Pyrzynska determined Au in geochemical reference samples, utilising microcolumn enrichment and FI-AAS detection (138). The microcolumn was packed with the cellulose sorbent Cellex T. The detection limit for this method was 2.2 $\mu g\ l^{-1}$ and the precision obtained at the 20 $\mu g\ l^{-1}$ level was 2.6 %. No significant interferences due to the presence of common inorganic ions in natural waters were observed. Moreover, the presence of Pt ions did not affect the Au signal. These results suggest a preferential uptake of Au by Cellex T. The method was applied to the certified reference materials platinum metal ore SARM 7 and pyrite ore RUS-1. The results obtained are in good agreement with the certified values. The procedure was also applied to the recovery of Au from seawater samples. The recovery obtained was 97 %.

Di and Davey utilised a microcolumn of α-amino pyridine bonded to a cross linked polyphenylethene, to preconcentrate and separate Pd, Pt and Ir with FI-AAS detection (139). Two mechanisms were proposed for the retention of the analytes. These were solvation and ion exchange. The effect of pH on the recovery of the analytes indicated that Pt and Ir were not affected by pH between 1 and 5, but the recovery of Pd significantly decreased below pH 2. Hence Pt and Ir were retained mainly by the solvation mechanism and Pd by ion exchange. Therefore Pt and Ir can be separated from Pd merely by adjusting the pH of the sample. An eluent comprising of 0.5 $Mg(ClO_4)_2$, 0.5 M $HClO_4$, 0.5 M HCl was utilised for elution. However selective elution of the analytes can be achieved utilising the following eluents in series: (1) 0.5 M $HClO_4$, 4 M HCl for Ir; (2) 0.1 M CH_3COONa, 0.5 M HCl for Pd; and (3) 0.5 $Mg(ClO_4)_2$, 0.5 M $HClO_4$, 0.5 M HCl for Pt. The analytes Pd, Pt and Ir were separated from potential interferences utilising 2 M HCl as the carrier solution. This removed co-eluting analytes (alkali, alkaline earth and heavy metals) from the column, prior to elution of the analytes of interest. However, Fe at a concentration of 200 mg ml^{-1} significantly affected the recovery of the Pt, Pd and Ir. This interference was eliminated by the addition of 0.2 M

ethylenediaminetetraacetic acid (EDTA). The detection limits obtained for Pt, Pd and Ir by this method were 0.017, 0.009 and 0.11 μg ml^{-1} respectively. The technique was applied to the recovery of these analytes from selected certified reference materials, such as SARM 7. The recoveries obtained were acceptable.

Martin-Esteban *et al.* determined Al in tap water and dialysis solutions, using on-line microcolumn enrichment and FI-AAS and FI-ICP-MS detection (140). The microcolumn was packed with the reagent Chromotrope 2B, which was immobilised on the anion exchanger AG 1-X8. Detection limits of 10 and 0.1 μg l^{-1} were achieved for AAS and ICP-MS, respectively. Two linear sections were found for the calibration plot of concentration against AAS signal. This was assumed to be due to different binding mechanisms between Al and the column packing reagent. At low Al concentrations (< 500 μg l^{-1}), the supposition is that a chelate is formed between Al^{3+} and Chromotrope 2B. At high Al concentrations (500 - 2000 μg l^{-1}), it is assumed that Al is hydrolysed to $Al(OH)_3$. This precipitate is most likely adsorbed by Chromatrope 2B. This reagent is highly selective, as Al was completely separated from Pb, Zn, Ni, Cd, Ca, Mg, Cr and Cu using this technique. The analytes Fe(II) and Fe(III) were partially retained by the resin but no interference was observed on the Al signal. The method was applied to the determination of Al in tap water and dialysis solutions. The results were compared to those obtained by electrothermal AAS and showed good agreement.

1.6.6 Activated Alumina

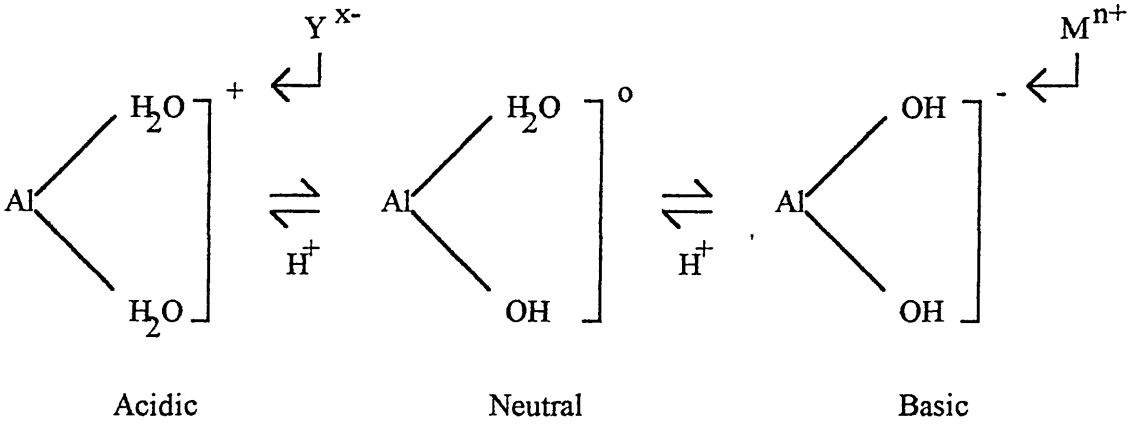


Fig.1.26 Deposition/elution process for ions on activated alumina.

Activated alumina offers a novel route for analyte enrichment, since it can function as both an anion and cation exchanger (see Fig.1.26).

Cox *et al.* utilised a microcolumn of activated alumina, for the on-line speciation of Cr(VI) and Cr(III), by FI-ICP-ES (141). The alumina was used in the acidic form, to ensure retention and enrichment of Cr(VI). The Cr(III) was not retained and thus passed directly to the ICP-ES for determination. The detection limits achieved by this technique were 1.4 and 0.2 $\mu g\ l^{-1}$, for Cr(III) and Cr(VI) respectively. An acidic carrier stream of 0.1 M HNO_3, assured the efficient retention of Cr(VI). The eluents NH_4OH and KOH, at concentrations above 1 M, indicated efficient elution of Cr(VI). However, further investigation showed that KOH had a greater detrimental effect on the alumina column, and hence NH_4OH was selected as the eluent. Studies indicated that only 86 % of the total Cr(VI) retained, was recovered in the first elution, however this was reproducible. The technique was applied to the analysis of the certified reference water 1643a issued by the National Bureau of Standards (NBS), and the British Geological Survey sample water C2. The combined result for Cr(III) (14.8 ± 1.0 ng g^{-1}) and Cr(VI) (1.96 ± 0.32 ng g^{-1}), was in close agreement with the total certified value for Cr (17 ± 2 ng g^{-1}) in the NBS sample.

McLeod *et al.* determined phosphorous in steels, utilising on-line microcolumn preconcentration and FI-ICP-ES detection (57). The column was packed with activated alumina in the acidic form, which was used for analyte enrichment and matrix removal. A detection limit of 0.6 mg l^{-1} was attained and an RSD of 1.6 % at the 20 mg l^{-1} level. The effect of varying acid strengths (0, 0.01, 0.1, 1, 10 % v/v) on the retention of PO_4^{3-} was investigated. HNO_3 concentrations < 0.01 % indicated incomplete retention. Therefore an acid strength of 0.1 % was selected. Microcolumn lengths between 1-10 cm and carrier flow rates up to 2.6 ml min^{-1}, had little effect on analyte retention. A column of 2.5 cm and a carrier flow rate of 1 ml min^{-1} were chosen. The effect of various eluents on the elution of PO_4^{3-} was studied. The eluent NH_4OH was ineffective but KOH and NaOH indicated efficient elution of PO_4^{3-}. The eluent concentration was varied in the range 0.1-2 M. Concentrations of KOH below 0.5 M indicated incomplete

elution, hence 0.5 M was selected. The elution of PO_4^{3-} was not significantly affected by varying the eluent volume between 50-400 µl. Experiments indicated that 90 % of the PO_4^{3-} retained was recovered in the first elution, however 200 µl injections of eluent, provided reproducible results. Reasonable agreement with the certified value of P in the steel sample BCS 408 (0.043 %) was obtained by this technique (0.041 %).

Cox and McLeod utilised a microcolumn of activated alumina in the basic form, to preconcentrate and determine Cr(III), by on-line FI-ICP-ES (142). The technique was applied to the analysis of urine samples. A detection limit of 0.05 µg l^{-1} and an RSD of 2.4 %, at the 10 µg l^{-1} level, were achieved. The pH range observed for quantitative Cr(III) retention was 2-7. The effect of carrier concentration on the retention of Cr(III) was investigated. Efficient retention was attained for NH_4OH concentrations in the range 0.02-0.1 M. However, concentrations of 0.05 M or above reduced the elution efficiency, hence 0.02 M was selected. The eluent HNO_3 at a concentration of 2 M, was required to achieve > 93 % recovery of Cr. It was observed that the Cr signal was enhanced, in matrix matched standard solutions. This was possibly due to the retention and subsequent elution of the alkaline earth elements, with the analyte signal. Hence, the enhanced signal was simply increased background noise, produced as a result of stray light and ion-electron recombination, by intense emitters such as Ca and Mg. Close agreement with the certified value of Cr in the urine sample 2670 (0.085 ± 0.006 µg ml^{-1}), which was issued by the National Bureau of Standards, was achieved by this technique (0.079 ± 0.004 µg ml^{-1}).

Cook *et al.* utilised activated alumina microcolumns to determine the oxyanions arsenate, borate, chromate, molybdate, phosphate, selenate and vanadate, by FI-ICP-ES (143). Retention and elution efficiencies were calculated for each species. Quantitative retention was obtained for each of the oxyanionic species, with the exception of borate. The species were further sub-divided into three classes, according to their elution characteristics. Effective elution was not achieved for arsenate or vanadate, even with the use of strong alkali (1 M KOH). Selenate and phosphate indicated effective elution with the use of strong alkali, and molybdate and chromate indicated effective elution

with the use weak alkali (1 M NH_4OH). Hence, under the experimental conditions utilised in this study, the former class were irreversibly bound to activated alumina. Activated alumina compared favourably with conventional ion-exchange resins. No significant volume changes were observed on elution, in comparison to Chelex-100, and sharp transient peaks were obtained.

Cox *et al.* utilised on-line microcolumn preconcentration and FI-ICP-ES, for the determination of sulphate in natural waters, seawater and boiler feed waters (144). Activated alumina in the acidic form, was packed into the microcolumn and used for SO_4^{2-} enrichment. A detection limit of 2.8 $\mu g\ l^{-1}$ was attained for this procedure and a sampling frequency of 4 h^{-1}. The frequency could be increased however, by increasing the sample flow rate. The eluents, KOH at a concentration of 0.5 M or NH_4OH at 2 M, produced a > 80 % recovery of SO_4^{2-}. The eluent NH_4OH was selected, as alumina did not deteriorate as quickly with this reagent. The effect of potential interfering species, Ca, PO_4^{3-} and Cl^-, on the analyte signal was studied. The species had no effect. The results obtained by this technique and by conventional ICP-ES, for natural waters and seawater samples were presented. The results were in close agreement, indicating that the results obtained for boiler feed waters were valid. The concentration of SO_4^{2-} in these samples precluded their determination by direct analysis.

McLeod *et al.* used FI-ICP-ES with on-line microcolumn enrichment, for the determination of the analytes Cr(III), Cr(VI), Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn, in certified reference waters (145). The microcolumn was packed with activated alumina in the acidic form, for the preconcentration of Cr(VI), and in the basic form, for the enrichment of the cationic analytes. The standard reference water 1643a issued by the National Bureau of Standards was analysed by this technique, for Cr(VI) and Cr(III). The combined results were in close agreement with the total certified Cr value. The complexing agent tartrate was utilised in the preconcentration of the cationic analytes. The use of this reagent ensured high retention efficiency over a wide pH range, increased the capacity of the column and extended the sampling times that could used, increasing the sensitivity of the technique. The results obtained by this technique, for the certified

river water SLRS-1, were in reasonable agreement with the reported values (see Table 1.2). The exceptions were Cd, Co and Pb, these were considered to be due to contamination in the sample preparation and/or processing.

Analyte	FI-ICP-ES µg/l	Certified Value µg/l
Cd	0.028	0.015 ± 0.002
Co	0.058	0.043 ± 0.01
Cu	3.1	3.58 ± 0.3
Fe	33.3	31.5 ± 2.1
Mn	1.3	1.77 ± 0.23
Ni	1.1	1.07 ± 0.06
Pb	0.7	0.106 ± 0.011
Zn	1.23	1.34 ± 0.2

Table 1.2 Analytical data obtained for SLRS-1 by the microcolumn enrichment technique with ICP-ES detection. The microcolumn contains activated alumina in the basic form. Reference 145.

Zhang *et al.* utilised a microcolumn of activated alumina in the basic form, to enrich and quantify Pb in potable waters, by FI-AAS (146). A detection limit of 0.36 µg l^{-1} was attained and RSD values of 1.4 and 12 %, for 40 and 4 µg l^{-1} Pb, respectively. The sample flow rate was studied over the range 1-6 ml min^{-1}. No significant effect on the analyte signal was observed, for microcolumns of 2 and 6 cm in length. However, incomplete retention occurred for a 1 cm column, above 3 ml min^{-1}. As the eluent flow rate was increased to 5 ml min^{-1} the analyte peak height increased. Above this flow rate no significant increase was observed. Therefore, a sample and eluent flow rate of 5 ml min^{-1} and a 6 cm column, were selected for further studies. It was shown that > 95 % of the Pb retained, was recovered in the first elution. The effect of pH on the retention of Pb was investigated, with and without the addition of the complexing agents, acetate, citrate and tartrate. A clearly defined pH range, for the maximum retention of Pb, was observed for each system. The addition of tartrate was selected, due to the slightly enhanced sensitivity observed for Pb, using this reagent. The enrichment capability of the microcolumn was studied. A linear relationship between absorbance and sampling time was found up to 8 min. The effect of the matrix cations Ca, Mg, Na and K, on the

analyte signal was investigated. The cations produced no interference, indicating the selectivity of alumina for Pb, in their presence. Complete recovery of Pb was attained from tap, ground, river and the certified reference water 1643a, which was issued by the National Bureau of Standards. Reasonable agreement was obtained by this technique and ICP-MS, for the analysis of the above samples.

Furuta *et al.* utilised FI and a spectrally segmented photodiode array ICP-ES, for the determination of Mo in seawater (147). A microcolumn of activated alumina in the acidic form was incorporated in the FI manifold, to obtain molybdate enrichment. A detection limit of 0.2 $\mu g\ l^{-1}$ and RSD values of 2 and 5 %, for Mo concentrations of 500 and 10 $\mu g\ l^{-1}$ respectively, were attained. The enrichment capability of the microcolumn was studied. A linear relationship between emission intensity and sampling time was observed, up to 10 min. It was shown that only 87 % of the Mo retained, was recovered in the first elution. The pH range for maximum retention of Mo was between 2-4. The analyte signal was not affected by the presence of a high concentration NaCl matrix. However, reduced retention efficiency was observed, for the seawater reference material NASS-2. This was possibly due to competition for available sites, from matrix anions such as SO_4^{2-} and PO_4^{3-}. A standards addition procedure was therefore adopted for the analysis of NASS-2. The result obtained was in close agreement with the certified value.

Coetzee *et al.* used on-line microcolumn preconcentration and FI-AAS detection, for the determination of Ag in borehole water (148). Activated alumina in the basic form was packed into the microcolumn and utilised for the enrichment of Ag. A detection limit of 2.9 $\mu g\ l^{-1}$ and an RSD of 5 %, for Ag concentrations above 10 $\mu g\ l^{-1}$, were attained. Ammonia solution (0.15 M), was utilised to regenerate the alumina to the basic form, following each determination. This reagent was not used as the carrier however. Excess ammonia prevented the retention of Ag, possibly due to the formation of $Ag(NH_3)_2^+$, which was not retained by the column. Water was therefore used as the carrier and flushed the excess ammonia from the column before analysis. The effect of sample pH on the absorbance of Ag was investigated. Maximum absorbance was observed at pH 4. The sample flow rate was varied for different column lengths. A 3 cm

column, at a flow rate of 5 ml min^{-1}, indicated optimum absorbance. The optimum elution flow rate was 5 ml min^{-1}. The enrichment capability of the alumina column was studied. A linear relationship between absorbance and sampling time was observed, up to a sampling period of 7 min for a 100 μg l^{-1} standard solution and 5 min for a 500 μg l^{-1} standard solution. The effect of matrix cations, Na, Mg and Ca on the analyte signal was investigated. A significant decrease in absorbance was observed, when the cations were present in solution at concentrations above 0.5 M. The technique was applied to the analysis of borehole waters. A standard addition procedure was adopted. The results obtained were in satisfactory agreement with known values.

Sperling *et al.* utilised a microcolumn of activated alumina in the acidic form, to preconcentrate and quantify Cr(III) and Cr(VI) in water samples, by on-line FI-AAS (149). Selective retention was possible, using the Clark-Lubs buffer system. Cr(III) was retained at pH 7 and Cr(VI) at pH 2. The species were eluted and determined with 1 M HNO_3 and 0.5 M NH_4OH, respectively. A sampling frequency of 55 h^{-1} was attained and detection limits of 1 and 0.8 μg l^{-1} for Cr(III) and Cr(VI). Initially the flame conditions were optimised for Cr determination. The effect of various buffers, at selected pH values, on the retention of Cr(III) and Cr(VI) was studied. The optimum pH for Cr(III) retention was pH 7, which was presumed to be due to the adsorption of the uncharged species, $Cr(OH)_3$ on the neutral alumina surface. The presence of the buffer enhanced the signal. The optimum pH range for Cr(VI) retention was 1-5.6. It was suggested that the negatively charged species, $[HCrO_4]^-$ was adsorbed by acidic alumina. The presence of the buffer suppressed the signal. Clark-Lubs buffer at a concentration of 0.2 M was selected for further studies. The effect of sample flow rate on Cr retention was investigated. A flow rate of 4 ml min^{-1} was selected, as the Cr signal did not deteriorate at this rate, the maximum possible for this FI system. A buffer flow rate of 0.5 ml min^{-1} ensured optimum retention of Cr. Ammonia solution at a concentration of 0.5 M and HNO_3 at 1 M, ensured maximum elution of Cr(VI) and Cr(III) respectively, at a flow rate of 2.2 ml min^{-1}. The retention efficiency was calculated to be 80 % for Cr(III) and 92 % for Cr(VI). The effect of the matrix cations,

Pb, Cu, Cd, Ni, Mn, Zn, Fe and Al, on the determination of Cr(III) was investigated. No significant interference was observed, from levels present in natural waters. However, higher concentrations of Al and Fe, indicated significant interference. Matrix anions had a significant effect on the retention of Cr(VI). This was dependent upon the concentration of the competing anions in relation to chromate, their affinity for activated alumina and the availability of active sites. However, it was possible to determine Cr(VI) in natural waters, as the alumina column could tolerate nitrate, sulphate, phosphate and molybdate at 5000, 1000, 100 and 20 fold excesses respectively, compared to chromate. Recoveries of Cr(III) and Cr(VI) from a selection of drinking, river and lake waters were in the range 90-106 %. The Cr(III) result obtained by this technique for the reference waters 1643a and c, issued by the National Institute of Standards and Technology, indicated close agreement with the total Cr value. Cr(VI) was not detected.

Yamada *et al.* utilised on-line microcolumn enrichment, for the determination of S in high purity iron samples, by FI-ICP-ES (150). The microcolumn was packed with activated alumina. A detection limit of 0.3 g g^{-1} was achieved. The S present in the sample was oxidised to SO_4^{2-}, with the use of HNO_3 and HCl. Five types of activated alumina, with different particle sizes (p.s.), were investigated. Acidic alumina 90, activity I and activity II-III (Merck), indicated optimum adsorption of SO_4^{2-} and lowest reagent blanks. The eluent 2 M NH_4OH ensured > 90 % of the sulphate retained, was recovered in the first elution. The effect of matrix species on the retention of sulphate was investigated. The maximum concentrations of the species, Si, Mn, P, Ni, Cr, Mo, Cu, V, W, Co, Al and Se, that did not interfere with the retention of sulphate, were reported. The acids used in the dissolution procedure suppressed the retention of sulphate. It was therefore necessary to adopt three standard addition procedures, for the analysis of JSS certified reference steel samples. The results obtained were in close agreement with the certified values for sulphate.

Cantarero *et al.* determined Pt in natural water samples, using on-line microcolumn enrichment and FI-AAS detection (151). The microcolumn was packed with acidic alumina. A detection limit of 0.02 mg l^{-1} was achieved and precision at the

0.1 mg l^{-1} level was 9 %. The predominant species of Pt in natural waters is $[PtCl_6]^-$. Hence key experimental parameters were optimised in order to maximise the recovery of this species, using acidic alumina. Quantitative retention of Pt was achieved for carrier concentrations (HNO_3) within the range 0.01-0.1 M. A concentration of 0.01 M was selected. The effect of sample pH on the retention efficiency indicated that pH 2.5 was optimum. Efficient elution was achieved with 2 M NH_4OH. Sample flow rates up to a maximum of 4 ml min^{-1} produced effective retention of Pt. A sample flow rate of 3 ml min^{-1} was selected to avoid problems with back pressure. The maximum flow rate for the complete elution of Pt was 1 ml min^{-1}. The smallest volume of eluent to achieve complete elution of Pt was 25 µl. The effect of potentially interfering anions (Cl^-, Br^-, I^- F^-, PO_4^{3-}, SO_4^{2-}) on the recovery of Pt was studied. No interference effects were observed at the concentrations of these anions found in natural waters. The exception was Cl^-, which significantly decreased Pt recovery at concentrations of 1000 mg l^{-1}. The technique was applied to the determination of Pt in spiked tap water samples. Recoveries between 97-103 % were achieved, which indicated that the technique was suitable for the trace determination of Pt in natural waters.

Dadfarnia and McLeod utilised microcolumns of activated alumina in the basic form, to enrich and determine U in natural waters, by FI-ICP-MS (152). A preconcentration factor of 40, and a detection limit of 4 ng l^{-1} was achieved. Precision at the 50 ng l^{-1} level was 4.5%. Incomplete retention of U was initially observed. This was assumed to be due to the formation of anionic species, which activated alumina could not retain. The complexing agent sodium acetate was added to sample and standard solutions, in an attempt to prevent hydrolysis. Complete retention of U was then observed. The effect of the buffer concentration was investigated. Incomplete retention was observed at concentrations below 0.25 M. Therefore, a concentration of 0.3 M was selected for further studies. The effect of sample pH was investigated. Incomplete retention of U was observed below pH 7. This was attributed to loss of active sites under acidic conditions. A pH of 8 was selected. Sample flow rates greater than 4 ml min^{-1} produced incomplete retention. A flow rate of 3.5 ml min^{-1} was thus

chosen. A linear relationship was observed between signal response and sample volume, for U standard solutions and seawater samples, between 1-12 ml. This indicated that U was preferentially retained by activated alumina, from the presence of matrix cations such as Na, K, Ca and Mg. The technique was applied to the certified reference materials NASS-1 and SLRS-1. Good agreement with the certified value was obtained for NASS-1, but poor agreement was found for SLRS-1. Spiked recovery experiments were also carried out on a seawater sample from the North Sea, and selected mineral waters. Greater than 99 % recovery was obtained. It should be noted that the level of U found in one of the mineral water samples, was greater than the maximum permissible level (20 $\mu g\ l^{-1}$) set by the Canadian regulatory authority.

Ebdon *et al.* determined the trace analytes As, Cr, Se and V in biological samples, by ICP-MS using on-line elimination of interference and preconcentration by FI (153). A microcolumn of acidic activated alumina was utilised to perform enrichment and matrix elimination. Detection limits between 1.2 (V) and 65 $\mu g\ l^{-1}$ (Se) were achieved without preconcentration. The Se detection limit was reduced to 1 $\mu g\ l^{-1}$ with preconcentration. The initial experiments were performed using AAS, to ensure that the analytes were retained by alumina. Standards were prepared containing 6 % v/v HNO_3, 6 % v/v 60 % NaOH and 0.2 % m/v potassium persulphate, and diluted to volume with Tris buffer. This ensured the analytes were converted to oxyanions. An interference study was performed in which the effects of NaCl (1 % w/v) were determined, with and without the microcolumn present. In the absence of the microcolumn Cl^- severely interfered with the determination of the analytes. The interference was substantially reduced when the column was utilised. The technique was applied to the certified reference materials, 9 Sargasso Seawater, Tort-1, Dorm-1 and Dolt-1, issued by the National Institute of Environmental Studies. Selenium was not detected due to sensitivity limitations, and V and Cr indicated reasonable agreement with the certified values. Arsenic indicated close agreement with the certified value for Sargasso, but poor agreement for the biological samples. This was assumed to be because the As was present in these samples as the extremely stable compound arsenobetaine, which is

known to withstand many acid digestion procedures. Thus the sample was subjected to photolysis by ultraviolet light and re-analysed. Good agreement with the certified values was then obtained for As. Se was preconcentrated using the microcolumn technique and the samples were re-analysed. Good agreement with the certified values was obtained. Tests showed between 98-109 % recovery for the analytes in a spiked sample.

Trojanowicz and Pyrzynska utilised microcolumn preconcentration to determine Co in oriental tobacco leaves by FI-AAS (154). The microcolumn was packed with 1-nitroso-2-naphthol-3,6-disulphonate-modified alumina. A detection limit of 0.44 $\mu g\ l^{-1}$ was achieved and precision at the 10 $\mu g\ l^{-1}$ level was 2.3 %. The effect of sample and elution flow rate on the analyte signal was investigated. A sample and elution flow rate of 1.6 and 2.7 ml min^{-1} respectively, were selected as optimum. The smallest eluent volume to achieve complete recovery of Co was 0.1 ml of 3 M or 0.2 ml of 0.1 M NaOH. The effect of sample pH on the Co signal was investigated from pH 2-10. Maximum retention was achieved at pH 2. A column length of 50mm was selected as it improved the recovery of Co utilising optimum conditions compared to a 20 mm column. The effect of potentially interfering ions (alkali, alkaline earth and heavy metals) on the Co recovery was studied. No interferences were observed. This result suggested that Co was preferentially retained in the presence of Fe, Cu and Ni, which form stable complexes with this column packing reagent. The technique was applied to the determination of Co in the certified reference material (CRM) CTA-OTL-1 (oriental tobacco leaves) and the recovery of Co in synthetic seawater. The result obtained for the CRM was in good agreement with the certified value and the recovery from the seawater sample was 97 %.

In summary, the major developments of on-line microcolumn preconcentration with atomic spectrometric detection have arisen from the modification of the FI configuration and the optimisation of on-line microcolumn preconcentration performance parameters. The FI manifold has been developed considerably, from the single line, single column configuration, to encompass dual column sampling and PC controlled preconcentration units. These systems are highly efficient, achieving high sampling

frequencies with low sample and reagent consumption. Performance parameters affecting retention efficiency have been optimised. These are column packing material, sample pH, sample flow rate, analyte concentration, matrix concentration, ionic strength, buffer or complexing agent, and the microcolumn parameters, length, internal diameter and particle size of packing material. Performance parameters affecting elution efficiency have also been optimised. These are elution flow rate and the eluent parameters, nature, strength and volume. The procedures thus optimised are highly sensitive, providing reproducible, precise and accurate results.

1.7 Aims and Scope of This Study

Despite great improvements in the sensitivity of modern analytical instrumentation, separation techniques such as solvent extraction, ion-exchange and coprecipitation are frequently used to overcome matrix interferences and/or enhance sensitivity through enrichment of the analyte (60-62). Manually operated separation procedures are generally time-consuming, involve high sample and reagent consumption, and are susceptible to contamination. However, with the introduction of flow injection (FI) analysis, traditional chemical separation procedures have been scaled down and incorporated on-line. There has been a considerable amount of research carried out in recent years in which a number of chemically different microcolumn systems have been employed with FI-ICP-ES. The majority have been limited to laboratory based experiments on standard reference materials. The work reported in this thesis is concerned with the ultratrace analysis of high purity materials and a range of natural waters (mineral, river, reservoir), using microcolumn enrichment, flow-injection and ICP-ES procedures. The inherent advantages of using on-line microcolumn preconcentration in combination with FI-ICP-ES has been discussed in section 1.6.

It is intended to provide new methodology for the ultratrace analysis of high purity alkali metal salts (CsI, KBr, NaCl, NaF, $LiNO_3$). Activated alumina microcolumns will be utilised to retain and enrich trace analytes (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the presence of relatively concentrated matrices (1 % w/v), prior to elution and

determination. This procedure simultaneously isolates the analytes from these matrices. This technique overcomes sensitivity limitations and possible difficulties arising from matrix interferences.

The microcolumn enrichment technique with ICP-ES detection will also be applied to the ultratrace determination of eleven analytes present in natural waters (mineral, reservoir). The underlying aim of this study is to determine if measurements obtained utilising activated alumina microcolumns with FI-ICP-ES are equivalent to existing measurement techniques. The determination of dissolved/filterable species of the analytes present in natural waters is currently achieved by a multi-element analysis technique (graphite furnace AAS, AAS, ICP-ES, ICP-MS etc), following the filtration of the sample in the field through 0.45 μm membrane filters, and acidification of the filtrate. Suspended species are collected on the filter, digested and analysed by a conventional multi-element technique. Total recoverable species are analysed by a multi-element analysis technique, usually following an appropriate digestion procedure but without filtration of the sample. Experiments will be devised in an attempt to ensure that the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in selected natural waters are determined by the microcolumn enrichment procedure with FI-ICP-ES detection.

It is also proposed to utilise microcolumns of activated alumina as field sampling tools. Samples will be collected in the field and processed through the alumina microcolumns, effectively immobilising the analytes to be determined. Hence an alumina microcolumn sampling stage to effect concentration and isolation prior to analytical measurement is at the core of the investigation. The overall aim is to extend the application of alumina microcolumns, and in particular to provide a new multi-element field sampling device which gives high sample integrity and preconcentration.

This study therefore explores a number of sample types of varying complexity to determine the critical parameters and conditions which need to be addressed to achieve the overall goals.

2 Experimental

2.1 Reagents

All reagents were of Aristar grade and Milli Q de-ionised water was used throughout to dilute solutions. All reagents and standard solutions were stored in pre-cleaned Nalgene bottles. Multi-element standards were prepared using suitable dilutions of 1000 mg l^{-1} Spectrosol aqueous standards, purchased from BDH chemicals. The required multi-element standard solutions were prepared daily from a 100 mg l^{-1} stock solution, which had been stored at 4 ^{o}C for no longer than 3 months, and contained barium, cadmium, calcium, cobalt, chromium, copper, iron, magnesium, manganese, nickel, lead, vanadium and zinc. The Group 1 salts lithium nitrate, sodium fluoride, sodium chloride, potassium bromide, caesium iodide and caesium chloride were prepared daily at a concentration of one percent, w/v. The carrier was 0.02 M ammonium hydroxide, and was prepared from concentrated ammonia solution. The eluent was 2 M nitric acid, and was prepared from concentrated nitric acid. Any adjustment of pH in the diluted solutions was achieved using ammonium hydroxide or nitric acid solutions. Complexing agent solutions (tartaric acid and acetic acid 0.025 M) were prepared as required.

2.2 Preparation of Alumina Microcolumns

The activated alumina was purchased from BDH (Brockman Grade 1). It was sieved to achieve a particle size in the range 150-180 μm. The microcolumns were constructed from 8 cm lengths of 0.6 mm internal diameter Teflon tubing. A length of tubing was taken and a piece of sponge inserted 1 cm from one end. The alumina was scooped into the tube, until it was packed 1 cm from the opposite end, where another piece of sponge was inserted. A 2 cm length of 0.6 mm external diameter Teflon tubing was then placed in each end of the microcolumn, to ensure the alumina remained in place. The microcolumns prepared were conditioned in the FI system for around 10 minutes. During which time the carrier, 0.02 M ammonium hydroxide and the eluent, 2 M nitric acid were passed through the column intermittently.

2.3 Flow Injection Manifolds

2.3.1 Single Valve System

The FI system illustrated in Fig.2.1 consisted of a peristaltic pump (Gilson Minipuls), which maintained a constant flow rate. A valve (Omnifit, low pressure, Teflon rotary), which contained an eluent loop. A microcolumn which contained activated alumina. The carrier was ammonium hydroxide. The eluent was nitric acid.

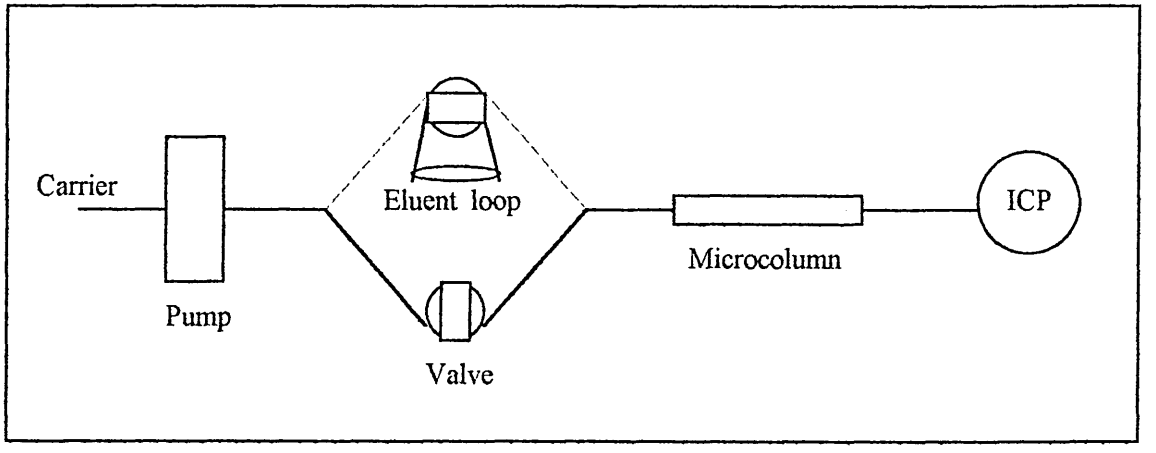


Fig.2.1 Schematic diagram of a single valve flow injection trace enrichment manifold.

The procedure for obtaining analytical data, for a sample (caesium iodide, 1 % w/v, multi element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 100 μg l^{-1}), adjusted to pH 5 will be detailed, for a 2 minute sampling period. As shown in Fig.2.1, the carrier, 0.02 M ammonium hydroxide was continually pumped, at 1 ml min^{-1}, through the FI system. The carrier flows through the valve, which is initially in the load position, and hence the solution does not travel through the 250 μl loop. The carrier then passes through the activated alumina microcolumn, which maintains active sites in the basic form. Finally the carrier is aspirated into the ICP-ES. To retain the trace analytes contained in 2 ml of the sample, the tubing is removed from the carrier solution and placed in the sample for 2 minutes. Following this time period, the tubing is returned to the carrier solution. The sample travels through the valve in load position, the microcolumn, and into the ICP-ES. The trace analytes are retained by the column and the matrix constituents, in this case caesium iodide, pass directly into the ICP-ES. The

carrier is monitored following the retention step. This is an attempt to determine if incomplete retention of any of the analytes has occurred, and to ensure matrix components are completely flushed from the column. During this time, the 250 µl loop is loaded with eluent, 2 M nitric acid, ready for the elution step. To elute the trace analytes from the alumina column, the valve is switched to the inject position, expelling the contents of the loop into the carrier stream. The plug of 2 M nitric acid passes through the microcolumn, eluting the retained analytes from the column, which travel to the ICP-ES for detection. An emission/time profile for each analyte is recorded. The emission intensity calculated is directly related to the area of the transient signal. The elution procedure is repeated on two more occasions, to ensure complete removal of analytes from the column. The deposition and elution procedure are repeated in duplicate or triplicate.

2.3.2 Dual Valve System

The FI system illustrated in Fig.2.2 consisted of a peristaltic pump (Gilson Minipuls), which maintained a constant flow rate. Valve 1, (Omnifit, low pressure, Teflon rotary), which contained an eluent loop. An activated alumina microcolumn was incorporated within the loop of valve 2. The carrier was ammonium hydroxide. The eluent was nitric acid.

The procedure for obtaining analytical data, for a sample (caesium iodide, 1 % w/v, multi element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 100 µg l^{-1}), adjusted to pH 5, will be detailed for a 5 minute sampling period. The carrier, 0.02 M ammonium hydroxide is continually pumped at 1 ml min^{-1}, through this system. The carrier flows through both injection valves, which are firstly in the load position. Therefore the solution does not travel through the 250 µl loop or the microcolumn. Finally, the solution travels to the ICP-ES. The trace analytes contained in 5 ml of the sample are retained as it is pumped through the second valve, as indicated in Fig.2.2 for 5 minutes. This solution travels directly through the microcolumn and then to waste. Hence, the trace analytes are retained by the column and the matrix constituents, in this

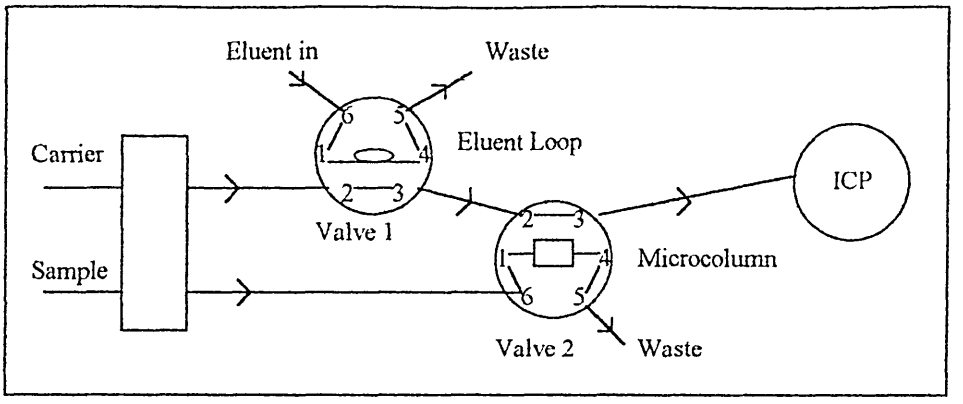


Fig.2.2 Schematic diagram of a dual valve flow injection trace enrichment manifold. Position 1:- Valve 1 and 2 are in load position. The sample is processed through the alumina microcolumn for retention of desired analytes. The 250 µl loop is filled with eluent.

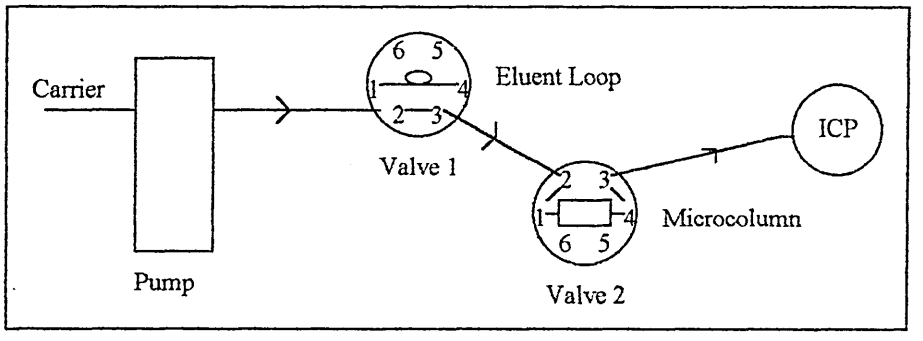


Fig.2.3 Position 2:- Valve 1 is in load position, valve 2 is in inject position. The microcolumn is on-line.

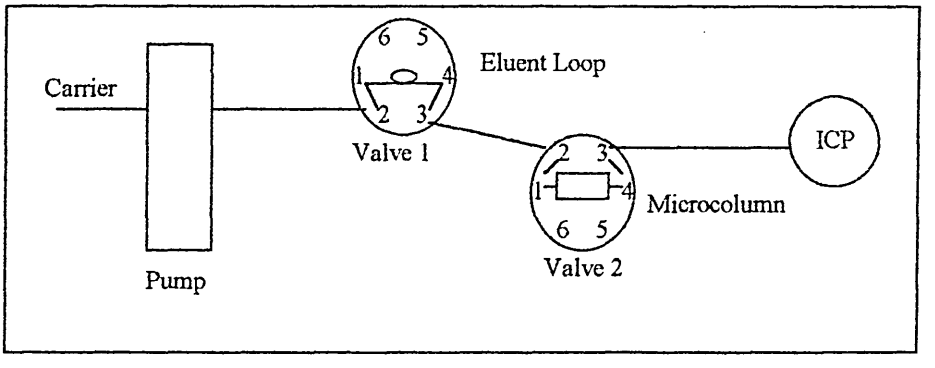


Fig.2.4 Position 3:- Valve 1 and 2 are in inject position. The eluent is expelled from the loop. Elution of retained analytes from the alumina microcolumn is achieved.

example caesium iodide, pass directly to waste. Following the retention step, valve 2 is switched to the inject position, placing the loaded alumina microcolumn on-line (see Fig.2.3). The carrier therefore passes through valve 1 as before, but travels through the microcolumn contained in the sample loop of valve 2 before the ICP-ES. The carrier is monitored twice following the switching of the valve. This is an attempt to monitor incomplete retention of any analyte and to ensure the remaining matrix material is flushed from the column. During the sampling period, the 250 µl loop of in valve 1 is filled with eluent, (2 M nitric acid). To elute the trace analytes from the alumina microcolumn, valve 1 is switched to the inject position, expelling the contents of the loop into the carrier stream, (see Fig.2.4). The plug of 2 M nitric acid passes through the microcolumn, eluting the retained analytes from the column, which travel to the ICP-ES for detection. An emission/time profile for each analyte is recorded. The emission intensity calculated is directly related to the area of the transient signal. The elution procedure is repeated on two more occasions, to ensure complete removal of every analyte from the column. The deposition and elution procedure is repeated in duplicate or triplicate.

2.4 Performance Parameters for On-Line Microcolumn Preconcentration

In developing flow injection microcolumn preconcentration techniques, a number of key experimental parameters may influence the deposition and\or elution efficiencies. Maximum deposition\retention is achieved on the alumina microcolumn, if all the trace analytes present in a sample, are completely retained on the column. The deposition efficiency is then deemed to be 100%. Factors which may affect deposition are:-

a) sample pH.

b) flow rate.

c) analyte concentration, matrix concentration and ionic strength.

d) microcolumn parameters, including the length of microcolumn, the internal diameter of the microcolumn and particle size of the packing material.

Complete elution is achieved from an alumina microcolumn, if the trace analytes present on the column, can be completely removed in the elution step. Factors which affect elution include:-

a) flow rate.

b) eluent parameters including the nature of the eluent, the strength of the eluent and the volume of eluent.

The analytical performance of an ICP instrument is assessed by considering basic performance parameters, such as the limit of detection, the lower limit of quantitative determination, precision, analytical range, wavelength coverage, resolving power and speed of analysis. Some of these parameters may also be applied to the flow injection microcolumn preconcentration technique with ICP detection, to assess the analytical performance of the combined system.

The limit of detection is the concentration of analyte which produces a signal equal to k multiplied by the standard deviation of the background noise level. IUPAC convention states k = 3. The limit of detection is dependent upon the overall system performance, such as the ICP source, sample introduction system, sample type and laboratory environment.

The lower limit of quantitative determination is the concentration below which an analyte cannot be reliable determined. It is estimated from multiplying the limit of detection by a factor of 5 to 10, and corresponds to the lower limit of analytical range.

The precision is a measure of the reproducibility of the results, and is expressed as the relative standard deviation. It is calculated using the equation below and is given as a percentage.

$$RSD = (\text{standard deviation} / \text{mean}) \times 100$$

2.5 Laboratory Procedures

The procedure utilised to calculate the retention and elution efficiencies for the microcolumn enrichment technique will be detailed as follows: Maximum retention (100 %) of the analytes is achieved, if the analytes present in solution are completely retained

in the retention step. Maximum elution (100 %) of the analytes is achieved if the entire proportion of the analytes retained is completely removed in the first elution. Using the procedure detailed in section 2.3.1, a 250 µl volume of a multi-element standard (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 500 µg l^{-1}, tartaric acid, 0.025 M), adjusted to pH 8 was processed in the FI system. The time/elution profile for each analyte was recorded for the retention step and three consecutive elutions. A 250 µl volume of the standard (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 500 µg l^{-1}, nitric acid, 5 M, tartaric acid, 0.025 M) was also processed in the FI system, without the alumina microcolumn in place. The time/intensity profile for each analyte was recorded. The retention efficiency for each analyte is calculated by 100 - (the area of the peak observed during the retention step (if any)) / (the area of the peak obtained without the column in place) x 100. The elution efficiency for each analyte is calculated by (the area of the peak obtained on the first elution with the column in place) / (the area of the peak obtained without the column in place) x 100.

The procedure utilised to calculate the limit of detection and the relative standard deviation for the microcolumn enrichment technique will be detailed as follows: A standard solution (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg l^{-1}, tartaric acid 0.025 M) was prepared and adjusted to pH 8. The solution (10 ml), was processed in the FI system ten times as described in section 2.3.1. Tartaric acid 0.025 M was processed similarly and used as the blank. The mean and standard deviation of the net intensities produced for both solutions were calculated. The mean intensity of the blank solution is taken away from the mean intensity calculated for the standard solution (this value is **A**). The value calculated for 3 x the standard deviation of the blank solution is **B**. Hence **B** is solved from the knowledge that the value calculated for **A** is equivalent to 50 µg l^{-1}. The relative standard deviation is calculated from the mean and the standard deviation obtained for the standard solution using the equation:

$$RSD = (\text{standard deviation} / \text{mean}) \times 100$$

2.6 Microcolumn Field Sampling Procedure

Alumina microcolumns were inserted separately into the flow injection manifold, depicted in Fig.2.1. To ensure any possible sources of contamination had been removed before analysis, three, 250 µl injections of 2 M HNO_3 were processed through each column. The columns were taken to the field sampling site (e.g. Redmires or Langsett Reservoir, Bay of Biscay etc), and conditioned at the site with the passage of 2 ml of 0.02 M ammonium hydroxide through each column. A sample of water was collected from the reservoir outflow for example. A proportion of this sample was taken and tartaric acid was added to a concentration of 0.025 M. The pH was adjusted to 8, before 10 ml of the prepared sample was processed through an alumina microcolumn. The remaining sample was acidified with 1 % nitric acid. The columns and samples were returned to the laboratory. The columns were incorporated into the FI system depicted in Fig.2.1. The retained analytes were eluted into the ICP-ES for determination.

2.7 Inductively Coupled Plasma-Emission Spectrometry Instrumentation

The Spectroflame combined simultaneous/sequential ICP-ES, was utilised for the majority of the experimental work. The instrument is equipped with a 16 channel Paschen-Runge polychromator and two Paschen-Runge monochromators. The radio frequency, free-running plasma generator, operated at an output power of 1.2 kW and a frequency of 27.12 MHz. The generator provided energy to the fully demountable plasma torch, which was surrounded by a water-cooled induction coil, and created a magnetic field for plasma containment. Argon gas is passed through this field and is ionised to form the plasma. Liquid samples are nebulised into the double-pass spray chamber, with the use of a cross-flow nebuliser. The aerosol produced travels up the injector tube to the torch with the nebuliser gas stream. The atoms and ions are excited, producing light emissions which are characteristic of the analytes. The light energy emitted is directed through the entrance slits of the spectrometers, utilising optical fibres. It is then diffracted by the grating, re-focussed on the exit slits and projected on to photomultiplier tubes (PMTs). The light energy is converted to electrical signals by the

Operating Parameters	
Frequency / MHz	27.12
Output Power / kW	1.2
Ar Flow Rate / l/min	
Coolant	18-20
Intermediate	1
Nebuliser	0.5
Observation Height / mm	16

Table 2.1 The Spectro ICP Operating Parameters

Instrumentation	
Nebuliser	Cross-flow
Spray Chamber	Double-pass
Torch	Fully Demountable
Generator	Free-running
Spectrometer	Paschen-Runge

Table 2.2 The Spectro ICP Instrumentation

Analyte	Wavelength/nm
Ba	455.403
Ca	317.933
Cd	226.502
Co	228.616
Cr	267.716
Cs	445.531
Cu	324.754
Fe	259.94
K	766.49
Li	460.286
Mg	285.213
Mn	257.61
Na	589.592
Ni	231.603
Pb	220.351
V	311.071
Zn	213.856

Table 2.3 The analyte spectral lines utilised in the experimental investigations.

PMTs. The information is finally processed by computer. The plasma operating conditions are given in Table 2.1. The Spectro ICP model P instrumentation is

summarised in Table 2.2. The spectral lines of the trace analytes studied in this investigation are detailed in Table 2.3.

2.8 Inductively Coupled Plasma-Mass Spectrometry Instrumentation

The main components and arrangement of the ICP-MS (VG PlasmaQuad) is shown in Fig.2.5.

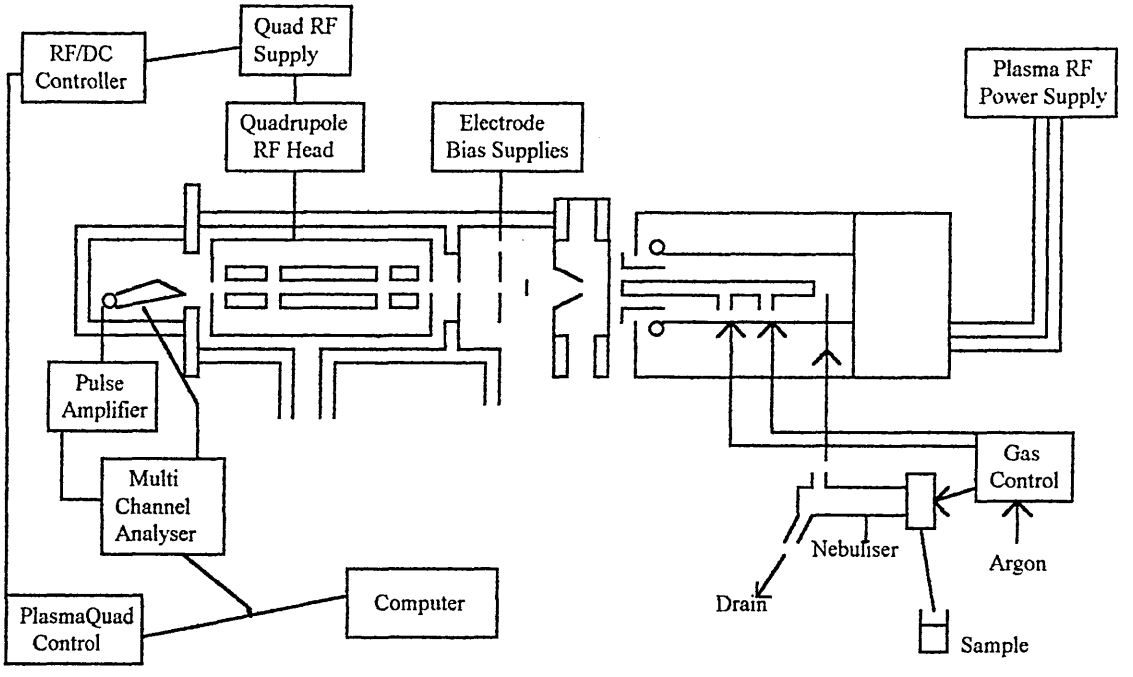


Fig.2.5 Schematic Diagram of an ICP-MS System

In basic operation, the sample is dispersed into an aerosol and carried by a stream of gas to the plasma discharge. The aerosol is injected into the base of the high temperature plasma, which is sustained by a radio frequency field. The sample is dissociated, atomised and ionised through a transference of energy from the plasma. The central portion of the plasma is extracted into a low pressure region through a sampling orifice. The sample is transported as a supersonic jet and a portion of this passes through a skimmer cone orifice, where there is a further reduction in pressure. Positive ions are extracted *via* a series of electrostatic lenses and are transported to a quadrupole mass filter. Ions of a predetermined mass to charge ratio are transmitted to an ion detector. Naturally occurring elements have a unique pattern of almost integer mass to

charge ratios, for their stable isotopes. Hence analytes in the sample can be identified. The concentration of the analytes in the sample is directly related to the ion count. The ICP-MS operating parameters are given in Table 2.4 and the isotopes studied in this investigation are given in Table 2.5.

Operating Parameters	
Frequency / MHz	27.12
Forward Power / W	1350
Reflected Power / W	< 10
Torch	Fixed
Spray Chamber	Double Pass
Nebuliser	Meinhard
Ar Flow Rate / l /min	
Coolant	15
Intermediate	1.7
Nebuliser	0.78
Ion Lens Default Settings	
Extraction	1.5
Collector	7.7
L1	7.7
L2	5.4
L3	5
L4	3.85
Measurement Time	5 min
Detector Mode	Peak Jump

Table 2.4 The VG PlamaQuad Operating Parameters

Analyte	Isotope
Ba	135
	137
Cd	106
	111
Co	59
Cr	52
	53
Cu	63
	65
Ni	60
	62
Mo	98
Pb	206
	207
	208
V	51
Zn	66
	67
	68

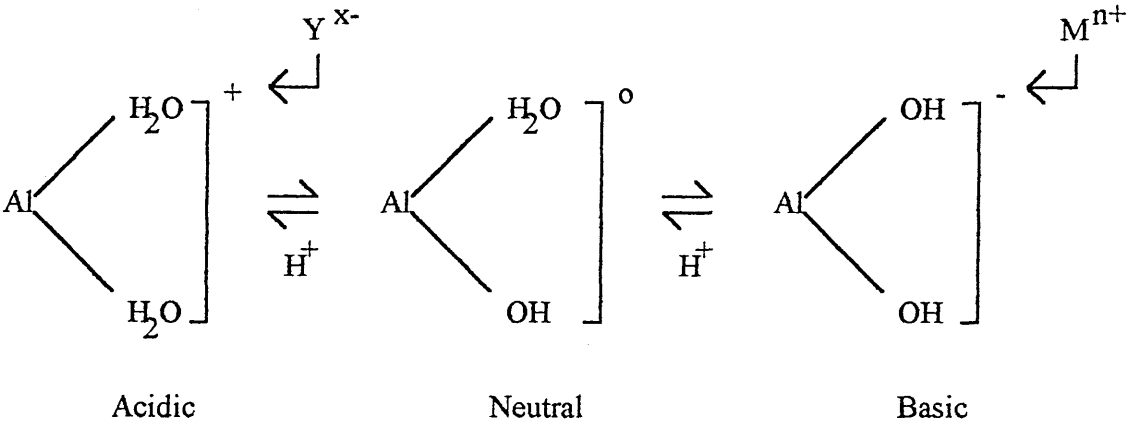
Table 2.5 The VG PlasmaQuad isotopes utilised in this investigation

3 Ultratrace Analysis of High Purity Salts

3.1 Caesium Iodide

Caesium iodide is produced by Merck Ltd. as a monocrystal growth, which is manufactured into lenses for use in scintillation equipment. The caesium iodide produced by this method is of high purity. However, it is expected that a highly pure sample of caesium iodide, contains impurities such as Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, at the sub $\mu g\ g^{-1}$ level. Therefore, a 1 % w/v solution of pure CsI contains impurities at the low $\mu g\ l^{-1}$ level, which is similar to the limit of detection capable by conventional ICP-ES analysis, making measurement improbable. Furthermore a 1 % w/v solution may cause nebuliser tip blockage and contributes to analyte suppression. In order to minimise such effects and overcome the sensitivity limitations, on-line microcolumn separation/preconcentration with ICP-ES detection is considered a viable technique, for the study of impurities in pure caesium iodide.

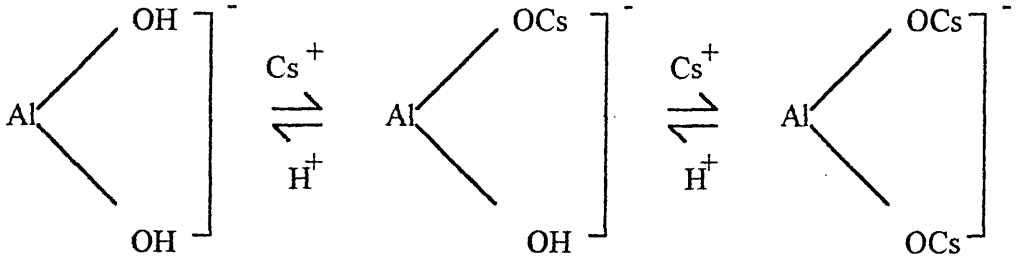
As previously discussed, activated alumina can function as both a cation and anion exchanger.



Hence, to retain cationic trace analytes the alumina must be maintained in its basic form. This is achieved by the continual passage of dilute ammonium hydroxide (0.02 M), through the column, as described in the experimental section 2.3.1.

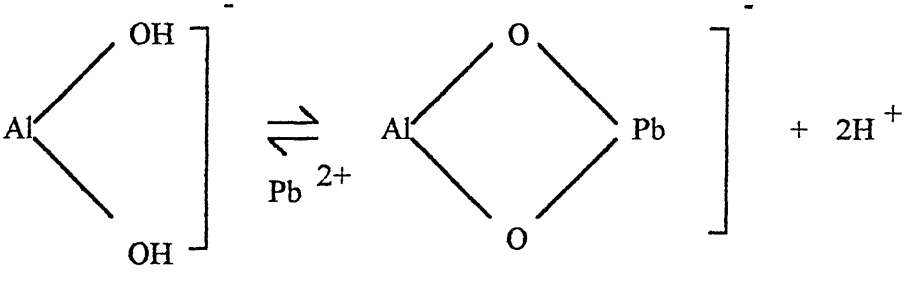
As the sample, (caesium iodide, 1 % w/v, multi element spike Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Zn, 100 $\mu g\ l^{-1}$) is processed through the column, it is possible that H^+ is displaced by Cs^+ at some sites. Studies have shown (see section

3.1.3), that the presence of CsI improves the retention of desired analytes, in comparison with a simple aqueous standard of the same analyte concentrations. Hence, the presence of CsI maintains the number of active sites throughout the column, and does not impair the retention of multi-valent cations.

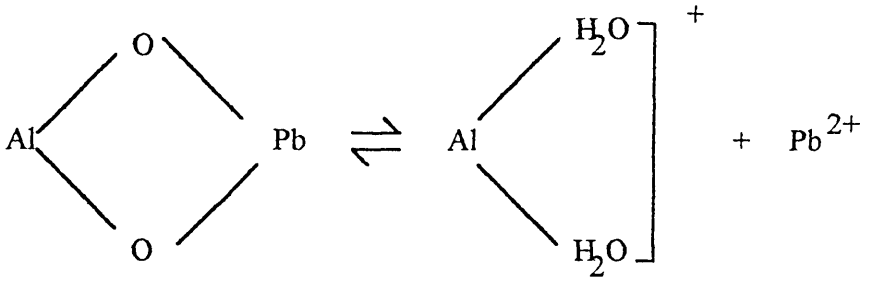


Basic Basic Basic

Because univalent ions form weak complexes with activated alumina, trace analytes in solution, such as Pb^{2+} displace Cs^{+} and H^{+}, forming stronger, more stable complexes. Effective separation from high concentrations of mono-valent matrix cations is thereby achieved. The adsorption of trace analytes on to activated alumina has been discussed by Hohl and Stumm (155), who proposed the following mechanism:



The passage of the sample through the column thus results in the retention of desired analytes, whilst the matrix, caesium iodide, is virtually un-retained. The retained analytes are then eluted from activated alumina by passage of 2 M nitric acid through the column. The acid is strong enough to displace the analytes, reverting the alumina temporarily to its acidic form. The alkaline carrier solution following the nitric acid plug, would almost instantly revert the alumina back to its basic form, ready for the next deposition/elution sequence. The eluted analytes would then be detected by ICP-ES.



3.1.1 Retention/Elution of Analytes

The ability of activated alumina to retain the trace analytes Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, in the presence of caesium iodide (1 % w/v) and a calibration standard solution was studied. Using the procedure described in section 2.3.1, a 250 µl volume of the sample, (caesium iodide, 1 % w/v, multi element solution spike, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 µg l^{-1}), and a calibration standard solution were processed using the FI system. The time/elution profiles for the sample solution are displayed in Fig.3.1. The plots show that following the injection of sample, only background levels of the analytes are detected. This indicates effective retention of the analytes by activated alumina. Following the injection of eluent, a transient signal was observed for each analyte, indicating that the retained analytes were subsequently eluted.

In summary:-

1. The analytes Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn are retained by activated alumina, in the presence of a CsI (1 % w/v) matrix.
2. The analytes are subsequently eluted from activated alumina with the injection of 250 µl of eluent (2 M HNO_3).

3.1.2 Effect of pH on Analyte Retention

In section 1.6 performance parameters which affect analyte retention on preconcentration sorbents, were considered in detail. They include sample flow rate, matrix concentration, and microcolumn parameters such as length. However, the parameter which showed the greatest influence on the retention of trace analytes, was

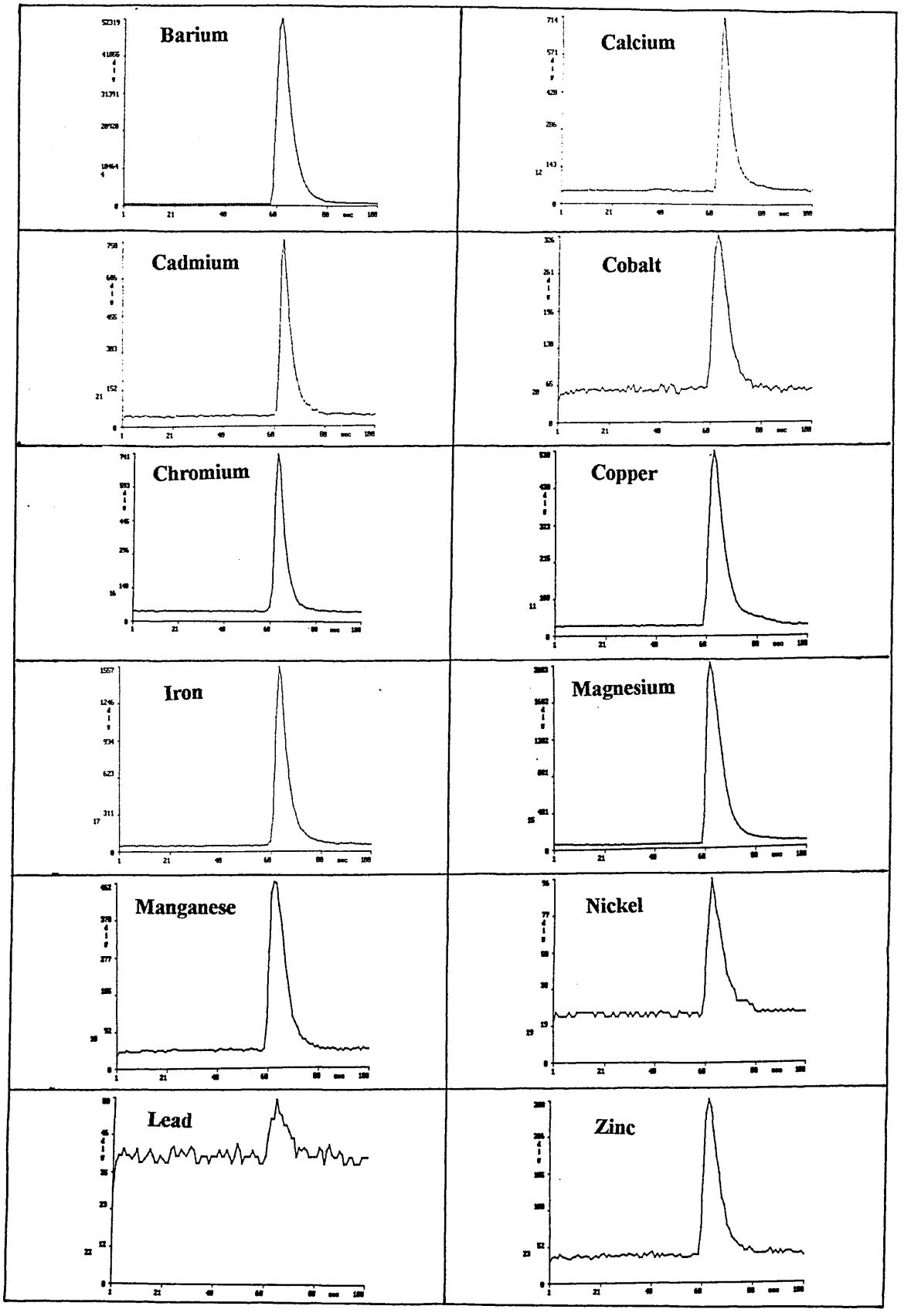


Fig.3.1 The emission (y-axis)/time (x-axis) response for a 250 µl volume of sample (caesium iodide, 1% w/v, multi element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 µg/l) and a 250 µl injection of eluent (nitric acid 2 M).

sample pH. Therefore, the effect of sample pH on the retention of the trace analytes was investigated at the outset. Samples were prepared (caesium iodide, 1 % w/v, multi element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 $\mu g\ l^{-1}$) and adjusted to pH 3, 4, 5, 6, 7, 8, 9 and 10 respectively, using dilute solutions of HNO_3 and NH_4OH. Using the procedure described in section 2.3.1, a 5 ml volume of the sample and a standard solution were processed for each pH adjustment. The data obtained are represented graphically in Fig.3.2. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus pH.

The analytes Cr, Cu, Fe, Pb and Zn were found to behave similarly. The plots show that pH has a much greater effect on the retention of these analytes for the aqueous standard solution, compared to the CsI matrix. The implication is, that the presence of CsI influences analyte retention. It is possible, as discussed previously in section 3.1.1, that CsI maintains basic sites, ensuring greater retention of these analytes from this matrix, in relation to the standard solution. Greatest retention occurs between pH 3 and 5 and pH 9 and 10 for these analytes, in the presence of the standard. Retention by activated alumina is much more uniform over the pH range 3 to 10 for these analytes, in the presence of CsI.

The analytes Cd, Co, Mn and Ni indicated similar behaviour. The plots show that these analytes have similar retention/elution behaviour, in the presence of both a CsI matrix and an aqueous standard. Greatest retention of the analytes Cd, Co, Mn and Ni occurred between pH 4 and 7.

The analytes Ba, Ca and Mg exhibited similar behaviour. These plots also indicate that pH has a much greater effect on retention of the analytes Ba, Ca and Mg for the aqueous standard, compared to the CsI matrix. Greatest retention occurs between pH 8 and 10 for these analytes, in the presence of the standard solution, whereas retention is more uniform from pH 3-10, in the presence of CsI.

This study shows that pH has a significant effect on the retention of the analytes (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) by activated alumina. Also that

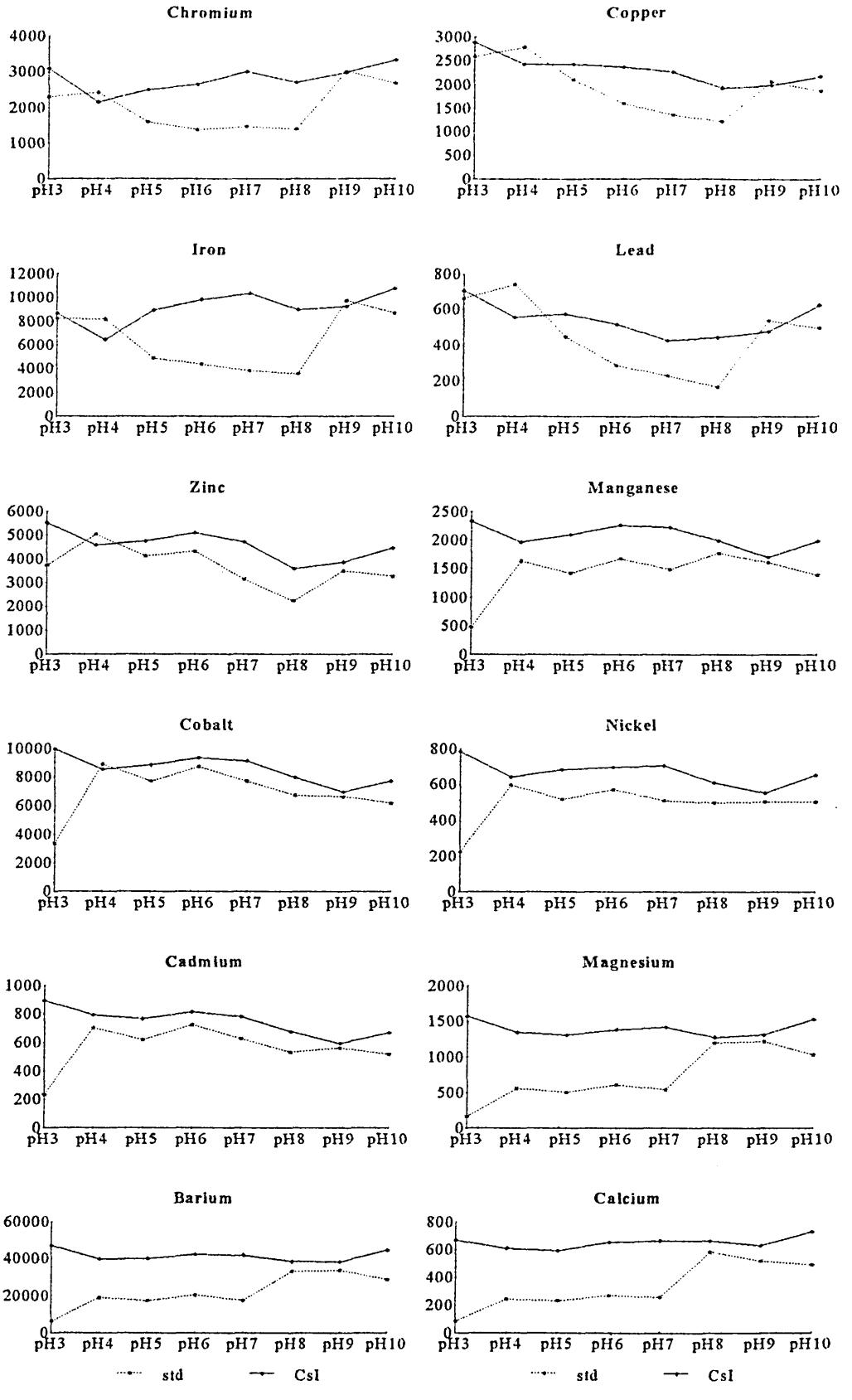


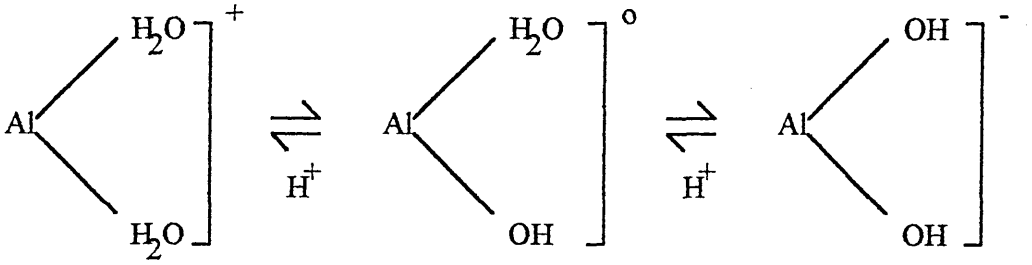
Fig. 3.2 The effect of pH on retention of trace analytes. The sample volume was 5 ml. Sample (caesium iodide, 1 % w/v, multi element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 µg/l). Multi-element standard (100 µg/l). The single valve procedure detailed in section 2.3.1 was utilised.

these analytes have different retention/elution behaviour, in the presence of the CsI matrix or a simple aqueous standard. This implies that the analytes can be split into groups, according to their behaviour with respect to retention/elution from activated alumina. These are:-

Group A:- Cr, Cu, Fe, Pb and Zn; Group B:- Co, Cd, Mn, Ni; Group C:- Ba, Ca, Mg.

In summary:-

1. Analyte retention is almost always greater in the presence of CsI.
2. Variations with pH are generally much less marked in the presence of Cs^+.
3. In almost all instances there is a significant change from pH 3 to 4. This is probably due to a marked shift to the right, of the equilibria:



4. For the analytes Cr, Cu, Fe, Pb and Zn there is a distinct increase in retention in the absence of Cs^+ from pH 8 to 9. It is possible that these analytes are preferentially retained at pH 9.
5. The analytes Ba, Ca and Mg show a marked increase from pH 7 to 8 in the absence of Cs^+. It is possible that these analytes are preferentially retained at pH 8.
6. The pH at which the analytes are effectively retained in the presence of both the standard solution, and the CsI matrix is 9. However a pH of 5 was selected for further studies, in an attempt to provide information concerning analyte affinities with activated alumina.

3.1.3 Enrichment Capability

Activated alumina has been investigated by a number of research groups, as a microcolumn packing material (see section 1.6.6). Therefore information provided in the

literature was utilised and applied to this study, with respect to experimental parameters such as sample and eluent flow rate, microcolumn parameters, (length and i.d.) and eluent nature and strength. The exception was sample pH, which has been discussed above and a value of 5 selected. Therefore, using the procedure described in section 2.3.1, volumes of 2.5, 5, 7.5 and 10 ml of the sample (caesium iodide, 1 % w/v, multi element spike Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 $\mu g\ l^{-1}$), and of a standard solution were processed. Graphical representation of the data are displayed in Fig.3.3. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus sample volume.

The plots produced indicate reasonably linear relationships between signal intensity and sample volume for the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni. Pb and Zn, in the CsI matrix and the analytes Cr, Cu, Fe, Pb and Zn in the standard solution. This implies effective deposition/elution of these analytes, for processing sample volumes up to 10 ml. The graphs for the remaining analytes Ba, Ca, Cd, Co, Mg, Mn and Ni in the standard solution and Ba, Ca and Mg in the CsI matrix, were non-linear. This suggests incomplete retention by activated alumina, for sample volumes greater than approximately 2 to 5 ml for these analytes.

These results add further support to the proposal that CsI influences the retention of the analytes by activated alumina, by maintaining active sites, compared with the aqueous standard solution. It appears that the pH of 5 reverts active sites throughout the alumina microcolumn to their neutral or acidic form, in the presence of the standard solution, hindering retention of the analytes Cd, Co, Mn, Ni, Ba, Ca and Mg above a sample volume of 2 to 5 ml. The data also indicates that the analytes can be placed in order of affinity, with respect to retention by activated alumina. The order is:-

Cr, Cu, Fe, Pb, Zn > Cd, Co > Mn, Ni > Ba, Ca, Mg

The implication is, that on passage of a sample through the alumina column, active sites become occupied. Once all available sites have been filled, it is possible that the analytes Cr, Cu, Fe, Pb, Zn, Cd, Co, Mn and Ni begin to displace the analytes Ca, Ba and Mg.

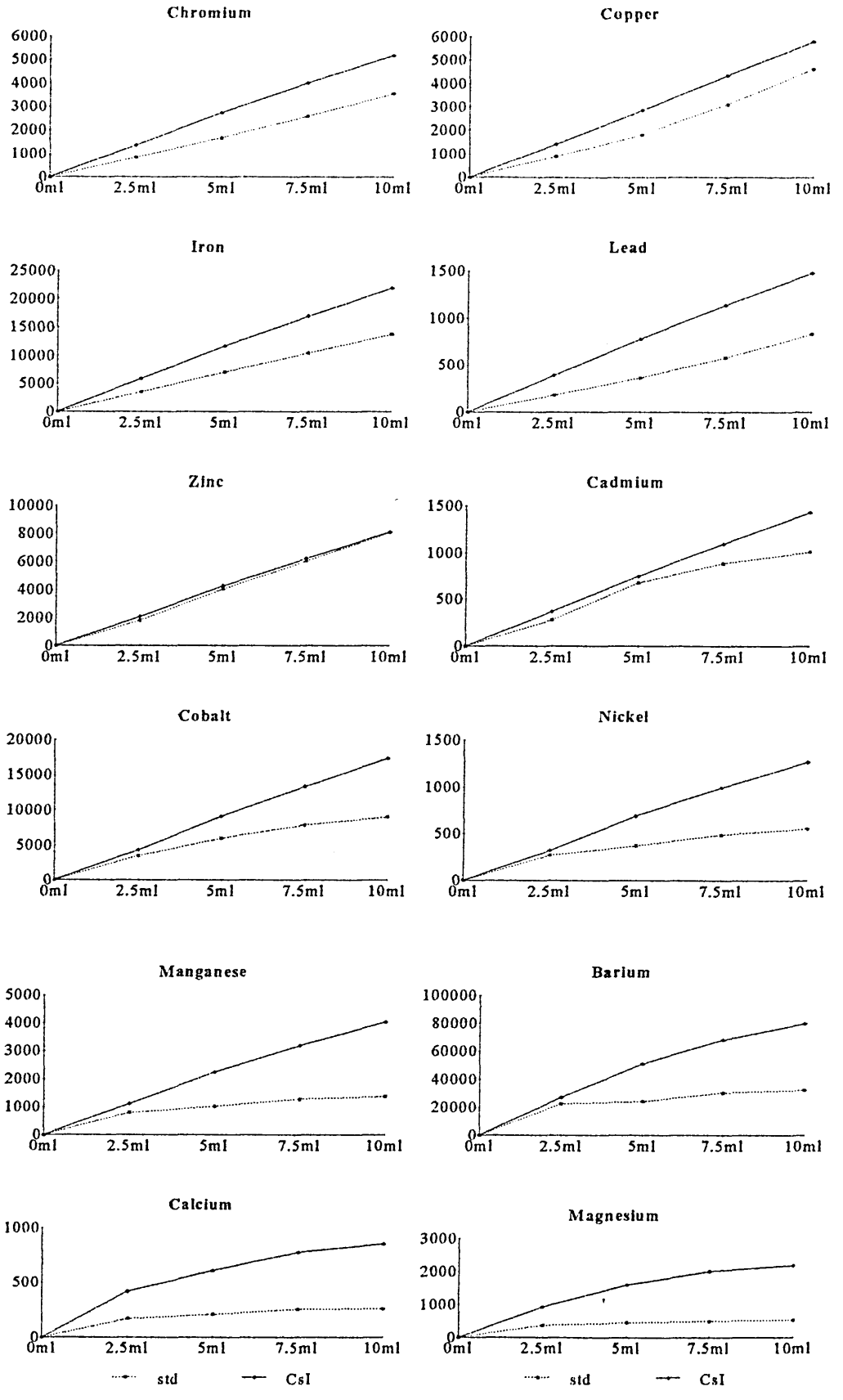


Fig. 3.3 The effect of sample volume on retention of the analytes. Sample (caesium iodide, 1 % w/v, multi element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn, 100 µg/l). Multi-element standard (100 µg/l).

This is feasible, as it was found that the former analytes are retained effectively by activated alumina from the CsI matrix, but latter are not. It appears that fewer sites are available for retention for the standard solution. Some sites may be reverted to their neutral form at pH 5, for processing volumes above 2 to 5 ml. Hence, as there are fewer available sites, it is possible that the analytes Cr, Cu, Fe, Pb and Zn, displace the analytes Cd, Co, Mn, Ni, Ba, Ca and Mg. This is suggested because it was found that only the former group are retained effectively by activated alumina from the standard solution.

In summary:-

1. The analytes Cr, Cu, Fe, Pb and Zn produce a linear relationship between sample volume and emission intensity in the presence of the standard solution, for processing volumes up to 10 ml.

2. The analytes Cd, Co, Ni, Mn, Ba, Ca and Mg produce a non-linear relationship between sample volume and emission intensity in the presence of the standard solution, for processing volumes up to 10 ml.

3. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn produce a linear relationship between sample volume and emission intensity in the presence of CsI (1 % w/v), for processing volumes up to 10 ml.

4. The analytes Ba, Ca and Mg produce a non-linear relationship between sample volume and emission intensity, in the presence of CsI (1 % w/v), for processing volumes up to 10 ml.

5. The analytes can be placed in order of affinity with respect to retention by activated alumina: Cr, Cu, Fe, Pb, Zn > Cd, Co > Mn, Ni > Ba, Ca, Mg

6. The analyte behaviour observed is different with respect to retention by activated alumina in the presence of the CsI matrix compared with a simple aqueous standard, for each analyte except Cr, Cu, Fe, Pb and Zn. Hence, a standard addition technique will have to be employed for the determination of the analytes in the CsI sample.

3.1.4 Recommendations for Analysis

The operational conditions recommended for analysis are given as follows:-
a pH of 5, a 10 ml sample volume, a 1 ml min^{-1} sample and elution flow rate and a 250 µl eluent volume (2 M nitric acid). A standard addition calibration procedure is also recommended. These conditions were selected from experimental investigations to give optimum sensitivity.

Samples were prepared (caesium iodide, 1 % w/v, multi-element spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 10 µg l^{-1}), (caesium iodide, 1 % w/v, multi-element spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 5 µg l^{-1}), (caesium iodide, 1 % w/v) and adjusted to pH 5. Using the procedure described in section 2.3.1, a sample volume of 10 ml of each sample was processed in the FI system. The data are represented graphically, plotting emission intensity (peak area) versus concentration, for each of the analytes in the CsI samples. This experiment was repeated on three occasions.

The results obtained are given in Table 3.1. Pb was not detected using this technique, due to sensitivity limitations. It is possible however that an increase in the sample volume used for enrichment, would result in the successful determination of this analyte.

Analyte	Concentration µg/g
Cd	0.19 ± 0.01
Co	0.06 ± 0.005
Cr	0.35 ± 0.05
Cu	0.22 ± 0.03
Fe	0.33 ± 0.03
Mn	0.16 ± 0.01
Ni	0.45 ± 0.02
Pb	
Zn	0.19 ± 0.02

Table 3.1 Determination of Trace Elements in CsI. (see text for Experimental Conditions).

3.2 Alkali Metal Salts

The microcolumn enrichment technique proved feasible for the determination of selected trace analytes in CsI. Hence studies were extended to a selection of the alkali metal salts. These were, potassium bromide, lithium nitrate, sodium fluoride and sodium chloride.

3.2.1 The Matrix Isolation Capability of Activated Alumina

The results shown in section 3.1.1 demonstrate the ability of activated alumina to retain the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, in the presence of a caesium iodide matrix, 1 % w/v. It is possible that the alkali metal salts $LiNO_3$, KBr, NaCl and NaF, behave similarly to CsI. Hence it is suggested that as the sample is processed through the column, H^+ is initially displaced by the appropriate species: Cs^+, Li^+, K^+ and Na^+. The trace analyte multi-valent cations subsequently displace these univalent ions, as they form stronger complexes with alumina. The trace analytes are therefore effectively retained by this procedure and simultaneously separated from the matrix. This was studied by examining the retention/elution behaviour of the analytes (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), in the presence of the above matrices. Samples containing each matrix were prepared (CsI, $LiNO_3$, NaF, NaCl, KBr, 1 % w/v, multi element spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100 $\mu g\ l^{-1}$), and adjusted to pH 5. Using the procedure described in section 2.3.1, a volume of 0.5 ml of each sample and standard solution was processed using the FI system. The time/elution profiles displayed in Fig.3.4 and 3.5, are typical examples of the emission behaviour observed.

The plots in Fig.3.4 confirm that matrix separation was achieved. Following the introduction of sample into the FI system, virtually all the Cs^+, K^+, Na^+ and Li^+ present, pass through the column directly into the ICP-ES for detection. A small proportion of the K^+, Na^+ and Li^+ present in the samples however, was retained on the column. This is recognised as a transient peak for these elements following the injection of eluent.

The plots in Fig.3.5 show the time/elution profiles for Cu in each of the above matrices. This is typical of the behaviour observed for the remaining analytes Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn. Thus the plots suggest that each analyte is retained on the

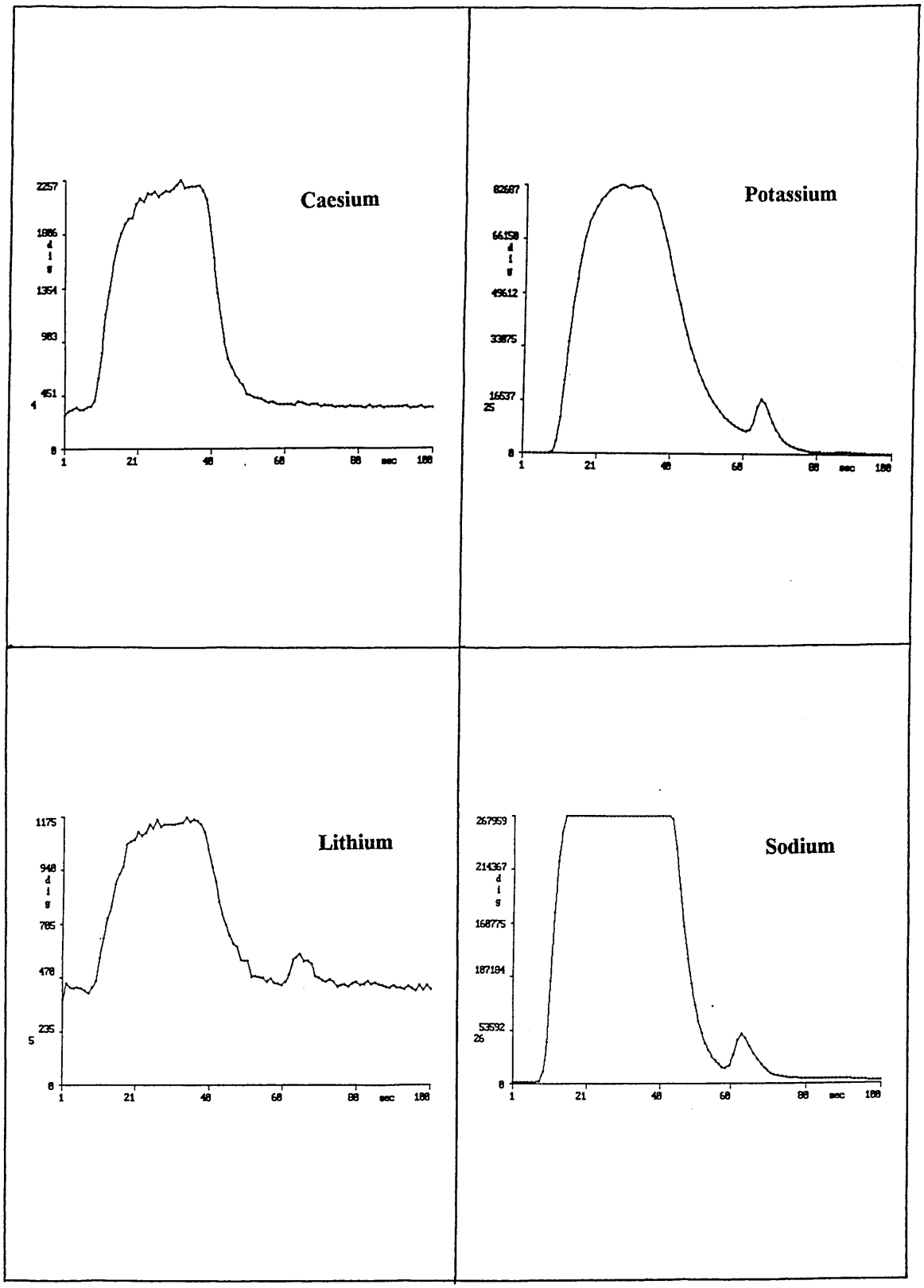


Fig.3.4 The emission/time response for Cs, K, Li and Na, for a 0.5 ml volume of sample (CsI, $LiNO_3$, KBr, NaF or NaCl, 1 % w/v, multi element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100 µg/l) and 250 µl injection of eluent (2M nitric acid).

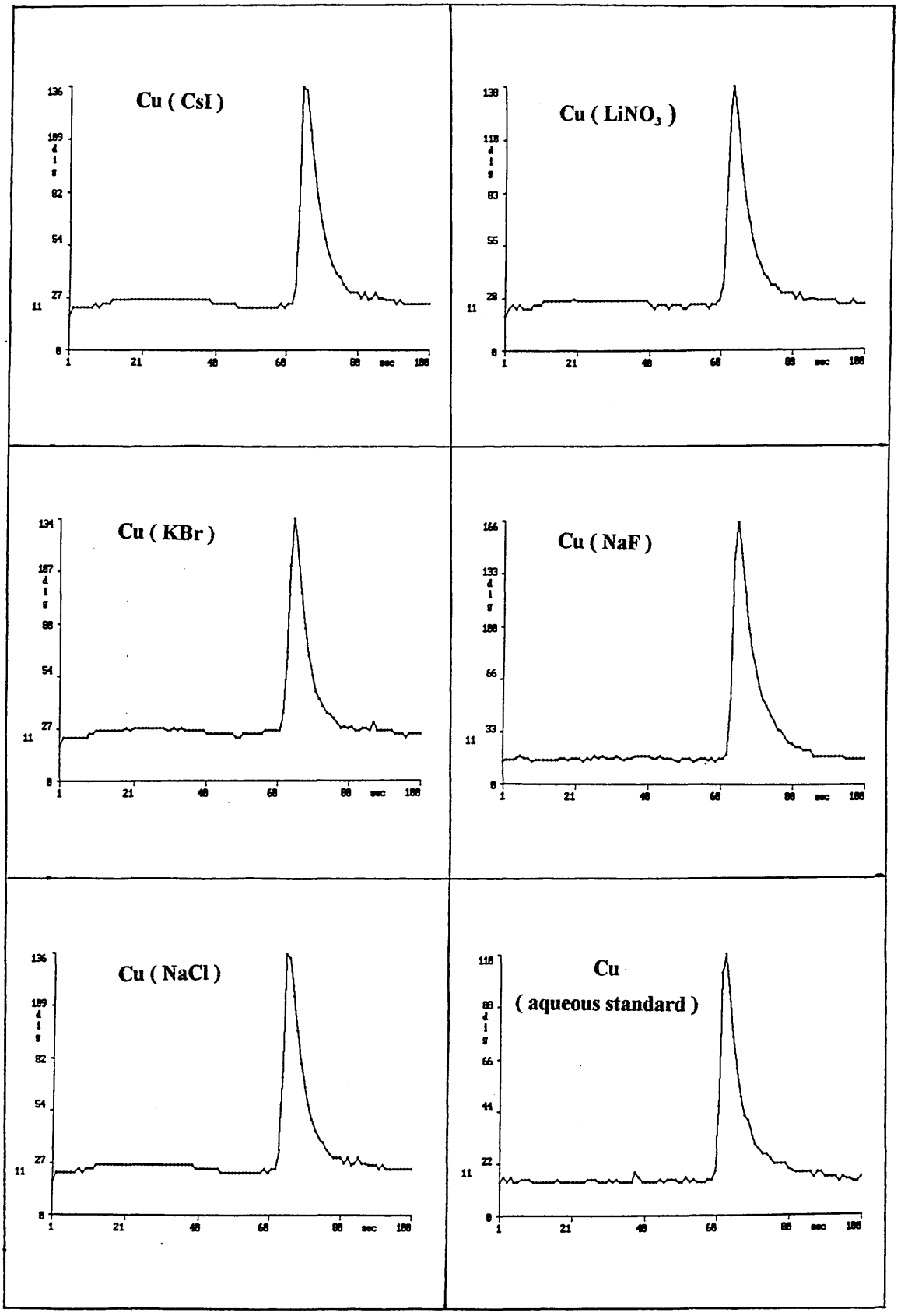


Fig.3.5 The emission/time response for Cu, for a 0.5 ml volume of sample (CsI, $LiNO_3$, KBr, NaF or NaCl, 1 % w/v, multi element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100 µg/l), or a 0.5 ml volume of a multi element standard (100 µg/l), and 250 µl injection of eluent (2 M nitric acid).

activated alumina in the presence of the KBr, $LiNO_3$, NaF, NaCl and CsI matrix. This is evident because following the introduction of sample, only background levels of the analytes were detected, indicating effective retention. A transient peak was produced for each analyte, following the injection of eluent, confirming that the retained analytes could be subsequently eluted. The plots also confirm that the analytes have similar retention/elution behaviour, whether present in a simple aqueous standard or in a complex solution. There is a greater concentration of copper in NaF than in the remaining matrices.

In summary:

1. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn are retained by activated alumina, in the presence of CsI, $LiNO_3$, KBr, NaCl, NaF (1 % w/v) and a standard solution.
2. The matrix cations (Cs^+, Li^+, K^+, Na^+) pass directly through the activated alumina microcolumn. Hence the matrix cations are not retained by activated alumina. The analytes are thus simultaneously separated from possible matrix interferences.
3. The analytes are subsequently eluted from activated alumina with a 250 µl injection of eluent (2 M HNO_3).

3.2.2 Effect of pH on Analyte Retention

Samples were prepared for each matrix (KBr, $LiNO_3$, NaF, NaCl, CsI, 1 % w/v, multi-element solution spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 100 µg l^{-1}), and adjusted to pH 2, 4, 6, 8 and 10, respectively. Using the procedure described in section 2.3.1, each sample (5 ml) and a standard solution (5 ml) were processed, for each pH adjustment. However, due to the relatively high dissolved solids content of these samples, nebuliser tip and tubing blockage was encountered. The procedure was repeated for each sample, at pH 2, 3, 4, 5, 6, 7, 8, 9 and 10, using the dual-valve system described in section 2.3.2 This configuration allowed the sample to travel through the microcolumn and then directly to waste, in preference to through the microcolumn and into the ICP-ES.

The data obtained are presented in Fig.3.6. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus pH. Each analyte, except Pb, exhibited maximum retention/elution between pH 8 to 10, in the presence of CsI, NaF, NaCl, $LiNO_3$, KBr (1 % w/v, multi element solution spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 100 $\mu g\ l^{-1}$) and the corresponding aqueous standard. Hence, a pH of 8-10 was most effective for the retention of these analytes. However, the behaviour observed in this study was different to the behaviour previously observed for these analytes in the presence of a CsI matrix. In section 3.1.2, variations in the retention behaviour with pH were much less marked from the sample solution (CsI) compared to the aqueous standard, and the analytes could be tentatively grouped according to their retention behaviour. Differences in analyte behaviour are observed in this experiment, but to a lesser degree. The analytes Cu, Fe and Pb appear to be retained more readily by alumina than Zn and Cr at low pH, which are more readily retained than Cd, Co, Mn and Ni. These tentative groups are similar to those found previously, which were Cr, Cu, Fe, Pb, Zn >Cd, Co >Mn, Ni >Ba, Ca, Mg.

The effect of pH on the retention of trace analytes contained in pure CsI, was investigated in section 3.1.2 and in this section. The differences observed from these two experiments, were believed to be connected to the different FI systems used (single-valve for section 3.1.2 and dual-valve in this section), as every other parameter remained constant. It is possible that some of the analytes experienced memory and interference effects with the single-valved system, as the sample matrix passed through the microcolumn and directly into the ICP-ES. The results from this investigation appear feasible, as active sites may be more easily maintained under alkaline conditions, and hence optimum conditions for analyte retention are more readily provided. A pH of 8 was selected for further study. The dual-valved system was also selected, as the sample will pass through the microcolumn and the directly to waste, in preference to the ICP-ES, ensuring greater freedom from matrix interferences.

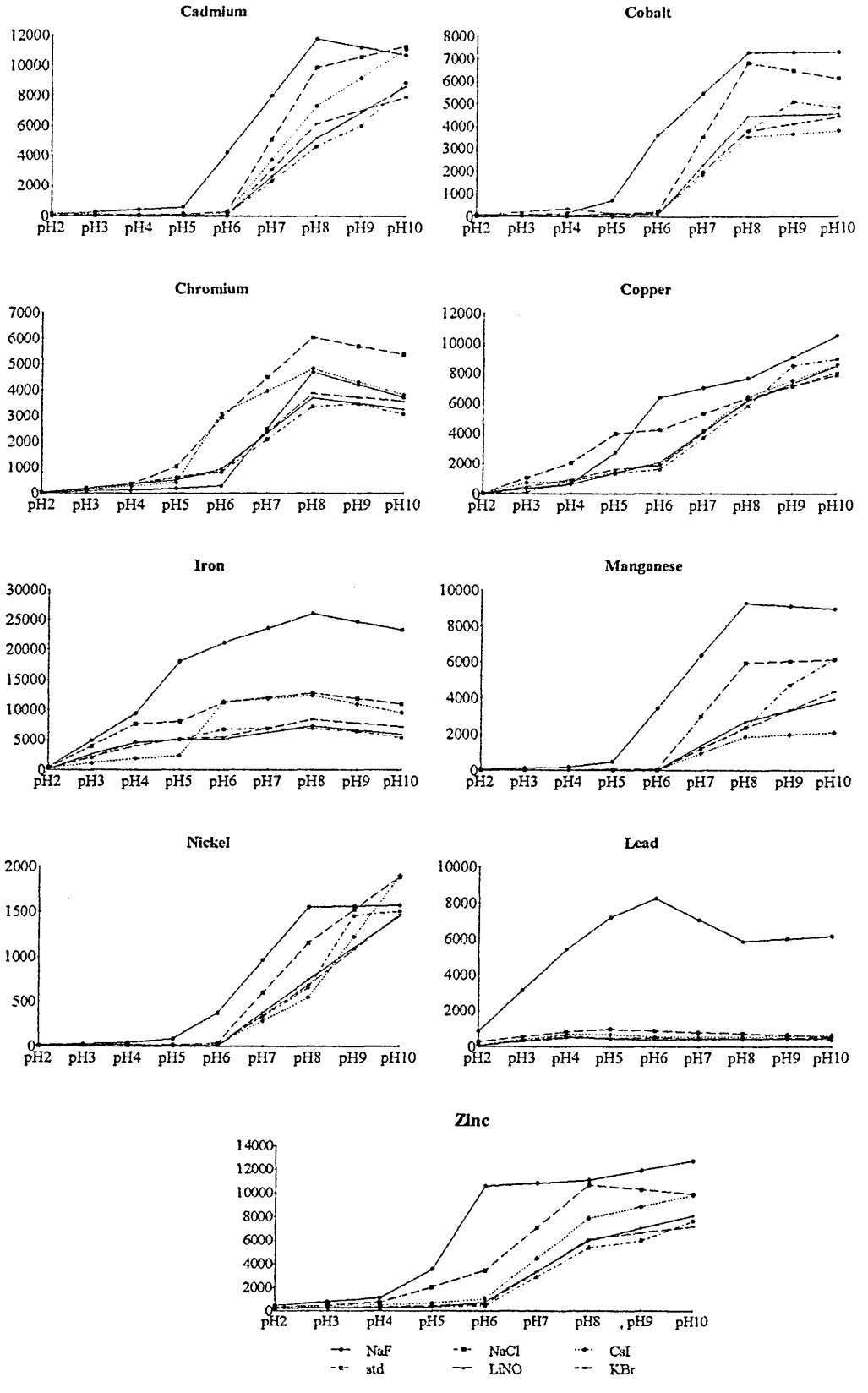
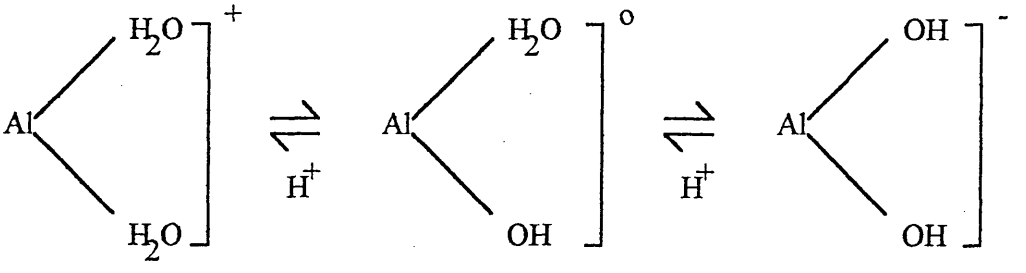


Fig.3.6 The effect of pH on retention of the analytes. The sample volume is 5 ml. Samples ($LiNO_3$, KBr, NaF, NaCl or CsI, 1 % w/v, multi-element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100 µg/l). Multi-element standard (100µg/l). The dual valve procedure detailed in section 2.3.2 was utilised.

In summary:

1. Incomplete analyte retention is observed for each analyte studied (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), in the presence of each matrix (CsI, KBr, $LiNO_3$, NaCl, NaF (1 % w/v)), between pH 2 and 5.

2. A significant increase in retention is observed for each analyte between pH 5 and 8, in the presence of the alkali salts and the standard solution. This is probably due to a marked shift to the right of the equilibria below:



3. Each analyte is effectively retained between pH 8 and 10, in the presence of the salts and the standard solution.

4. The analytes can be tentatively placed in order of selectivity, with respect to analyte retention: Cu, Fe, Pb > Cr, Zn > Cd, Co, Mn, Ni.

3.2.3 Enrichment Capability.

Utilising the conditions and procedure detailed in section 2.3.2, samples were prepared for each matrix and 4, 8, 12 and 20 ml aliquots processed. Graphical representations of the data are displayed in Fig.3.7. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus sample volume. The plots produced indicate a linear relationship between signal intensity and sample volume, for the analytes (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), in each alkali metal salt matrix (CsI, $LiNO_3$, KBr, NaCl, NaF, 1 % w/v). The analytes in the standard solution behaved similarly. Hence, effective retention/elution of the analytes, up to a 20 ml processing volume at pH 8, was achieved. It should be noted however that although the analytes are present in every

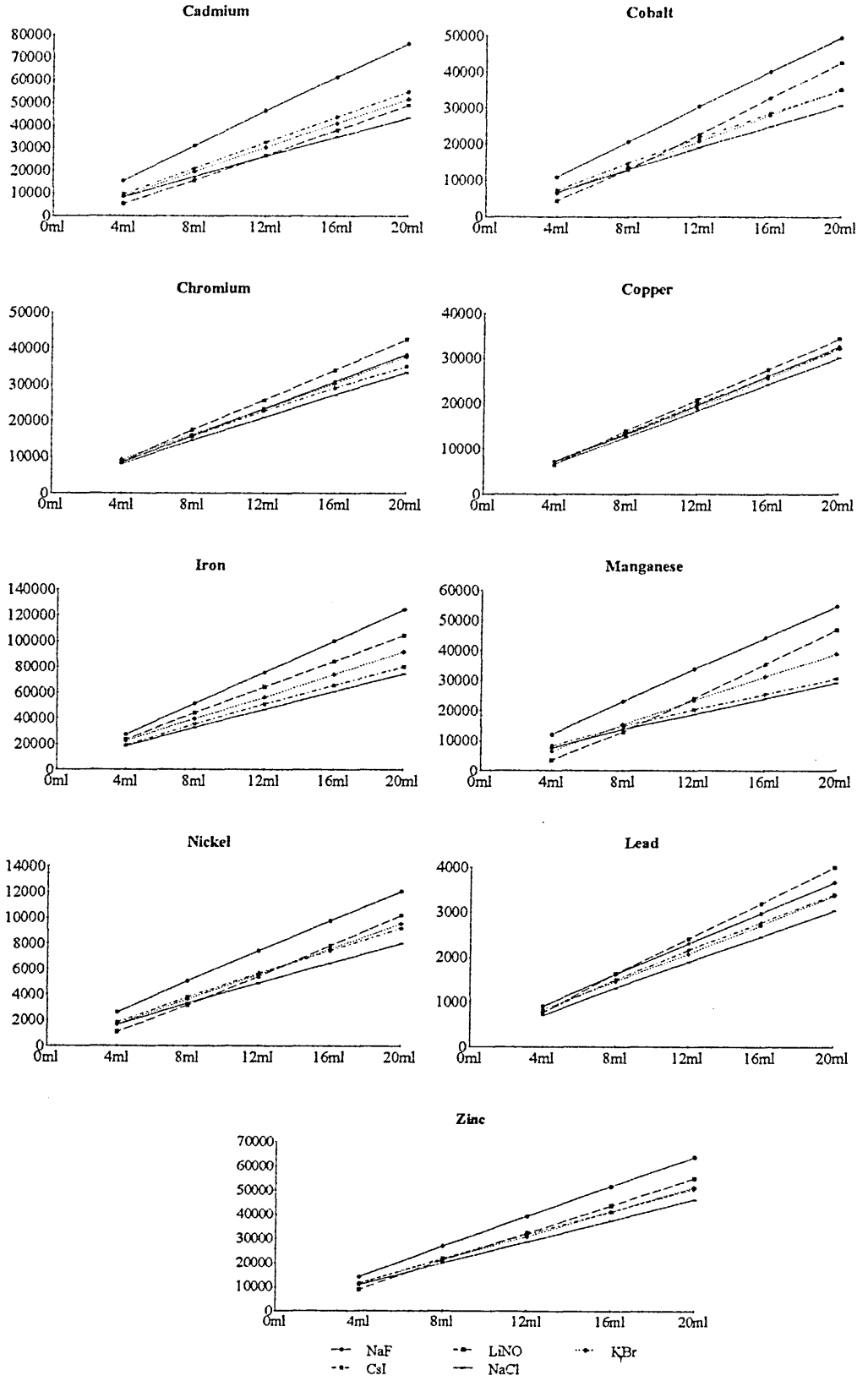


Fig.3.7. The effect of sample volume on the retention of the analytes by activated alumina. Samples ($LiNO_3$, KBr, NaF, NaCl or CsI, 1 % w/v, multi-element solution spike, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100 µg/l).

matrix at the 100 μg l^{-1} level, differences occurred in the analyte emission intensities obtained, particularly for processing volumes of 20 ml. This may have been due to a number of factors:-

a) The reagent NaF, provided by Merck Ltd., was of Analar grade. The remaining matrices were of Aristar grade. Hence, NaF may contain enhanced levels of trace impurities, and it is therefore possible that increased analyte emission intensities would be obtained for NaF.

b) The study was carried out over a 3 day period. Plasma conditions may have varied slightly each day, producing the observed discrepancies in the emission intensities.

c) The differences observed in the analyte intensities, may have been due to spectral interferences. Matrix constituents (Na^+, Li^+, Cs^+, K^+) may have been partially retained, and subsequently eluted with the analytes. Hence, the matrix ions may have contributed to the signals obtained. To ensure matrix constituents were completely flushed from the column, the carrier was allowed to flow through the column for 5 minutes before elution.

In summary:

1. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn produce a linear relationship between sample volume and emission intensity, in the presence of the alkali salts (CsI, KBr, $LiNO_3$, NaCl, NaF, 1 % w/v), and the standard solution, up to processing volumes of 20 ml.

2. The analytes exhibit similar retention/elution behaviour in the presence of each matrix and the standard solution. Hence a simple calibration procedure can be utilised to determine the analytes in these matrices.

3.2.4 Analytical Performance

The limit of detection for each analyte was calculated, using the microcolumn enrichment procedure with ICP-ES detection. The results were compared to those obtained by conventional ICP-ES analysis. The relative standard deviation (RSD) was calculated for each analyte, by both techniques. Hence, a standard solution (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 100 μg l^{-1}) was prepared and adjusted to pH 8. The solution (5

ml), was processed in the FI system ten times. De-ionised water was processed similarly and used as the blank. A multi-element standard solution (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, 10 mg l^{-1}) was analysed by conventional ICP-ES ten times. De-ionised water was analysed using the same procedure and utilised as the blank. The calculations and procedures used are detailed in sections 2.4 and 2.5. The results are given in Table 3.2 a) and b), and show that the limits of detection are significantly improved using the FI-ICP-ES technique, the exception is Fe. It appears that the activated alumina utilised in this investigation, was contaminated at the µg l^{-1} level with Fe.

Analyte	ICP-ES LD / µg/l	FI-ICP-ES LD / µg/l
Cd	3.2	0.25
Co	12	0.34
Cr	2.9	0.72
Cu	1.4	0.17
Fe	2.3	2.1
Mn	4.2	0.075
Ni	9.7	0.5
Pb	67	3.2
Zn	3.4	0.61

Analyte	ICP-ES % RSD	FI-ICP-ES % RSD
Cd	0.29	0.47
Co	0.21	0.58
Cr	0.26	0.54
Cu	0.33	0.55
Fe	0.21	0.54
Mn	0.32	0.26
Ni	0.29	0.47
Pb	0.46	2.9
Zn	0.4	1

Table 3.2 a) Limits of Detection (LD) and b) precision (%RSD), for conventional ICP-ES and microcolumn preconcentration, (5 ml of a multi-element standard Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 100µg/l).

3.2.5 Recommendations for Analysis

The operational conditions recommended for analysis are:-

a pH of 8, a 20 ml sample volume, a 1 ml min^{-1} sample and elution flow rate, and a 250 µl eluent volume (2 M nitric acid). Similar retention behaviour is observed for the analytes, when present in a complex matrix or a simple aqueous standard, using these conditions. A calibration graph can be produced, from simple standard solutions. The analyte concentrations present in the samples can then be determined from interpolation of the graph.

The analytes present in the alkali metal salts were determined using two different calibration methods: A simple aqueous standard and a standard addition calibration. Standard and sample solutions were prepared (CsI, $LiNO_3$, KBr, NaF, NaCl, 1 % w/v,

multi-element solution spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 50 μg l^{-1}), (CsI, $LiNO_3$, KBr, NaF, NaCl, 1 % w/v, multi-element spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 10 μg l^{-1}), (CsI, $LiNO_3$, KBr, NaF, NaCl, 1 % w/v, multi-element solution spike Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, 1 μg l^{-1}) and adjusted to pH 8. Using the procedure described in section 2.3.2, 20 ml of each sample was processed in the FI system on three separate occasions. The data were represented graphically, plotting emission intensity (peak area) against concentration, for each analyte present in each matrix and standard solution.

The results obtained by both calibration procedures are given in Table 3.3 a), b), c), d) and e). The first concentration was determined by simple interpolation from an aqueous standard calibration, and the second from a standard addition procedure. The results indicate close agreement between the two approaches. It is therefore possible to use activated alumina microcolumns to preconcentrate trace impurities present in high purity alkali metal salts and achieve accurate results for a range of trace impurities. The analyte Pb was not determined in CsI due to sensitivity limitations.

The results obtained are similar to those obtained by other workers utilising different column packing materials. Israel *et al.* (84) utilised a microcolumn of EDTrA-cellulose, to enrich and isolate the analytes Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn present in potassium nitrate and potassium acetate prior to ICP-MS detection. The results obtained were as follows for potassium nitrate (ng/g): Cd (<17); Co (<120); Cu (530); Fe (700); Mn (32); Ni (87); Pb (100); V (<90); Zn (465) and potassium acetate (ng/g): Cd (<17); Co (<120); Cu (<24); Fe (280); Mn (<20); Ni (<21); Pb (40); V (<90) and Zn (200). Beinrohr *et al.* (97) utilised a microcolumn of quinol-8-ol to enrich and isolate Cu present in NaCl, NaOH, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $MgSO_4$ and NH_4OH, prior to AAS detection. The results obtained for Cu were 38, <7, 14, 19, 32 and 25 ng/g respectively.

Analyte	CsI ng/g A	CsI ng/g B
Cd	76 ± 8	70 ± 8
Co	61 ± 14	59 ± 13
Cr	180 ± 3	200 ± 4
Cu	180 ± 11	220 ± 15
Fe	570 ± 10	620 ± 17
Mn	44 ± 1	43 ± 2
Ni	120 ± 17	140 ± 20
Pb	27 ± 21	30 ± 21
Zn	160 ± 10	170 ± 11

Analyte	KBr ng/g A	KBr ng/g B
Cd	57 ± 4	52 ± 5
Co	110 ± 10	110 ± 12
Cr	200 ± 1	220 ± 5
Cu	160 ± 5	190 ± 10
Fe	330 ± 6	380 ± 5
Mn	52 ± 2	51 ± 1
Ni	130 ± 11	150 ± 15
Pb	120 ± 2	130 ± 3
Zn	190 ± 13	210 ± 10

Analyte	LiNO3 ng/g A	LiNO3 ng/g B
Cd	18 ± 4	16 ± 6
Co	45 ± 9	43 ± 8
Cr	190 ± 10	210 ± 9
Cu	150 ± 5	190 ± 8
Fe	320 ± 5	370 ± 4
Mn	50 ± 1	49 ± 2
Ni	100 ± 8	120 ± 12
Pb	230 ± 4	260 ± 6
Zn	200 ± 8	220 ± 6

Analyte	NaCl ng/g A	NaCl ng/g B
Cd	22 ± 3	20 ± 2
Co	74 ± 15	71 ± 12
Cr	190 ± 10	210 ± 8
Cu	140 ± 5	170 ± 6
Fe	300 ± 4	330 ± 5
Mn	34 ± 2	34 ± 1
Ni	110 ± 2	130 ± 5
Pb	170 ± 20	190 ± 18
Zn	160 ± 5	180 ± 10

Analyte	NaF ng/g A	NaF ng/g B
Cd	200 ± 13	180 ± 10
Co	210 ± 15	200 ± 10
Cr	530 ± 15	550 ± 13
Cu	170 ± 5	210 ± 8
Fe	> 5000	>5000
Mn	> 5000	>5000
Ni	790 ± 20	780 ± 19
Pb	1100 ± 43	1200 ± 52
Zn	> 5000	>5000

Table 3.3 a), b), c), d) and e) Determination of Trace Analytes in a Selection of the Alkali Metal Salts. A:- Simple Aqueous Standard Calibration Procedure. B:- Standard Addition Calibration Procedure. See Text for Experimental Conditions.

3.3 Conclusions

1. A procedure for the successful determination of the trace analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, using a microcolumn of activated alumina in a FI-ICP-ES system has been developed.

2. The key experimental parameter sample pH was investigated and optimised at pH 8.

3. A dual-valve FI system was required, to minimise matrix interferences and prevent nebuliser and tubing blockage.

4. The capability of the technique for on-line enrichment of the analytes was demonstrated. The limit of detection determined for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn was 0.25, 0.34, 0.72, 0.17, 2.1, 0.075, 0.50, 3.2 and 0.61 $\mu g\ l^{-1}$ respectively, for a 5 ml sample volume.

5. The technique was successfully applied to the determination of these analytes in a selection of the alkali metal salts (CsI, KBr, $LiNO_3$, NaCl, NaF, 1 % w/v). For validity of measurement, the analytes were determined using two calibration techniques: A simple aqueous standard, and a standard addition calibration.

4 Analysis of Natural Waters - Laboratory Studies

Natural waters can be categorised as drinking (tap and mineral water), fresh (river, stream, lake and reservoir water) estuarine and seawater. The former two categories contain waters with relatively simple matrices, the latter two contain a relatively high concentration of dissolved organics and a concentrated salt matrix. Hence, natural water samples are highly complex materials, containing analytes in many physico-chemical forms and concentrations. Analytes such as calcium, magnesium, potassium and sodium are present in major quantities, and analytes such as cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead, vanadium and zinc exist at the $\mu g\ l^{-1}$ and the sub $\mu g\ l^{-1}$ level. Hence, due to the low concentration of these analytes serious losses of the analytes to container walls are experienced.

Although the total concentration of dissolved analytes may be similar in two water systems, the chemical forms of the analytes may be quite different. Some of the possible dissolved/filterable forms of trace analyte present in natural waters are shown in Table 4.1. The various physico-chemical forms of a trace analyte present in a water sample, are not necessarily in equilibrium with one another, but any procedure applied to the sample may disturb the equilibria and hence alter the speciation. The act of filtering the sample, which facilitates the provision of data for dissolved and total species concentration, or acidifying the sample for sample preservation will affect the equilibria.

The collection of a natural water sample is an arduous task due to the danger of contamination. The type and method of pre-cleaning of the sample bottles must be decided, along with other considerations such as sampling time, place and depth. If speciation measurements are to be performed, the water sample must not be acidified or frozen before storage. This is due to the possibility of irreversible change in the sample integrity and composition at the time of sampling. Storage at 4 ^{o}C is the preferred method, but the possibility of loss of trace analytes using only this condition for sample storage is a definite possibility.

Dissolved forms of trace analytes in a water sample are defined by convention as analyte which can pass through a 0.45 μm filter. The filtration step arbitrarily separates particulate forms of the analytes, from analyte in solution and forms associated with

colloidal particles. Open ocean seawater seldom requires filtration, due to a low concentration of particulate matter, but filtration is necessary for almost all fresh waters.

Physico-chemical Form	Possible Examples
Particulate	Retained by Filter
Simple Hydrated Ions	$Cd(H_2O)^{2+}$
Simple Inorganic Complexes	$Pb(H_2O)_4Cl_2$
Simple Organic Complexes	Cu-glycinate
Stable Inorganic Compounds	PbS, $ZnCO_3$
Stable Organic Compounds	Cu-fulvate
Adsorbed on Inorganic Colloids	Pb-MnO_2
Adsorbed on Organic Colloids	Cu-humic acid

Table 4.1 Possible Physico-chemical Forms of Analytes in Natural Waters. Reference 163.

Ion exchange has been utilised for trace analyte preconcentration of natural waters, because separations can be carried out with minimum sample manipulation. The iminodiacetic acid chelating resin, Chelex-100 has been applied to trace analyte determinations. Florence and Batley have used this resin to separate ionic from colloidally associated Cu, Pb, Cd and Zn (156, 157). Chelex-100 binds ionic metal strongly, but because it has a pore size of approximately 1.5 nm, large molecules and colloidal particles are excluded from the resin and are not retained. Hence the resin provides a simple, rapid and almost contamination free method for the separation of ionic and colloidally associated analyte. Trace analytes which are complexed by organic ligands, or adsorbed on organic colloidal particles can also be determined. Some methods are based on the assumption that the analytes can be successfully liberated from their organic complexes. These include ultraviolet irradiation and acid digestion. Others utilise neutral non-polar macroporous styrene-divinylbenzene copolymer resins, (e.g. Amberlite XAD-2) that have a high affinity for organometallic complexes. Groschner and Appriou (158) utilised a three column system which simultaneously preconcentrated

and differentiated between neutral hydrophobic organometallic complexes (C_{18} reversed phase), anionic complexes (Dowex) and labile cationic analytes (Chelamine). In contrast, activated alumina has been utilised to retain different analyte species (Cr(III) (142) and Cr(VI) (141)), humic acids (159-161) and organometallic species (162). Hence it is possible that activated alumina can retain dissolved, complexed and colloidal species of the trace analytes present in natural waters.

Independent studies utilising on-line microcolumn preconcentration with FI-atomic spectrometry have been applied to natural water samples (see section 1.4). Hartenstein *et al.* (65, 66) reported that only 10 % of the Mn value produced by conventional ICP-ES, was determined by the microcolumn enrichment technique for tap and rain water samples. This was reputed to be due to the possibility that only labile Mn species were retained by Chelex-100, and inert forms were not. Liu *et al.* (67) applied the microcolumn enrichment technique to Cu in river water samples, but the recovery obtained was poor. This was suggested to be due to the possibility that a proportion of the Cu was present in a form inaccessible to Chelex-100. Comber *et al.* (71) reported poor recovery of Cu from natural waters using Chelex-100 microcolumns. Cu was recovered from weak complexes easily, but on-line UV photolysis was required to liberate the Cu from strong complexes. Treit *et al.* (72) and Tabani and Kratochvil (73) utilised the macroporous reagent Dowex 50W-X8. This resin was reported to retain labile species of the analytes Ni and Cu, whilst bound species were not retained. Hewavitharana (74) used a similar procedure with Dowex to determine free Ca and Mg in the presence of complexed forms of these analytes. Milosavljevic *et al.* (89) utilised a microcolumn of resin 122 to perform on-line speciation. Free Cu ions were retained by this resin, but strongly complexed Cu was not. Malamas (91) utilised a microcolumn of 8-quinolinol to determine Cu in tap water samples. The results obtained were similar to those found by graphite furnace AAS, but it was not known how the reagent would perform when applied to samples containing strong soluble complexes, colloids or particles. In contrast Cox *et al.* (141, 142) have utilised microcolumns of activated

alumina to determine Cr species (Cr(III) and Cr(VI)) in natural waters The combined concentration of the two Cr species corresponded to the total Cr content.

Therefore the FI microcolumn preconcentration technique, developed for the analytical study of trace analytes in high purity alkali metal salts, was applied to the study of trace analytes present in selected mineral and reservoir water samples. The underlying aim of this study is to determine if measurements obtained utilising activated alumina microcolumns are equivalent to existing measurement techniques. The determination of dissolved/filterable species of the analytes present in natural waters is currently achieved by a multi-element analysis technique (AAS/ICP-ES/ICP-MS etc), following the filtration of the sample in the field through 0.45 μm membrane filters, and acidification of the filtrate. Suspended species are collected on the filter, digested and analysed by a multi-element analysis technique. Total recoverable species are analysed usually following an appropriate digestion procedure, by a conventional multi-element analysis technique without filtration of the sample. Experiments have been devised in an attempt to ensure that the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in selected natural waters, are determined by the microcolumn enrichment procedure with FI-ICP-ES detection.

This investigation focuses on a drinking water sample, (Buxton Mineral Water) due to its relatively simple matrix. The experiments were designed in an attempt to determine the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in this sample. The effect of the complexing agents acetic and tartaric acid, on the retention/elution of the analytes present in Buxton Mineral Water was studied. The effect of sample pH on species retention was also investigated. The influence of the complexing agents on the enrichment capability of microcolumn system was studied. The recommendations required for analysis are given, along with results for Buxton Mineral Water.

The optimised procedure was then applied to the determination of the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in a fresh water sample. Reservoir waters were selected, due to their accessibility and frequency

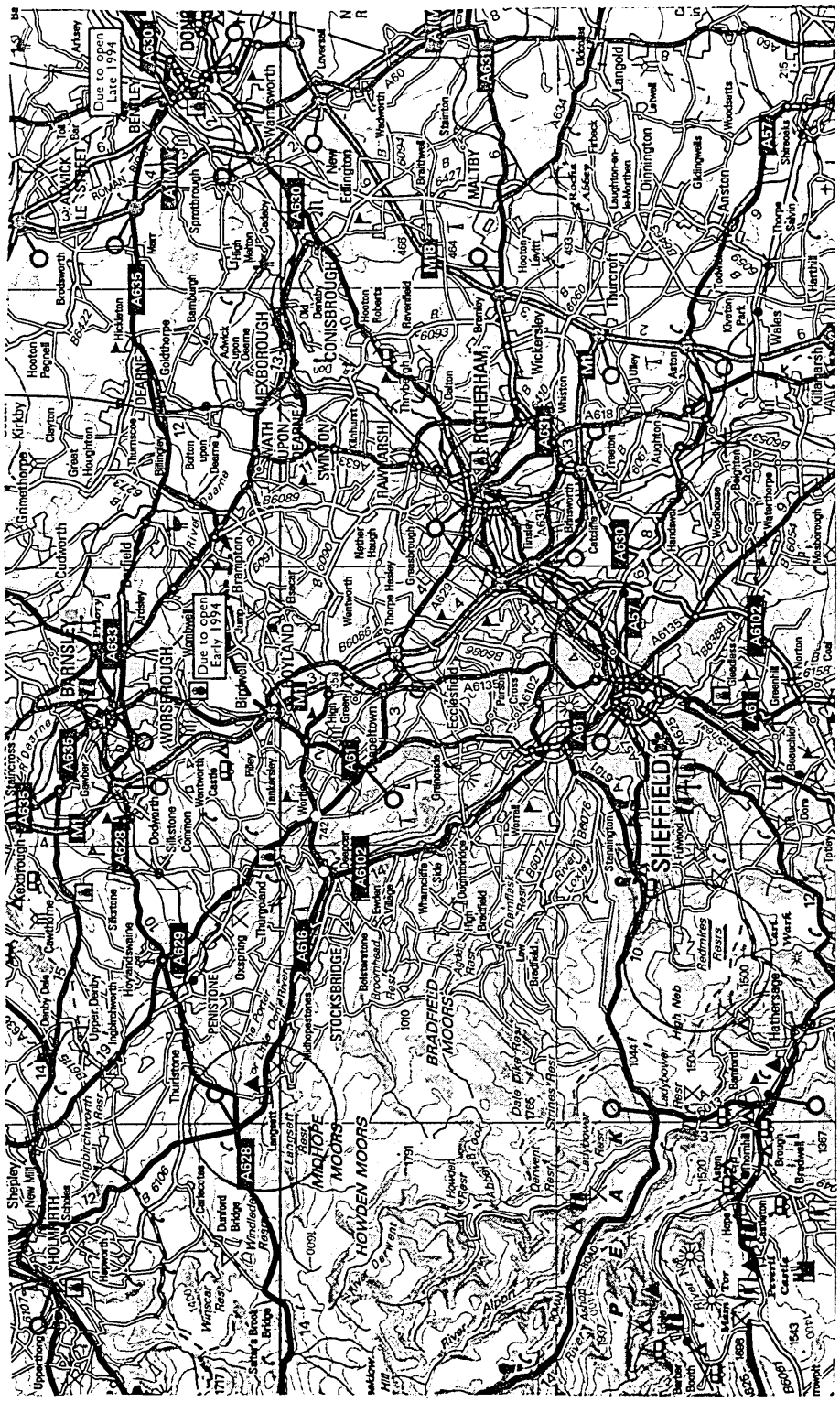


Fig.4.1 An Ordnance Survey map of the Sheffield area. The field sampling locations selected for this project are highlighted.

around the Sheffield area. These reservoirs are approximately situated to the southwest and northwest of Sheffield, respectively (see Fig.4.1). Redmires Reservoir has two main feeder streams, Wyming Brook and Fullwood Booth. Langsett Reservoir is fed by the Little River Don and two un-named trout streams. There are three reservoirs at Redmires, upper, middle and lower. The samples taken for this investigation were collected from the untreated upper reservoir. Langsett combines with Midhope Reservoir, however the samples collected for this investigation were from the untreated Langsett Reservoir Water. The effect of the complexing agents acetic and tartaric acid, on the retention/elution of the analytes present Langsett and Redmires reservoirs was investigated. The effect of eluent concentration on elution of the analytes was also studied. These reservoirs were selected for their contrasting composition. Redmires has low colour, turbidity and total organic carbon (i.e. low organic concentration) whereas Langsett has a high organic concentration. It is therefore assumed that the trace analytes will be present as different species in these two reservoirs. The analytical performance of the microcolumn enrichment technique with ICP-ES detection is discussed in terms of limits of detection capable with this procedure, precision and retention and elution efficiencies. The recommendations for analysis are given and the results obtained for the standard reference material SLRS-1. Typical determinand levels in Redmires and Langsett reservoirs are given in Table 4.2.

Determinand	Redmires	Langsett
pH	6.3	4.4
Turbidity / NTU	0.46	3.9
Colour / Hazen	29	66
Mg /mg/l	1.9	1.9
Ca / mg/l	5.4	3.2
Al / mg/l	0.37	0.45
Fe / mg/l	0.77	0.52
Mn / mg/l	0.11	0.11

Table 4.2 Typical Determinand Levels in Langsett and Redmires Reservoirs

4.1 Buxton Mineral Water

Experiments have been devised in this section in an attempt to ensure that the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in Buxton Mineral Water, are determined by the microcolumn enrichment procedure with FI-ICP-ES detection. Theoretically the chemical nature of activated alumina and the analyte ions in solution are both strongly dependent on pH. Hence under alkaline conditions, activated alumina represented as HL is converted to L^-, which reacts efficiently with analyte cations, (see section 3.1). However under alkaline conditions the reaction of some analyte ions may be inhibited due to hydrolysis.

$$[M(H_2O)_n]^{z+} + H_2O = [M(H_2O)_{n-1}\ OH]^{(z-1)+} + H_3O^+$$

As the pH is increased, the equilibrium in this equation will shift to the right. The hydroxyl ion will hydrolyse further to form a species containing up to z OH groups. This will result in precipitation of the analyte as an hydroxide. The approximate pH at which precipitation will begin, can be estimated. For example, investigations have indicated that the analyte Fe(III) is effectively retained by activated alumina at pH 8, (see section 3.). However, it is expected at this pH, that Fe could be present in Buxton water as the insoluble complex $Fe(OH)_3$ or as $[Fe(OH)_4]^-$ (163). Hence, it is in a form that is not available for reaction with activated alumina.

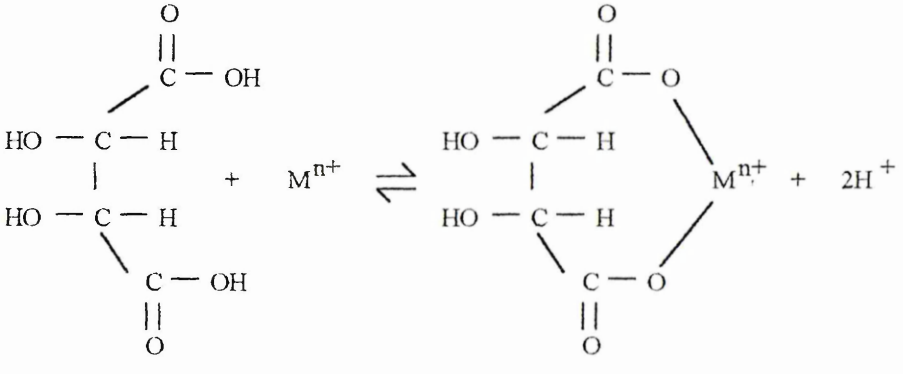
Mohammad *et al.* (102, 107) postulated that this difficulty could be surmounted, with the addition of an anionic buffer. The buffer thus utilised, forms a complex with the analyte in solution preventing the precipitation, or the formation of an anionic species, of the analyte. However, the buffer selected must not inhibit the reaction of the analyte with activated alumina. This approach was adopted in this work. The complexing agents acetic and tartaric acid were investigated, to determine if they could form strong enough complexes with the analytes present in Buxton water, to prevent analyte precipitation and/or anionic species formation but not inhibit the reaction between the analytes and activated alumina. Tartaric acid forms stronger complexes with the analytes than acetic acid, and this can be seen from a selection of their stability constants (see Table 4.3).

Analyte	Tartaric Acid log K	Acetic Acid log K
Ba	1.6	0.4
Cd	2.8	2.4
Co	2.1	1.9
Cu	6.5	3.2
Fe	7.5	3.2
Zn	8.3	1.5

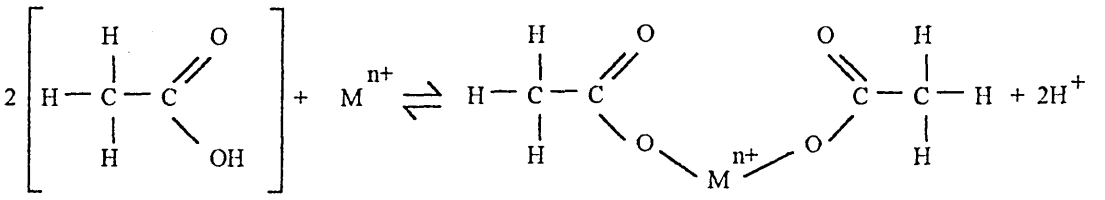
Table 4.3 Stability constants (expressed as log K values) for analyte binding reagents

4.1.1 The Influence of Complexing Agents on the Retention/Elution of Analytes

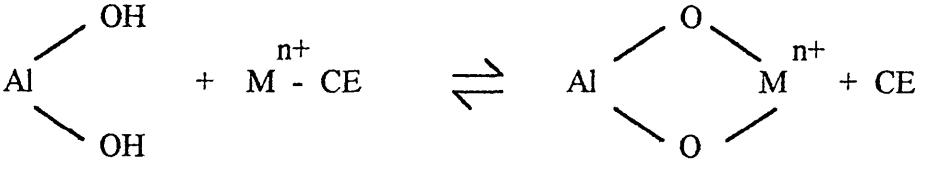
Initially acetic and tartaric acid were investigated, to evaluate their suitability as complexing agents, with respect to retention of the analytes by activated alumina. The complexing agent selected must ensure that the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are maintained in solution, in a form accessible to activated alumina without inhibiting their reaction with the column packing material. Hence, analyte complexes formed on the addition of the complexing agent to the sample and standard solutions, must prevent precipitation of the analyte and the formation of anionic species. The passage of these solutions through the column, must then result in the retention of the analytes by activated alumina, as detailed in section 3.1. The complexing agent should not inhibit retention by forming very strong complexes with the analytes. Hence, activated alumina must remain able to retain the trace analytes, when present in solution as analyte complexes.



Possible Analyte-Tartrate Complex Formation



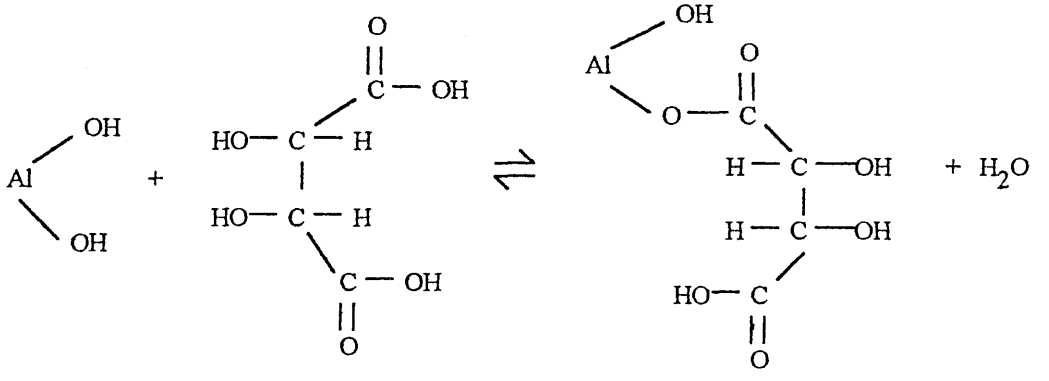
Possible Analyte-Acetate Complex Formation



* CE is the complexing agent

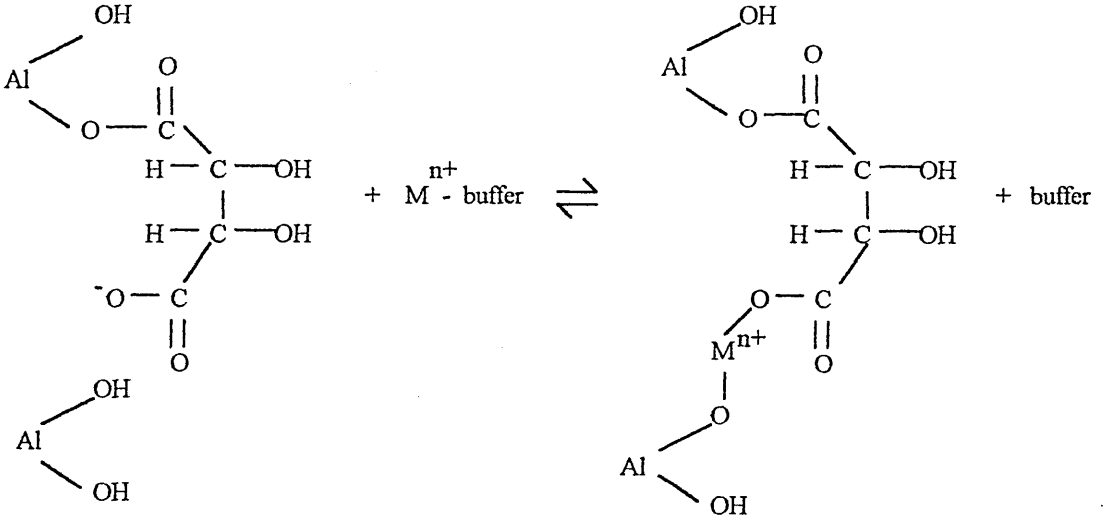
Proposed Retention of Analytes by Activated Alumina

This reaction is proposed for the majority of the analyte complexes formed which are of neutral charge and hence not in a form that alumina can retain under alkaline conditions. The exceptions are Fe^{3+} and Cr^{3+}. It is possible therefore, that these analytes may also be retained as analyte complexes. This suggests that Fe and Cr may be retained by alumina in a different form to the remaining analytes. Hence differences may be observed for these analytes. Furthermore, investigations by Kummert and Stumm (164) have suggested that organic acids are retained by activated alumina. Therefore, as the complexing agent is present in excess, it may also be retained.

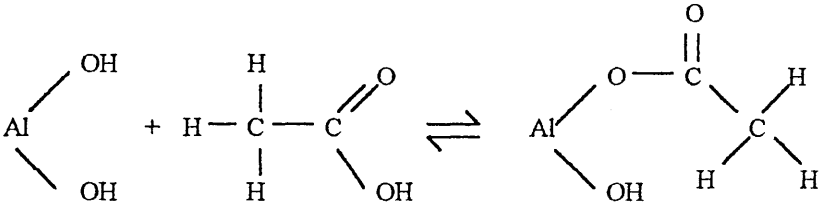


Tartaric Acid Retention by Alumina

Tartaric acid is a dicarboxylic acid, it is therefore possible, under the alkaline experimental conditions utilised for optimum analyte retention, that the second COOH group may de-protonate, producing an alternative reactive site for analyte retention. This will not occur for acetic acid. In fact, if acetic acid is used, it may hinder retention of the analytes, as it will compete for active sites. It is therefore possible that differences will be observed, with respect to analyte retention, with the use of different complexing agents.



Possible Alternative Site for Analyte Retention



Acetic Acid Retention by Alumina

The capability of activated alumina to retain the trace analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, in the presence of Buxton Mineral Water, was investigated. Using the procedure detailed in section 2.3.2, a volume of 0.5 ml of the sample, (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 $\mu g\ l^{-1}$) and a standard solution, adjusted to pH 8, were processed using the FI system. The procedure was repeated for Buxton Mineral Water

containing either 0.025 M tartaric acid or acetic acid. Typical time/elution profiles are displayed in Fig.4.2, 4.3, 4.4 and 4.5.

Fig.4.2 shows the time/elution profiles for Fe. The analyte Cr indicated similar retention/elution behaviour to the analyte Fe. The plots show that only background levels of the analyte Fe is detected, following the injection of sample. This indicates effective retention of the analyte from the standard solution, Buxton Mineral Water and Buxton Mineral Water which contains either 0.025 M tartaric acid or acetic acid. A transient signal was observed for the analyte, following the injection of eluent, indicating that the retained analyte could be subsequently eluted. However, the transient signal detected, differed for each matrix. A peak height of 1557 was obtained for 50 $\mu g\ l^{-1}$ Fe, present in the standard solution. The peak height for Buxton Mineral Water (50 $\mu g\ l^{-1}$ Fe spiked) was 1788. This increase suggests that the sample contained Fe at a detectable level. Buxton Mineral Water with added acetic acid, produced a peak height of 1761. This slight decrease may be due to competition for active sites by acetic acid, as discussed above, which resulted in incomplete retention of the analytes and/or slight suppression of the analyte signal in the presence of acetic acid. Buxton Mineral Water containing added tartaric acid produced a peak height of 750. However, although the height has more than halved, the peak width has doubled. It is therefore possible that Cr and Fe are retained as analyte-tartrate complexes, as discussed above. Thus these analytes form stronger complexes with alumina in the presence of tartrate, as shorter, broader peaks are observed on elution. It should be noted that the peak areas calculated for the profiles Fe (Buxton), Fe (Buxton/acetate) and Fe (Buxton/tartrate) in Fig.4.2 were virtually equivalent, that peak area is normally utilised for results generated in this study (see section 2.3.2) and hence peak heights are discussed here for comparison purposes only.

Fig.4.3 shows the time/elution plots for Cd. The analytes Co, Cu, Mn, Ni, Pb and Zn exhibited similar retention/elution behaviour to Cd. The plots indicate effective retention and elution of the analyte Cd, in the presence of the standard solution, Buxton Mineral Water and Buxton Mineral Water containing either 0.025 M acetic acid or

tartaric acid. The differences in peak height observed for the different matrices in Fig.4.2, were detected for Cd also. The peak height for the standard was 758, Buxton Mineral Water, 788, Buxton Mineral Water containing acetic acid, 762 and tartaric acid, 689. The peak width for sample containing tartaric acid was slightly broader than the remaining matrices. It is possible therefore, that the alternative active site proposed above, is produced and utilised. Hence, these analytes form slightly stronger complexes with alumina in the presence of tartrate, as slightly shorter, broader peaks are produced. It should be noted that the peak areas calculated for the four profiles in Fig.4.3 were virtually equivalent.

Fig.4.4 shows the time/elution profiles for Ca. The analytes Ca, Mg and Ba indicate retention/elution behaviour similar to Ca. Effective retention of Ca is observed for the standard solution only. Incomplete retention of Ca is observed for the remaining matrices. This is mainly due to the high concentration of this analyte (mg l^{-1} level) in Buxton Mineral Water. The peak height for the standard solution was 714, Buxton Mineral Water, 40841, Buxton Mineral Water containing acetic acid, 45041 and tartaric acid, 47268. The observed increase in peak height from 40841 to 47268, is due to increased retention of the analyte, which confirms that tartaric acid is an efficient complexing agent. It is able to prevent the precipitation of Ca, Ba and Mg at high pH and/or the formation of a species which alumina can not retain.

The analyte V behaves differently to every other analyte. The time/elution plots are shown in Fig.4.5. The analyte shows complete retention from every matrix. However, in the presence of the standard solution, Buxton Mineral Water and Buxton Mineral Water containing 0.025 M tartaric acid, the carrier solution (0.02 M NH_4OH), which follows the sample plug, elutes a proportion of the analyte retained. The proportion eluted decreases in the series Buxton + tartrate < Buxton < standard. It is possible that at pH 8, a proportion of the V is converted to species such as vanadate, which are weakly retained by alumina, in the presence of these matrices. Hence, in this situation, acetic acid is a more efficient complexing agent. It should be noted that the V retained, in the presence of Buxton Mineral Water containing tartrate, demonstrates

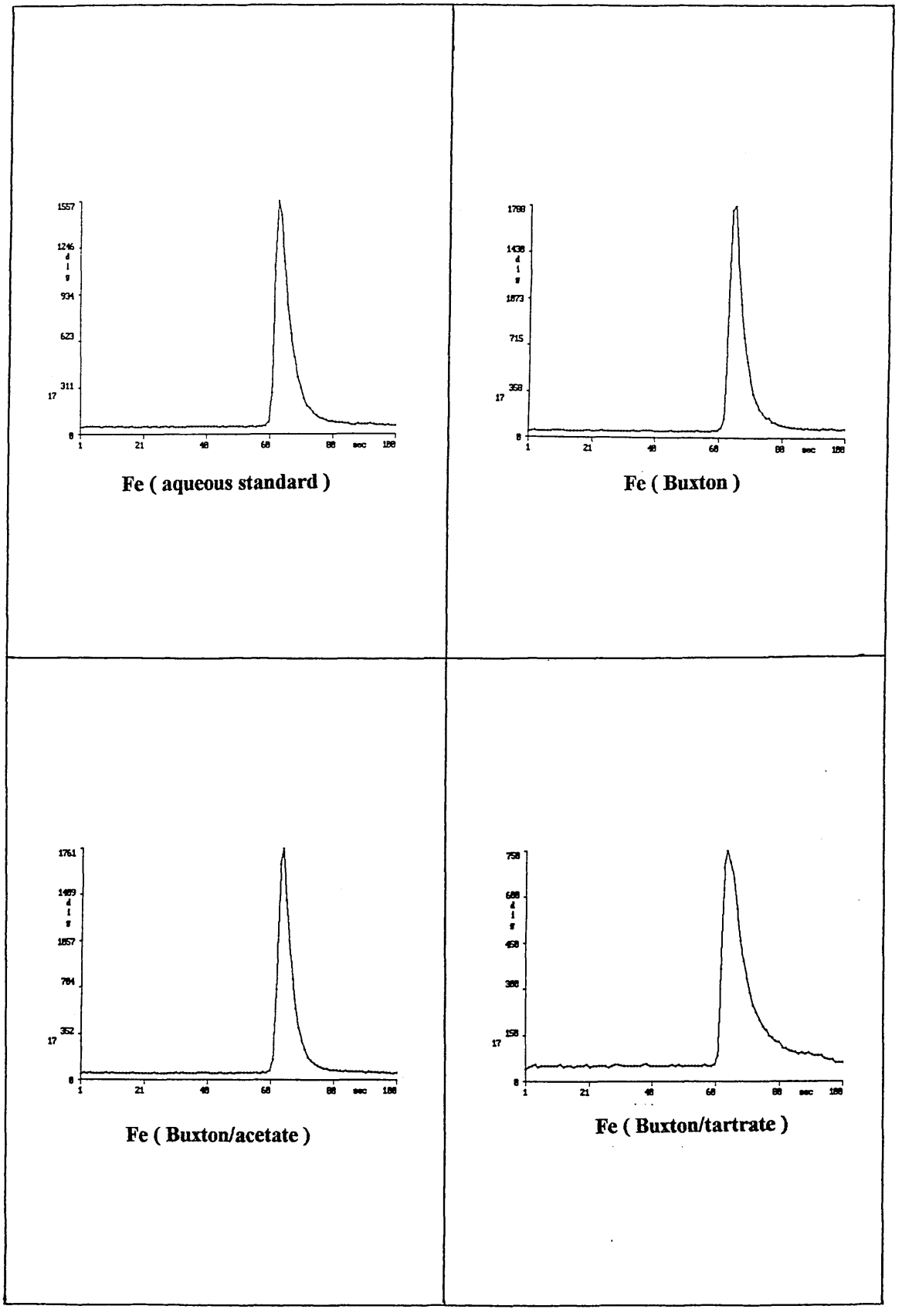


Fig.4.2 The emission/time response for Fe, for a 0.5 ml volume of sample. 1:- standard solution. 2:- (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). 3:- sample 2 containing acetic acid (0.025 M). 4:- sample 2 containing tartaric acid (0.025 M).

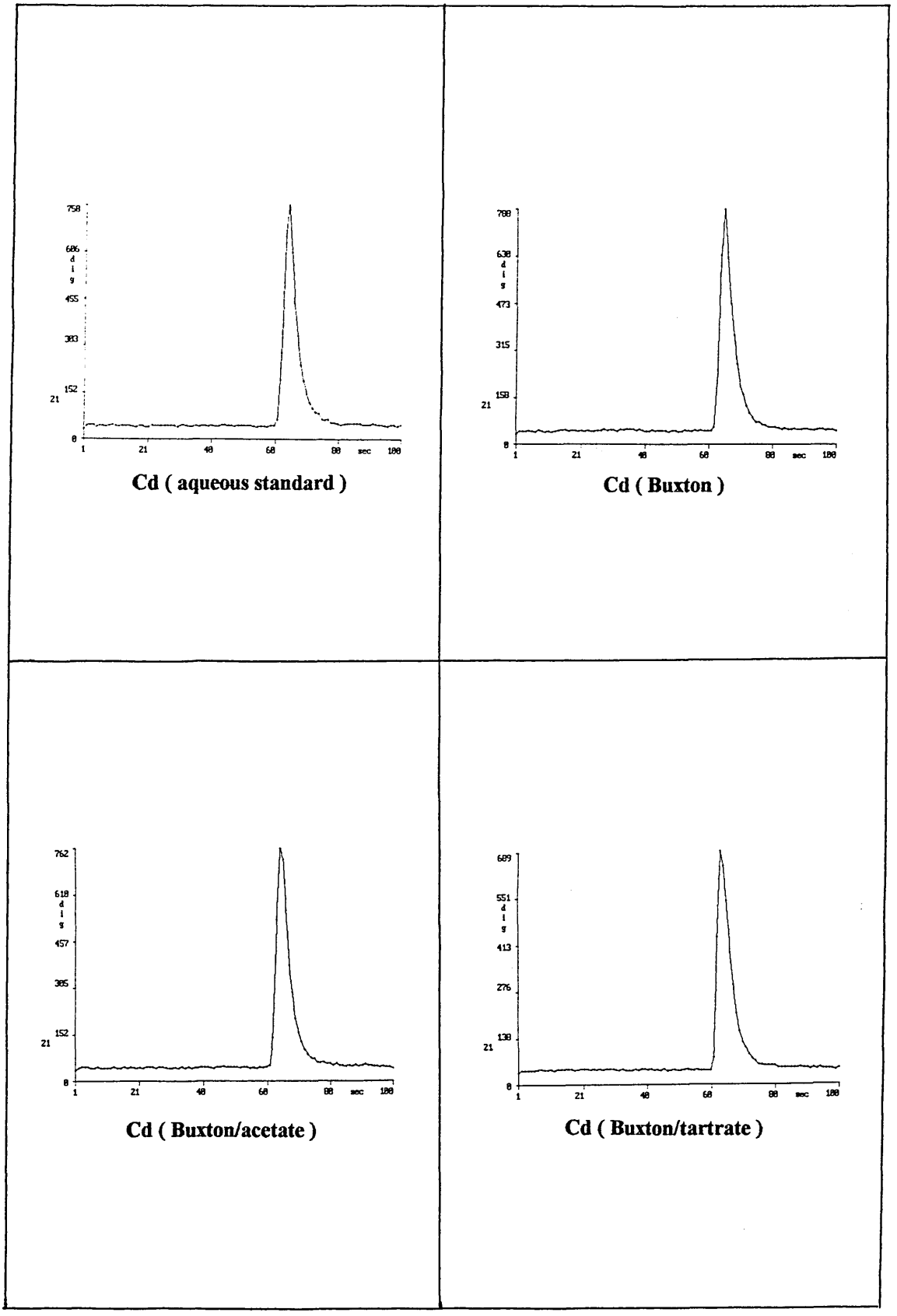


Fig.4.3 The emission/time response for Cd, for a 0.5 ml volume of sample. 1:- standard solution. 2:- (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). 3:- sample 2 containing acetic acid (0.025 M). 4:- sample 2 containing tartaric acid (0.025 M).

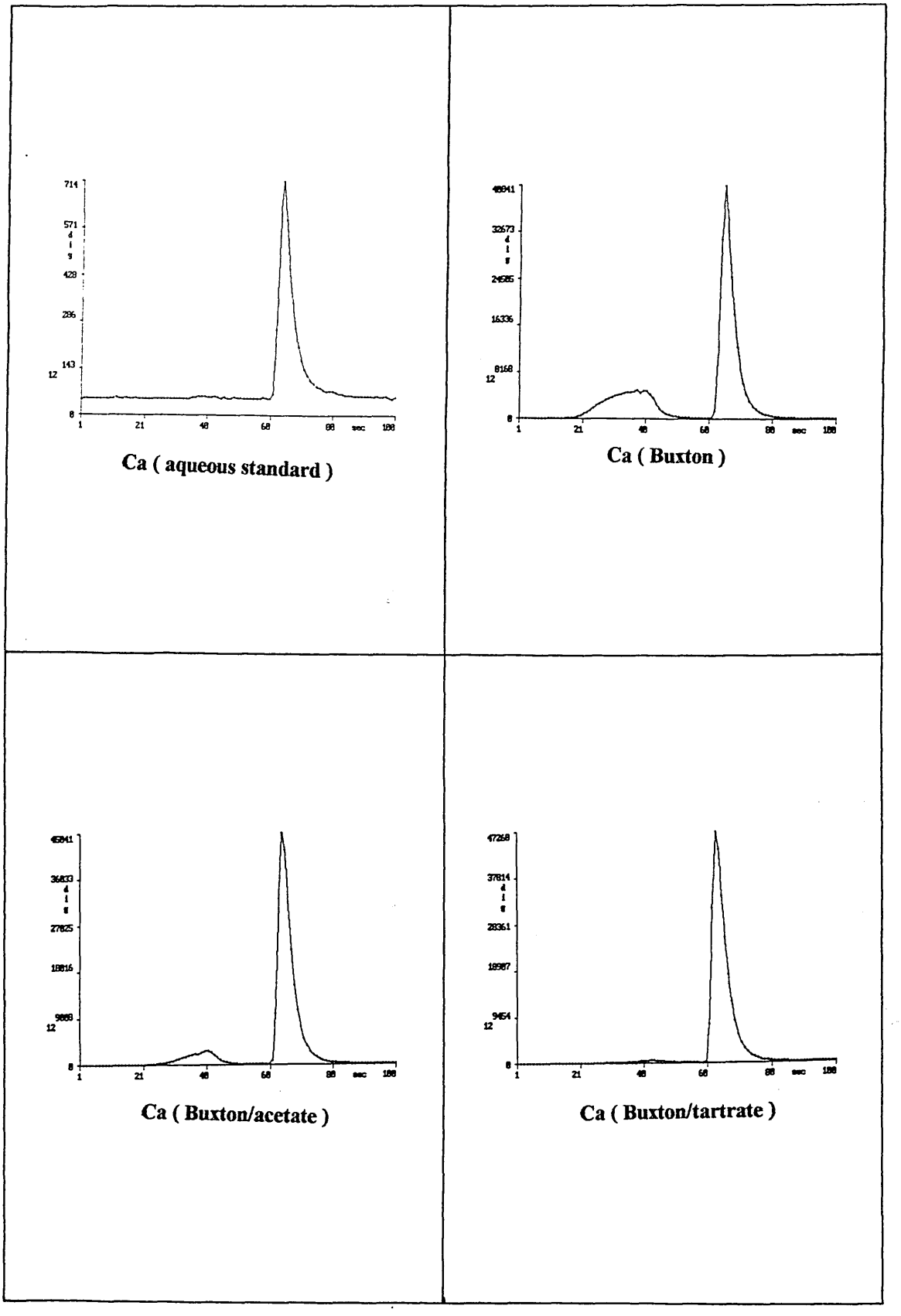


Fig.4.4 The emission/time response for Ca, for a 0.5 ml volume of sample. 1:- standard solution. 2:- (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). 3:- sample 2 containing acetic acid (0.025 M). 4:- sample 2 containing tartaric acid (0.025 M).

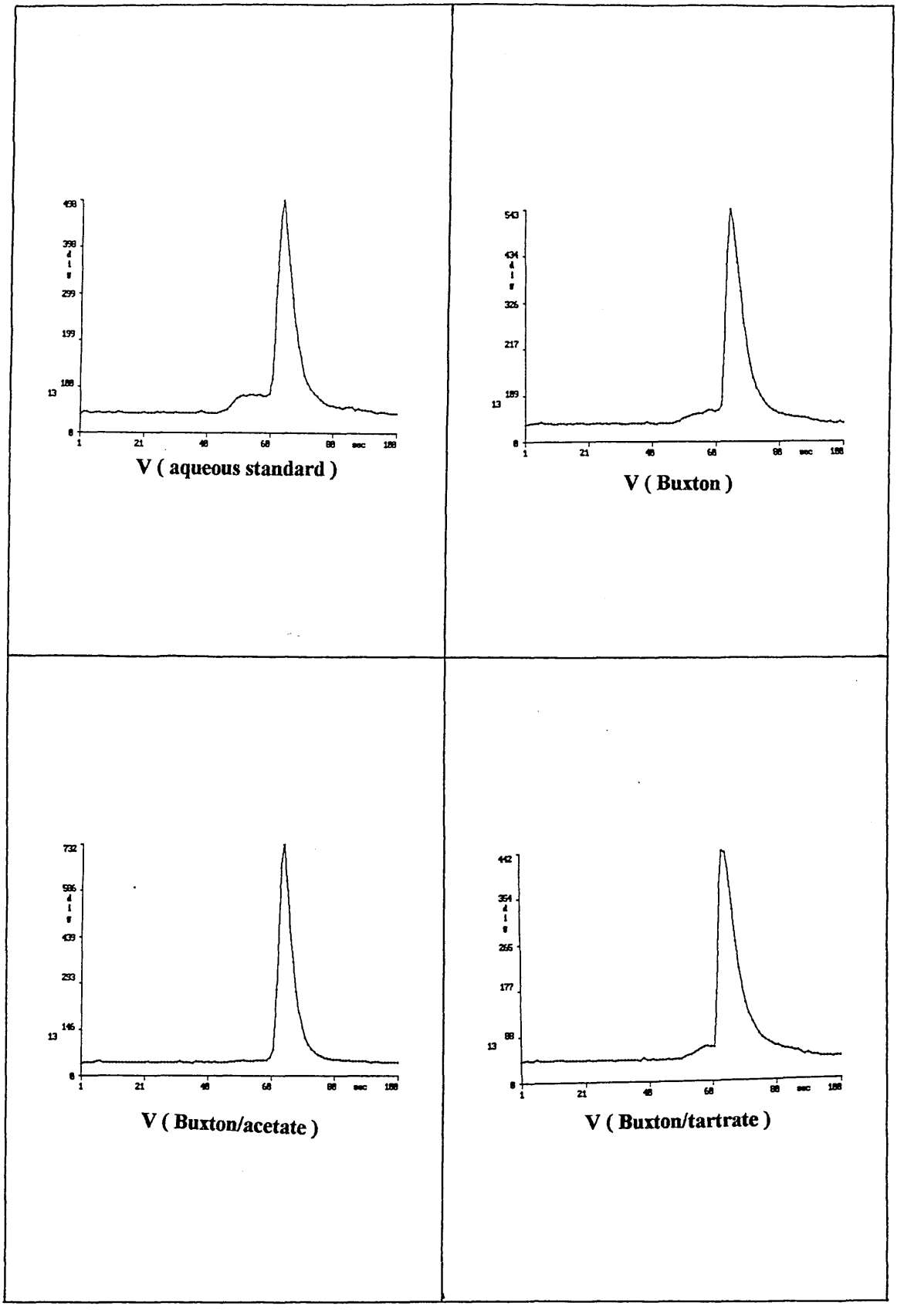


Fig.4.5 The emission/time response for V, for a 0.5 ml volume of sample. 1:- standard solution. 2:- (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). 3:- sample 2 containing acetic acid (0.025 M). 4:- sample 2 containing tartaric acid (0.025 M).

elution behaviour similar to Cr and Fe (see Fig.4.2).

In summary:

1. Every analyte (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn) present in the standard solution is effectively retained by activated alumina. However, a proportion of the analyte V is eluted by the carrier solution (0.02 M NH_4OH), which follows the sample zone. This is assumed to be due to the formation of V species at pH 8 which are weakly retained by alumina, and can therefore be easily eluted.

2. Every analyte retained in the presence of the standard solution is subsequently eluted from alumina with the injection of 250 µl of eluent (2 M HNO_3).

3. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are effectively retained by activated alumina, in the presence of Buxton Mineral Water. The remaining analytes (Ba, Ca and Mg), indicate incomplete retention. The analytes Ba, Ca and Mg are present in Buxton Mineral Water at the mg l^{-1} level (0.4, 55 and 19 respectively). The remaining analytes are present at the 50 µg l^{-1} level in this study. Therefore the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are selectively retained by activated alumina in the presence of high concentrations of Ba, Ca, Mg. The analyte V shows similar behaviour as detailed in 1. above. The proportion of V eluted by the carrier however was notably lower.

4. Every analyte retained in the presence of Buxton Mineral Water is subsequently eluted from alumina with the injection of 250 µl of eluent (2 M HNO_3). The peak height obtained for each analyte however, is notably greater than those found for the standard solution. This is assumed to be due to either a detectable presence of the analytes in the original sample and/or a clearer more controlled desorption process for the analytes retained in the presence of the sample.

5. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are effectively retained by activated alumina, in the presence of Buxton Mineral Water containing added acetic acid (0.025 M). The remaining analytes (Ba, Ca and Mg), indicate incomplete retention as detailed in 3. above. However, the proportion of Ba, Ca and Mg retained by activated alumina, notably improves with the addition of acetic acid. Also the analyte V is not

eluted by the carrier. Hence the presence of the complexing agent acetic acid improves retention.

6. Each analyte retained in the presence of Buxton Mineral Water containing added acetic acid (0.025 M), is subsequently eluted from alumina with the injection of 250 µl of eluent (2 M HNO_3). The peak height obtained for each analyte however, is slightly lower than those found for Buxton Mineral Water. This may be due slight suppression of the analyte signal in the presence of acetic acid.

7. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn are effectively retained by activated alumina, in the presence of Buxton Mineral Water containing added tartaric acid (0.025 M). The remaining analytes (Ba, Ca and Mg), indicate incomplete retention as detailed in 3. above. However, the proportion of Ba, Ca and Mg retained by activated alumina, significantly improves with the addition of tartaric acid. A proportion of the analyte V is eluted by the carrier as detailed in 1. However the proportion eluted is significantly lower than that found for the standard and Buxton Mineral Water. Hence the presence of the complexing agent tartaric acid improves retention.

8. Each analyte retained in the presence of Buxton Mineral Water containing added tartaric acid (0.025 M), is subsequently eluted from alumina with the injection of 250 µl of eluent (2 M HNO_3). The peak height obtained for each analyte however, is significantly lower than those found for Buxton Mineral Water, but the peak width has significantly increased accordingly. It is proposed that this is due to the formation of an alternative reactive site on activated alumina, in the presence of tartaric acid, which binds the analytes more strongly.

4.1.2 The Effect of pH on Species Retention

It has been shown that the chemical nature of the column packing material and the analyte ions in solution, are strongly dependent upon pH (92, 97). Furthermore, that reagents such as acetate and tartrate can be utilised as complexing agents to maintain the analytes in solution. Therefore, the effect of pH on species retention was investigated, with and without the use of the complexing agents acetic and tartaric acid.

A sample (Buxton Mineral Water, multi-element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 $\mu g\ l^{-1}$) and standard solution were prepared and adjusted to pH 3, 4, 5, 6, 7, 8, 9 and 10, respectively. Using the procedure detailed in section 2.3.2, a 5 ml volume of the sample and standard solution were processed in the FI system, for each pH adjustment. This experiment was repeated for Buxton Mineral Water containing either acetic acid or tartaric acid (0.025 M). The data obtained are represented graphically in Fig.4.6, 4.7 and 4.8. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus pH.

The plots in Fig.4.6 indicate different retention/elution behaviour for the analytes, in the presence of Buxton Mineral Water and a simple aqueous standard. They also indicate that pH has a greater effect on retention of the analytes, in the presence of the standard solution, compared to the sample. The analytes can be roughly separated into groups, by comparing their retention/elution behaviour. These are:-
Group 1:- Cr, Fe and V; Group 2:- Cu, Pb and Zn; Group 3:- Cd and Co; Group 4:- Mn and Ni; and Group 5:- Ba, Ca and Mg.
These groups are similar to those found in chapter 3. It is possible that the differences observed for the sample and standard solution, with respect to analyte retention, are related to the fact that the sample is a natural water and therefore contains natural complexing agents. Hence, these natural complexing agents, are able to maintain the analytes in a form that alumina can retain, producing the observed superior retention capability. The standard solution does not contain a complexing agent and hence poorer retention characteristics are observed. The pH selected for further investigations was 7. Certain analytes (Co, Mn, V and Ni) were retained more effectively at pH 9, however the matrix analytes Ba, Ca and Mg are retained effectively at this pH also, hence it was not selected.

The plots in Fig.4.7 indicate similar retention/elution behaviour for the analytes, in the presence of Buxton Mineral Water containing acetic acid (0.025 M) and a comparable standard solution. The analytes can be separated into groups, corresponding

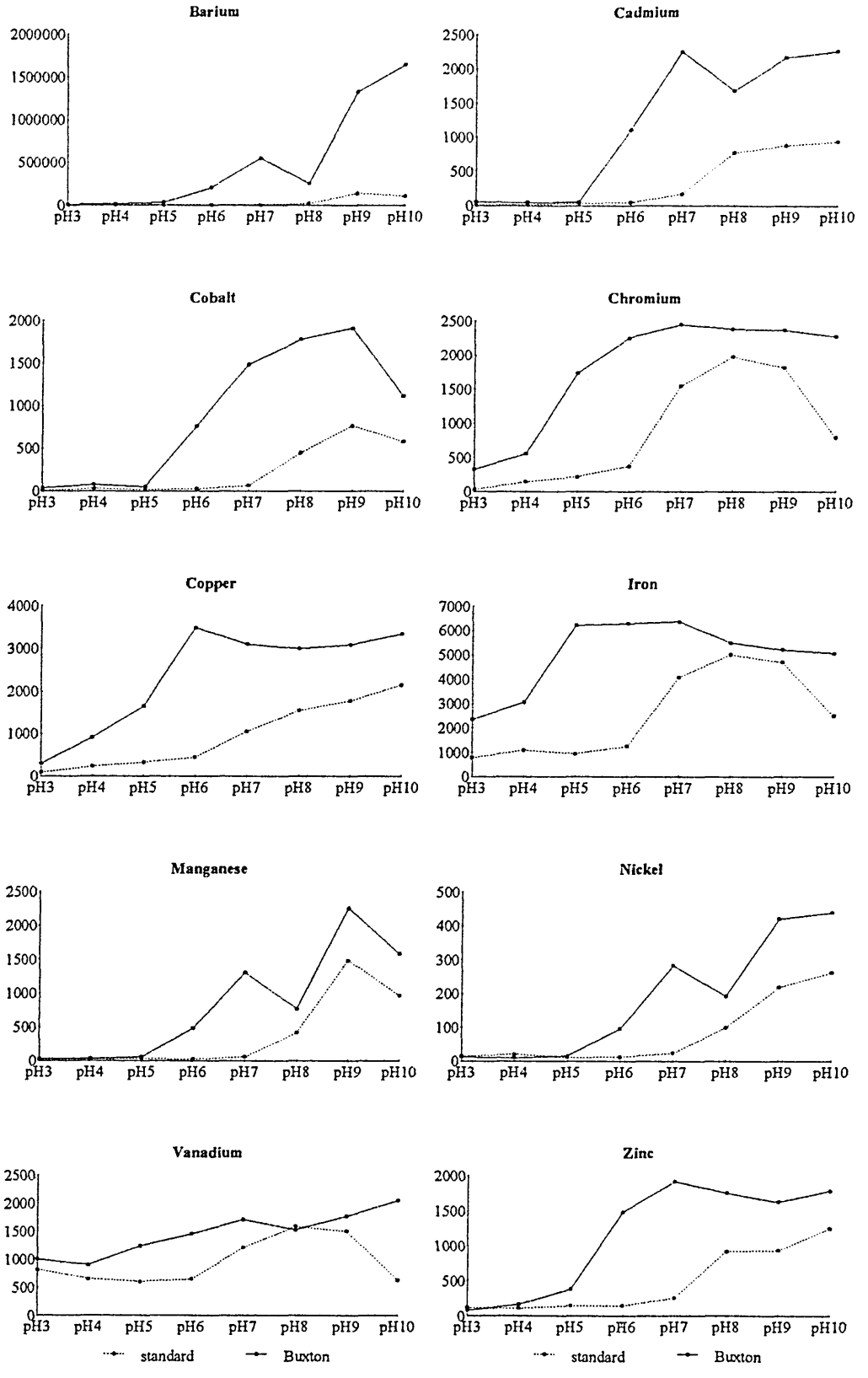


Fig.4.6 The effect of pH on retention of analyte species. The sample volume is 5 ml. Sample (Buxton Mineral Water, multi-element spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). Multi-element standard (50 µg/l)

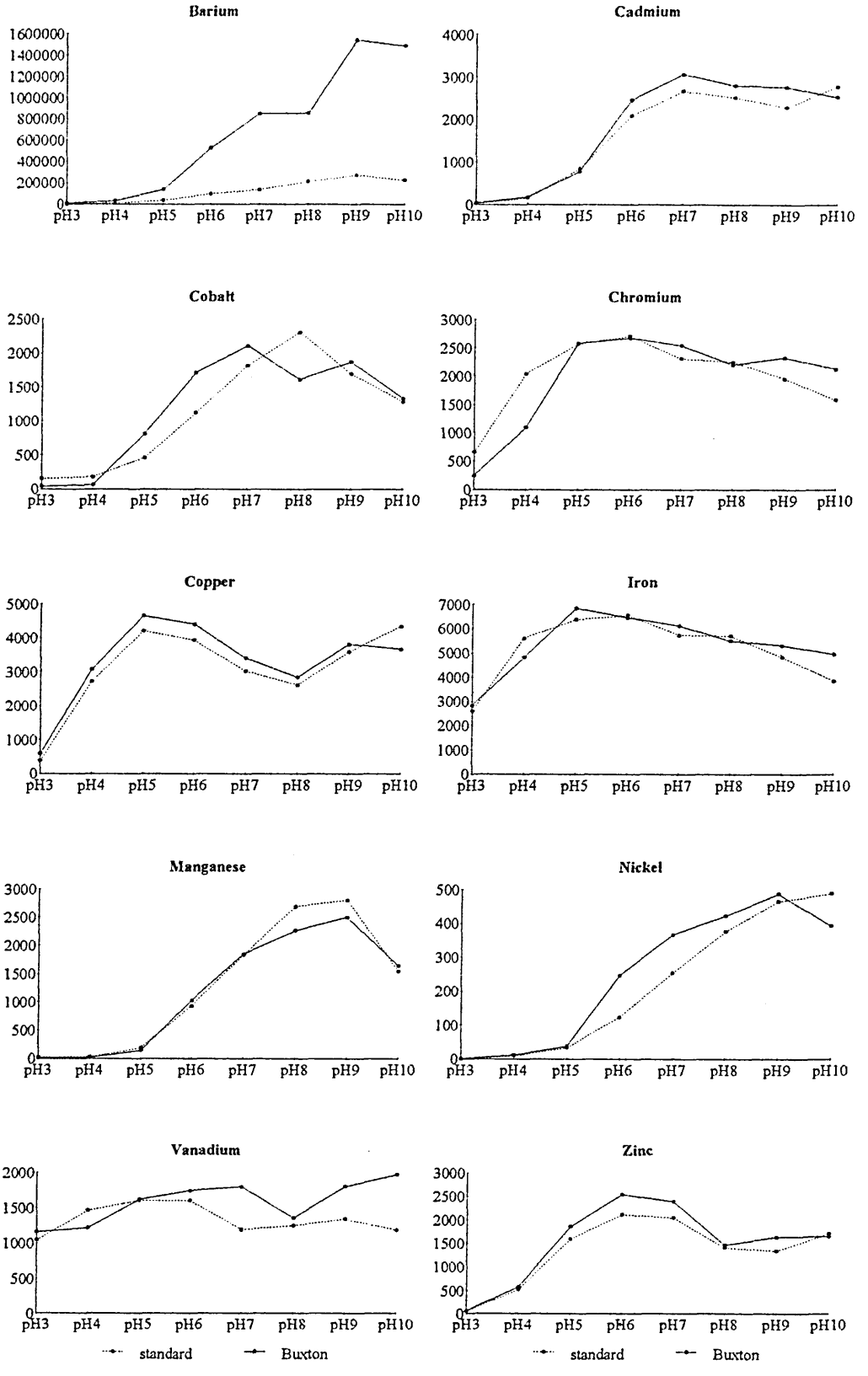


Fig.4.7 The effect of pH on retention of analyte species. The sample volume is 5 ml. Sample (Buxton Mineral Water, multi-element spike Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l, acetic acid, 0.025 M). Multi-element standard containing 0.025 M acetic acid.

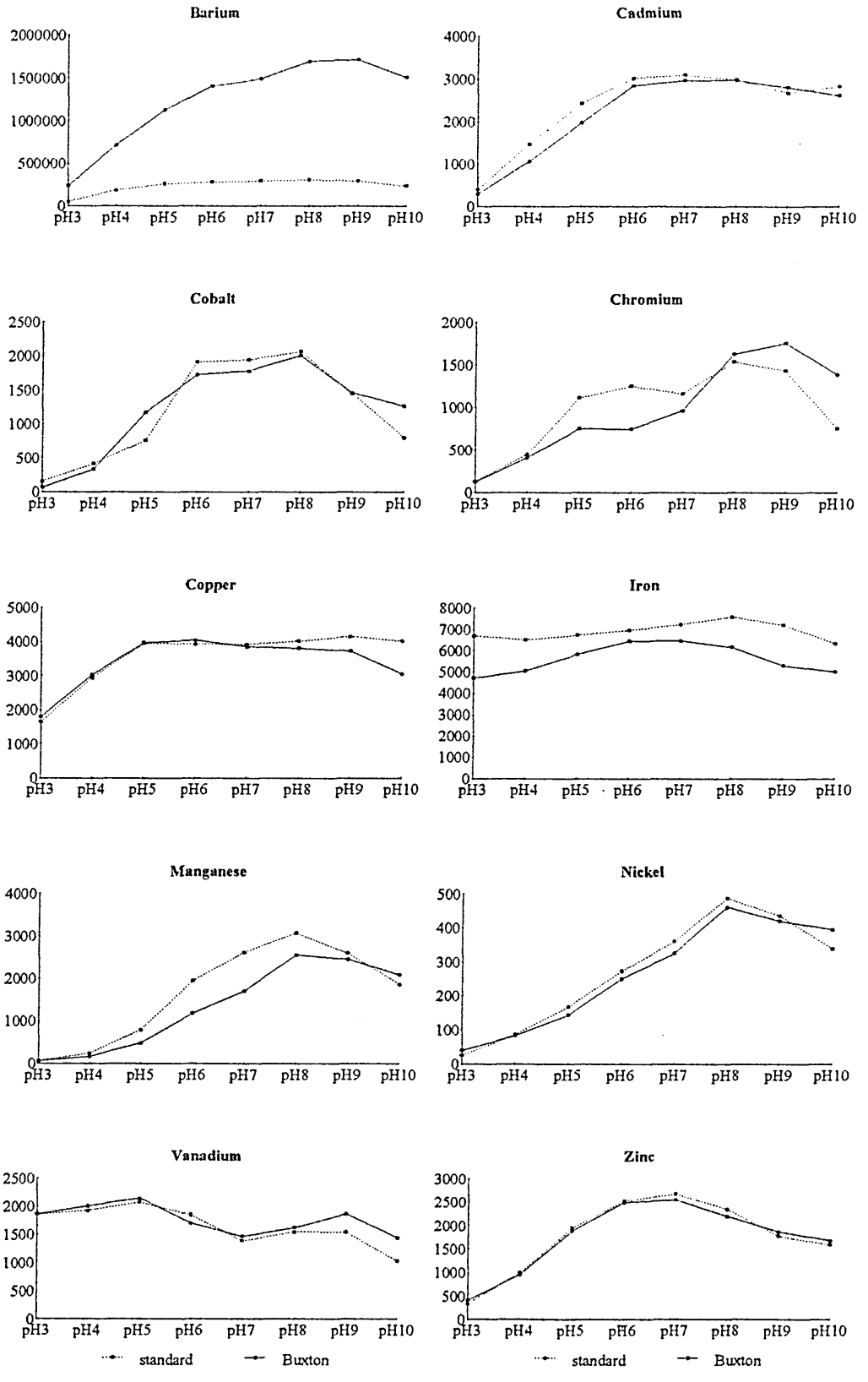


Fig.4.8 The effect of pH on retention of analyte species. The sample volume is 5 ml. Sample (Buxton Mineral Water, multi-element spike Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l, tartaric acid, 0.025 M). Multi-element standard containing 0.025 M tartaric acid.

to their retention/elution characteristics. The 5 groups are equivalent to those found for Buxton Mineral Water without complexing agent. However, the addition of complexing agent to the sample and standard solution, appears to have functioned as expected. Analyte-acetate complexes appear to have formed, maintaining the analytes in a form that activated alumina could retain, producing similar retention/elution behaviour, in the presence of the sample and standard. The pH selected for further study was 7. This was a compromise as certain analytes (Cr, Cu, Fe, Pb, V and Zn) exhibited greatest retention between pH 5-7 and others (Ba, Ca, Cd, Co, Mg, Mn and Ni) between pH 7-9.

The plots in Fig.4.8 also show similar retention/elution behaviour for the analytes, in the presence of Buxton Mineral Water containing tartaric acid (0.025 M) and an equivalent standard solution. However, the analyte groups, separated due to different retention/elution characteristics, have changed. The groups are:-

Group 1:- Cr; Group 2:- Cu, Fe, V and Pb; Group 3:- Co, Cd and Zn; Group 4:- Mn and Ni and Group 5:- Ba, Ca and Mg.

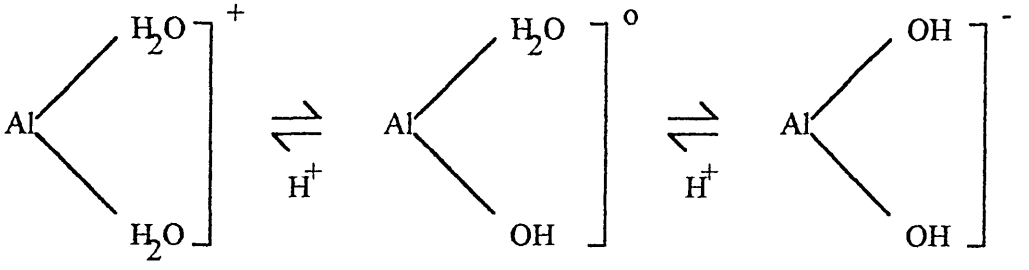
The differences in the analyte groups, may be due to the presence of the suggested alternative active sites. However, as above, the complexing agent appears to have functioned as expected, maintaining the analytes in a form alumina could retain and thus producing similar retention/ elution behaviour, in the presence of the sample and standard. The pH selected for further investigation was 8.

In summary for the analytes present in the standard and sample in the absence of complexing agent:

1. Analyte retention is always greater in the presence of Buxton Mineral Water, compared to a simple aqueous standard.

2. Variation with pH is much less marked in the presence of Buxton Mineral Water, compared to a simple aqueous standard.

3. A significant increase in retention is observed for every analyte between pH 6 and 9, in the presence of the standard solution, and between pH 4 and 9, in the presence of Buxton Mineral Water. These increases are probably due to a marked shift to the right of the equilibria below, which facilitates analyte retention:



4. Incomplete retention is observed for every analyte (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn), in the presence of the standard solution below pH 6, and in Buxton Mineral Water below pH 5.

5. Each analyte is effectively retained between pH 8 and 10, in the presence of the standard solution and Buxton Mineral Water.

6. The analytes can be tentatively placed in order of selectivity, with respect to analyte retention: Cr, Fe, V > Cu, Pb, Zn > Cd, Co > Mn, Ni > Ba, Ca, Mg.

In summary for the analytes present in the standard and sample with the addition of either acetic acid or tartaric acid:

1. The analytes (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) exhibit similar variations with pH, in the presence of the standard solution and Buxton Mineral Water containing added acetic acid or tartaric acid (0.025 M). The exceptions are Ba, Ca and Mg.

2. The variations with pH are much less marked for the standard and sample solutions containing added acetic or tartaric acid, compared to the same solutions in the absence of complexing agent.

3. Incomplete retention is observed for every analyte (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn), in the presence of the sample and standard solution containing acetic acid below pH 5, and tartaric acid at pH 3.

4. A significant increase in retention is observed for every analyte between pH 5 and 9, in the presence of the sample and standard solution containing acetic acid, and between pH 3 and 9 for the same solutions containing tartaric acid. These increases are probably due to a marked shift to the right of the equilibria described above, which facilitates analyte retention.

5. Every analyte is effectively retained between pH 8 and 10, in the presence of the sample and standard solution containing complexing agent. It is possible that the analytes are maintained in solution with the addition of complexing agent, which facilitates analyte retention.

4.1.3 The Influence of Complexing Agents on the Enrichment Capability

Utilising optimum experimental conditions and the procedure detailed in section 2.3.2, volumes of 2, 5, 10 and 15 ml of sample (Buxton Mineral Water, multi-element spike Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 $\mu g\ l^{-1}$) and standard solution were processed in the FI system. This procedure was repeated for Buxton Mineral Water containing either acetic acid or tartaric acid (0.025 M). Graphical representations of the data produced are displayed in Fig.4.9, 4.10 and 4.11. Hence the plots show emission intensity, which is the area calculated for the transient signal produced for each analyte on elution with nitric acid, versus sample volume.

The plots produced in Fig.4.9 indicate a linear relationship between signal intensity and sample volume for the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in the sample and the analytes Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn in the standard solution. Effective retention/elution of these analytes is therefore obtained, for processing sample volumes up to 15 ml. The remaining analytes Ba, Ca and Mg, present in the sample solution, produced a non-linear relationship. Hence, incomplete analyte retention was observed for these analytes, for sample volumes greater than 10 ml. This was possibly due to the high concentration of the analytes in the sample (mg l^{-1} level) and that activated alumina has least selectivity for Ba, Ca and Mg. However, only the analytes Cr, Cu, Fe and V indicate similar retention/elution behaviour, in the presence of the sample or standard solution. This is most probably due to activated alumina having greatest selectivity for these analytes. It is presumed as suggested above, that the superior retention/elution behaviour of the analytes, in the presence of the sample in comparison to standard solution, can be related to the presence of natural complexing agents in the sample. These natural complexing agents are able to maintain the analytes

in a form that activated alumina can retain. The absence of complexing agents in the standard, thus produces poor retention.

The plots produced in Fig.4.10 indicate a linear relationship between signal intensity and sample volume for every analyte in the standard solution containing acetic acid, (0.025 M) and every analyte except Ba, Ca and Mg in the sample. Effective retention/elution of every analyte, except Ba, Ca and Mg is therefore obtained. The remaining analytes (Ba, Ca and Mg), present in the sample solution containing acetic acid, produced a non-linear relationship. Hence, incomplete analyte retention was observed for these analytes, for sample volumes greater than 5 ml. This behaviour is similar to the study without complexing agent and has been discussed above. However, each analyte indicated similar retention/elution behaviour, in the presence of either the sample or standard solution. As suggested above, it is assumed that the addition of complexing agent to the sample and standard solution, has functioned as expected. Analyte-acetate complexes appear to have formed, maintaining the analytes in a form that activated alumina can retain.

The plots produced in Fig.4.11 also indicate a linear relationship between signal intensity and sample volume for each analyte in the standard solution containing tartaric acid, (0.025 M) and every analyte except Ba, Ca and Mg in the sample. Hence, as above effective retention/elution of each analyte, except Ba, Ca and Mg is obtained. Again every analyte indicated similar retention/elution behaviour, in the presence of either the sample or standard solution. Hence the complexing agent has functioned as initially proposed, maintaining the analytes in a form alumina could retain in both matrices and thus producing the similar retention/elution behaviour observed.

In summary:

1. Every analyte (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) exhibits a linear relationship between sample volume and emission intensity, in the presence of the standard solution with and without the addition of complexing agent, up to processing volumes of 15 ml.

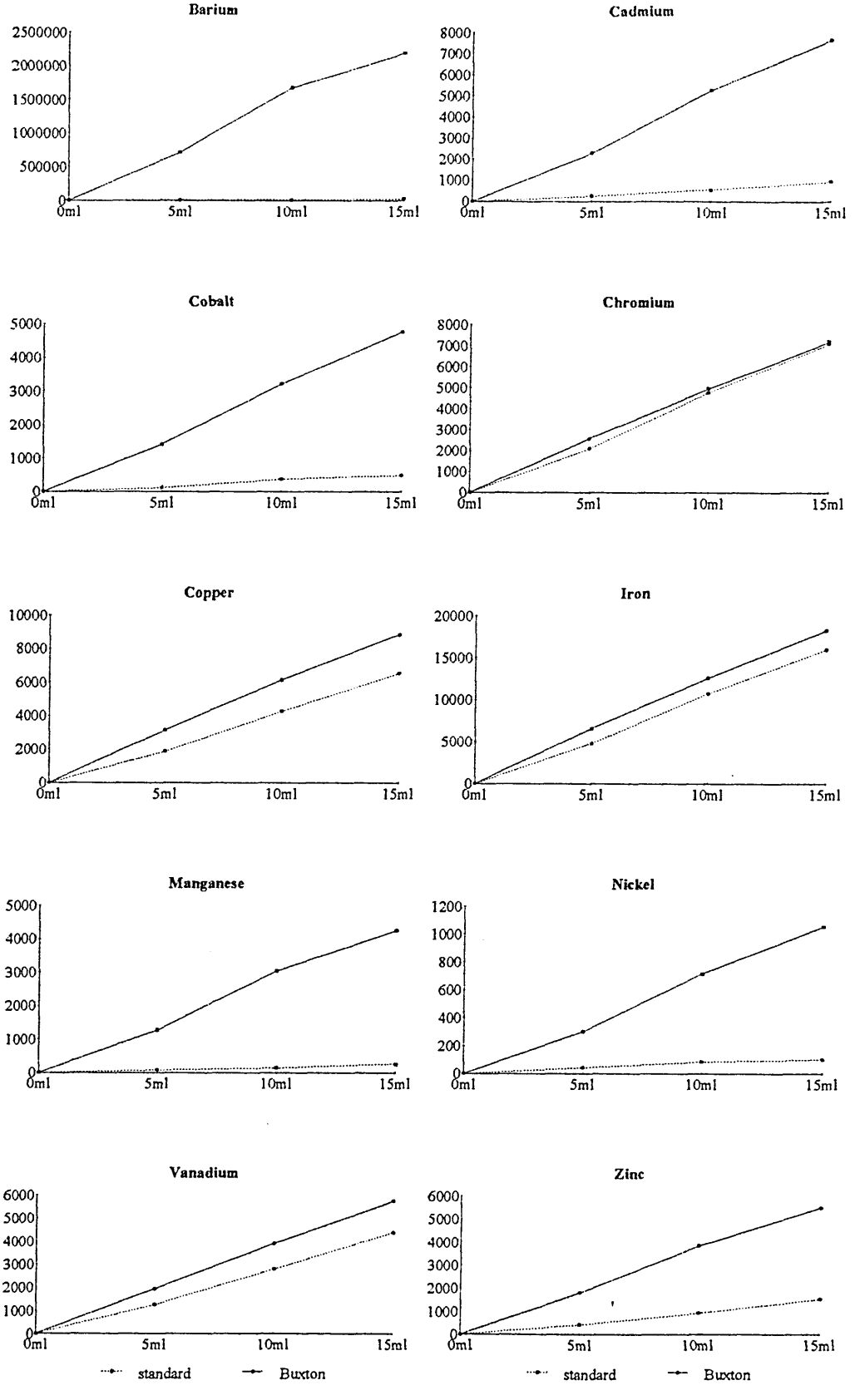


Fig.4.9 The effect of sample volume on the retention of the analytes. Sample (Buxton Mineral Water, multi-element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l). Multi-element standard (50 µg/l).

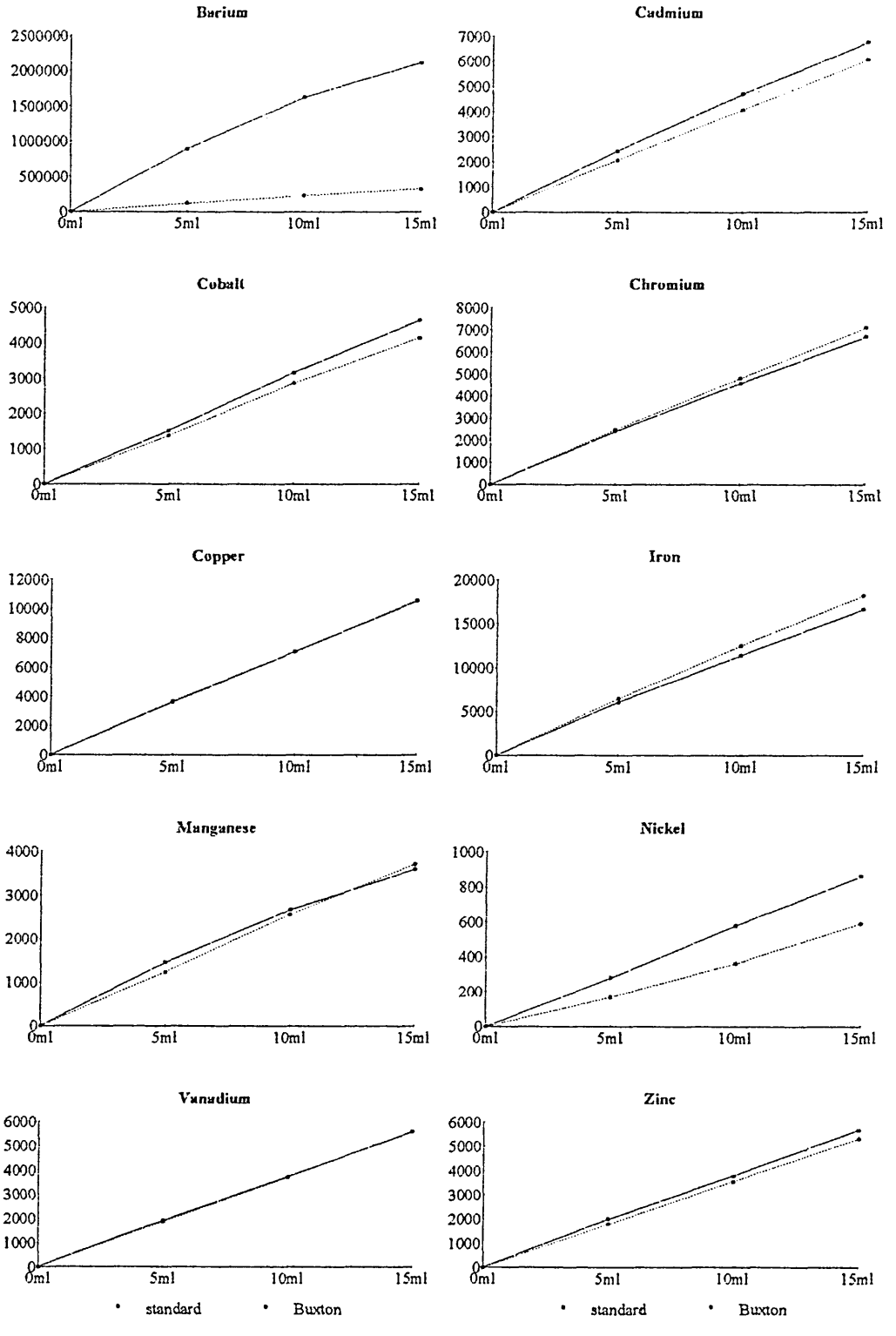


Fig.4.10 The effect of sample volume on the retention of the analytes. Sample (Buxton Mineral Water, multi-element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l, acetic acid, 0.025 M). Multi-element standard containing 0.025 M acetic acid (50 µg/l).

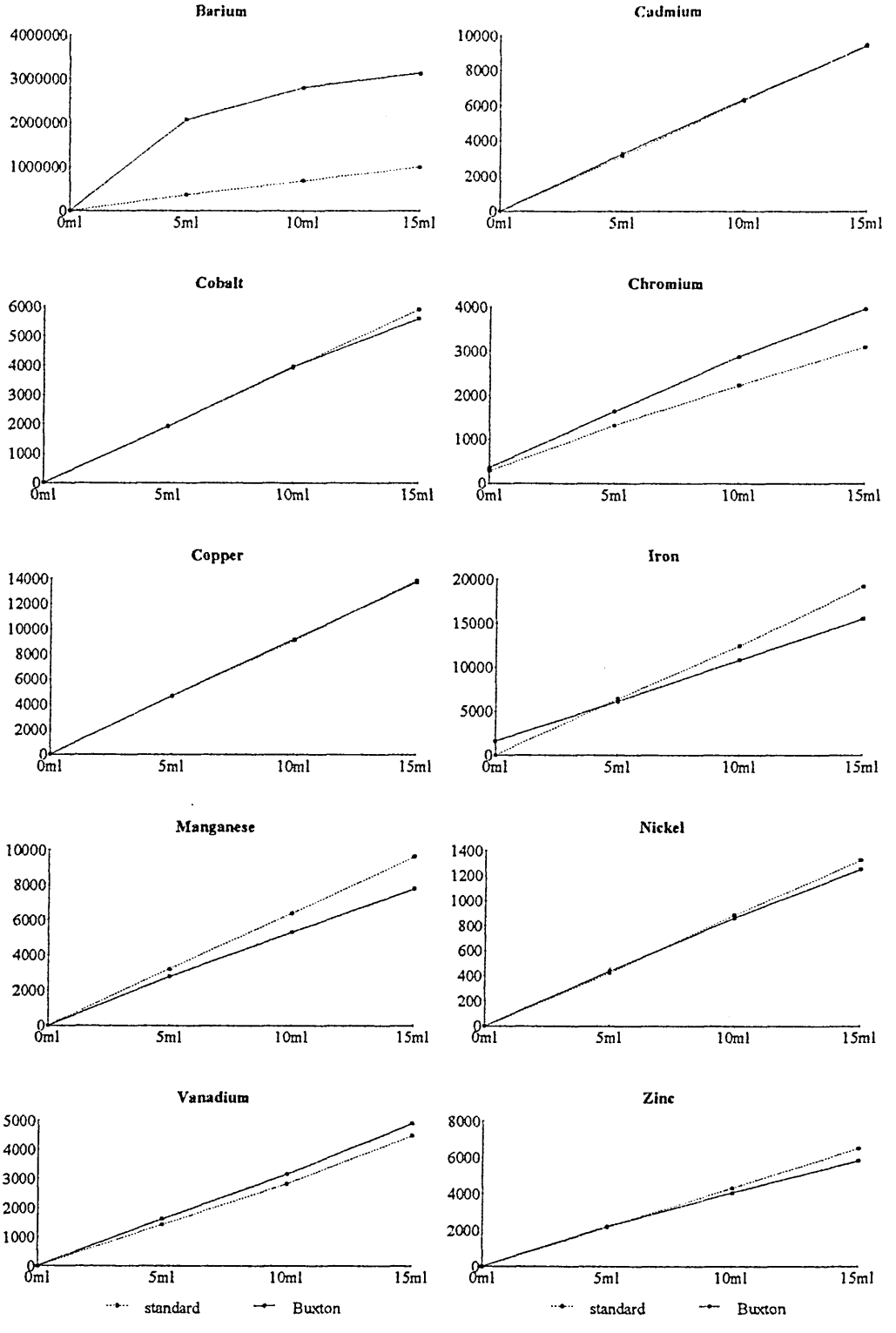


Fig.4.11 The effect of sample volume on the retention of the analytes. Sample (Buxton Mineral Water, multi-element solution spike, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg/l, tartaric acid, 0.025 M). Multi-element standard containing 0.025 M tartaric acid (50 µg/l).

2. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn produce a linear relationship between sample volume and emission intensity, in the presence of Buxton Mineral Water with and without the addition of complexing agent, up to processing volumes of 15 ml. The remaining analytes (Ba, Ca and Mg), produce a non-linear relationship. This is assumed to be due to their higher concentration in the sample (0.4, 55 and 19 mg l^{-1} respectively), compared to the remaining analytes (50 µg l^{-1} in this study), and because activated alumina has the least affinity for Ba, Ca and Mg.

3. The analytes (Ba, Ca, Cd, Co, Mg, Mn, Ni, Pb and Zn) exhibit different retention/elution behaviour in the presence of Buxton Mineral Water and the standard solution, without the addition of complexing agent. The remaining analytes (Cr, Cu, Fe and V), exhibit similar retention/elution behaviour. This is assumed to be because activated alumina has the highest affinity for Cr, Cu, Fe and V, and they are hence preferentially retained in the presence of the standard solution.

4. The analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn exhibit similar retention/elution behaviour in the presence Buxton Mineral Water and the standard solution, with the addition of complexing agent. The remaining analytes (Ba, Ca and Mg), exhibit different retention/elution behaviour. Therefore the analytes Ba, Ca and Mg cannot be accurately determined in Buxton Mineral Water by this technique. The remaining analytes can only be determined accurately with the addition of complexing agent.

5. The volume selected for the determination of trace analytes in Buxton Mineral Water was 10 ml. This volume is expected to provide adequate sensitivity with greater sample throughput than the larger volume (15 ml).

4.1.4 Recommendations for Analysis

The optimised operational conditions recommended for analysis are either:-

a pH of 7, a 10 ml sample volume, the addition of complexing agent (acetic acid at a concentration of 0.025 M), a 1 ml min^{-1} sample and elution flow rate, a 250 µl eluent volume (2 M nitric acid), and a carrier solution of 0.02 M ammonium hydroxide, or

a pH of 8, a 10 ml sample volume, the addition of complexing agent (tartaric acid at a concentration of 0.025 M), a 1 ml min^{-1} sample and elution flow rate, a 250 µl eluent volume (2M nitric acid), and a carrier solution of 0.02 M ammonium hydroxide.

Similar retention behaviour is observed for the analytes, in the presence of Buxton Mineral Water containing a complexing agent and a corresponding standard, using these conditions. Hence, a calibration graph can be produced from standard solutions and the analyte concentrations present in the sample can be determined from interpolation of the graph. A series of standard solutions were prepared (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, acetic acid, 0.025 M), at concentrations of 0, 1, 10 and 50 µg l^{-1} and adjusted to pH 7. Using the procedure described in section 2.3.2, a 10 ml volume of each standard was processed in the FI system. Buxton Mineral Water was also processed with and without a similar addition of acetic acid. The data were represented graphically, plotting emission intensity (peak area) versus concentration, for each of the analyte in the standard solutions, with and without blank subtraction. The concentrations of the analytes present in Buxton Mineral Water, were interpolated from the graph plotted with blank subtraction. The concentrations of the analytes present in Buxton Mineral Water containing acetic acid, were interpolated from the graph plotted without blank subtraction. This procedure was repeated using the complexing agent tartaric instead of acetic acid. The results obtained are given in Table 4.4 and 4.5. The concentrations obtained, for the analytes present in Buxton Mineral Water containing tartaric acid, are in good agreement with the concentrations determined without complexing agent. The concentrations obtained, for the analytes present in Buxton Mineral Water containing acetic acid, are in poor agreement with the concentrations determined without complexing agent. It is presumed that acetic acid is competing for active sites with the trace analytes. Under the conditions used in the two cases, tartaric acid is the most effective complexing agent.

In summary:

1. The concentrations determined for the analytes present in Buxton Mineral Water containing acetic acid, are in poor agreement with the concentrations determined without

complexing agent. This suggests that acetic acid is not a suitable complexing agent to use with Buxton Mineral Water.

Analyte	Buxton Mineral Water µg/l	Buxton Mineral Water with Tartaric Acid µg/l
Cd	1.8 ± 0.2	2.0 ± 0.1
Co	3.1 ± 0.3	3.1 ± 0.4
Cr	3.8 ± 0.2	3.5 ± 0.2
Cu	4.2 ± 0.1	4.0 ± 0.1
Fe	4.5 ± 0.1	4.3 ± 0.2
Mn	1.0 ± 0.2	0.8 ± 0.1
Ni	2.9 ± 0.3	2.5 ± 0.2
Pb	n.d.	n.d.
V	3.4 ± 0.2	1.9 ± 0.2
Zn	5.9 ± 0.2	5.1 ± 0.3

Table 4.4 The concentrations are determined by the FI microcolumn enrichment technique with ICP-ES detection. Buxton Mineral Water (10 ml), with and without the addition of tartaric acid, was analysed without and with blank subtraction, respectively. The uncertainties are based on 5 determinations.

Analyte	Buxton Mineral Water µg/l	Buxton Mineral Water with Acetic Acid µg/l
Cd	2.5 ± 0.3	1.0 ± 0.1
Co	1.3 ± 0.2	0.4 ± 0.1
Cr	2.4 ± 0.4	1.3 ± 0.1
Cu	4.7 ± 0.1	4.3 ± 0.2
Fe	4.1 ± 0.5	2.9 ± 0.3
Mn	1.0 ± 0.1	0.4 ± 0.1
Ni	2.3 ± 0.1	1.7 ± 0.2
Pb	n.d.	n.d.
V	3.6 ± 0.4	1.5 ± 0.1
Zn	3.7 ± 0.1	2.6 ± 0.2

Table 4.5 The concentrations are determined by the FI microcolumn enrichment technique with ICP-ES detection. Buxton Mineral Water (10 ml), with and without the addition of acetic acid, was analysed without and with blank subtraction, respectively. The uncertainties are based on 5 determinations.

2. The concentrations determined for the analytes present in Buxton Mineral Water containing tartaric acid, are in good agreement with the concentrations determined without complexing agent. This suggests that the complexing agent tartaric acid is an

effective complexing agent. The analytes are maintained in solution in a form activated alumina can retain, and the reaction of the analytes with the column packing material is not inhibited by this complexing agent. It is therefore selected for the determination of the analytes present in Buxton Mineral Water.

4.2 Reservoir Waters

The optimised procedures developed for the determination of trace analytes in Buxton Mineral Water were next applied to the determination of the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in a fresh water sample. Reservoir waters were selected, due to their accessibility and frequency around the Sheffield area. The study focuses on Langsett and Redmires, which were selected for their contrasting composition. Redmires has low colour, turbidity and total organic carbon (i.e. low organic concentration) whereas Langsett has a high organic concentration. It is therefore assumed that the trace analytes will be present as different analyte species in these two reservoirs.

4.2.1 The Influence of Complexing Agents on Retention/Elution

The optimum experimental conditions detailed in section 4.1.4, were utilised to investigate the influence of the complexing agents acetic and tartaric acid, on retention/elution of the analytes present in reservoir waters. Using the procedure detailed in section 2.3.2, a 10 ml volume of the samples (Redmires Reservoir Water), (Redmires, acetic acid, 0.025 M), (Redmires, tartaric acid, 0.025 M) were processed in the FI system. This procedure was repeated for Langsett Reservoir Water. Following the retention step, the second valve in the FI system, which contains the activated alumina microcolumn, is switched to the inject position. Carrier passes through the microcolumn and flushes any remaining matrix analytes from the column. This wash is monitored in an attempt to determine if a proportion of the trace analytes has not been retained. The carrier is monitored subsequently as a comparison, before the

microcolumn is eluted on three consecutive occasions. These five determinations are presented as bar charts in Fig.4.12 and 4.13 for Redmires and Langsett, respectively.

The addition of acetic acid to both Redmires and Langsett Reservoir Waters reduces retention of the analytes, compared to the sample without the addition of complexing agent. Utilising Fe as an example, the proportion of this analyte in the wash/carrier, is notably increased with the addition of acetic acid. Also, the proportion of Fe in the first elution is significantly reduced. This is presumed to be due to acetic acid competition for active sites on activated alumina, therefore incomplete retention is observed. Hence, the complexing agent is inhibiting the reaction of the analytes with the column packing material and is rejected from further study.

The diagrams indicate that the addition of tartrate to both Redmires and Langsett Reservoir Waters, improves retention of the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Utilising Fe as an example, the proportion of this analyte present in the wash/carrier, is significantly reduced with the addition of tartaric acid. Consequently, the proportion of Fe in the first elution is significantly improved. Notable improvement of the proportion, of every trace analyte in the first elution, is also observed for the remaining analytes, except V. It is assumed that the improvement is related to the effectiveness of tartaric acid as a complexing agent. This complexing agent appears to be maintaining the analytes in solution in a form activated alumina can retain. Also, the reaction of the analytes with the column packing material does not appear to be inhibited by the complexing agent.

However, although retention of the analytes has improved with the addition of tartaric acid to both samples, elution of the analytes has not. Utilising Fe as an example, the proportion of this analyte in the second and third elutions, has increased perceptibly, compared to the reservoir samples without complexing agent addition. This is assumed to be due to the retention of Fe-tartrate complexes, which form stronger bonds with alumina and are thus more difficult to elute. The remaining analytes indicate similar elution behaviour, but the effect is not as pronounced. This may be due to analyte retention, *via* the alternative reactive site suggested in section 4.1.1. The bonds thus

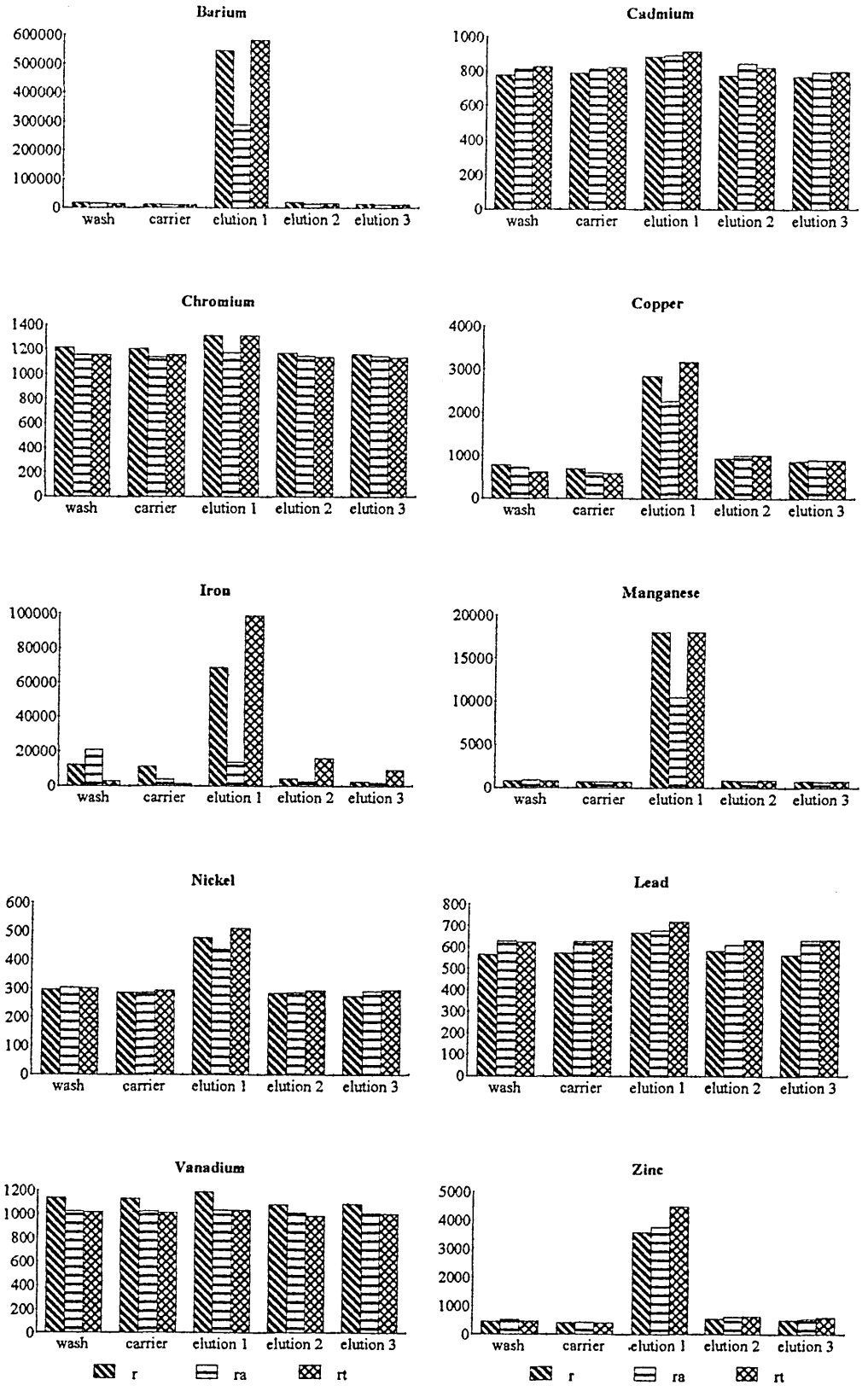


Fig.4.12 Bar chart illustrating the effect of complexing agent on the retention/elution of trace analytes present in Redmires Reservoir. r = Redmires; ra = Redmires + acetic acid; rt = Redmires + tartaric acid.

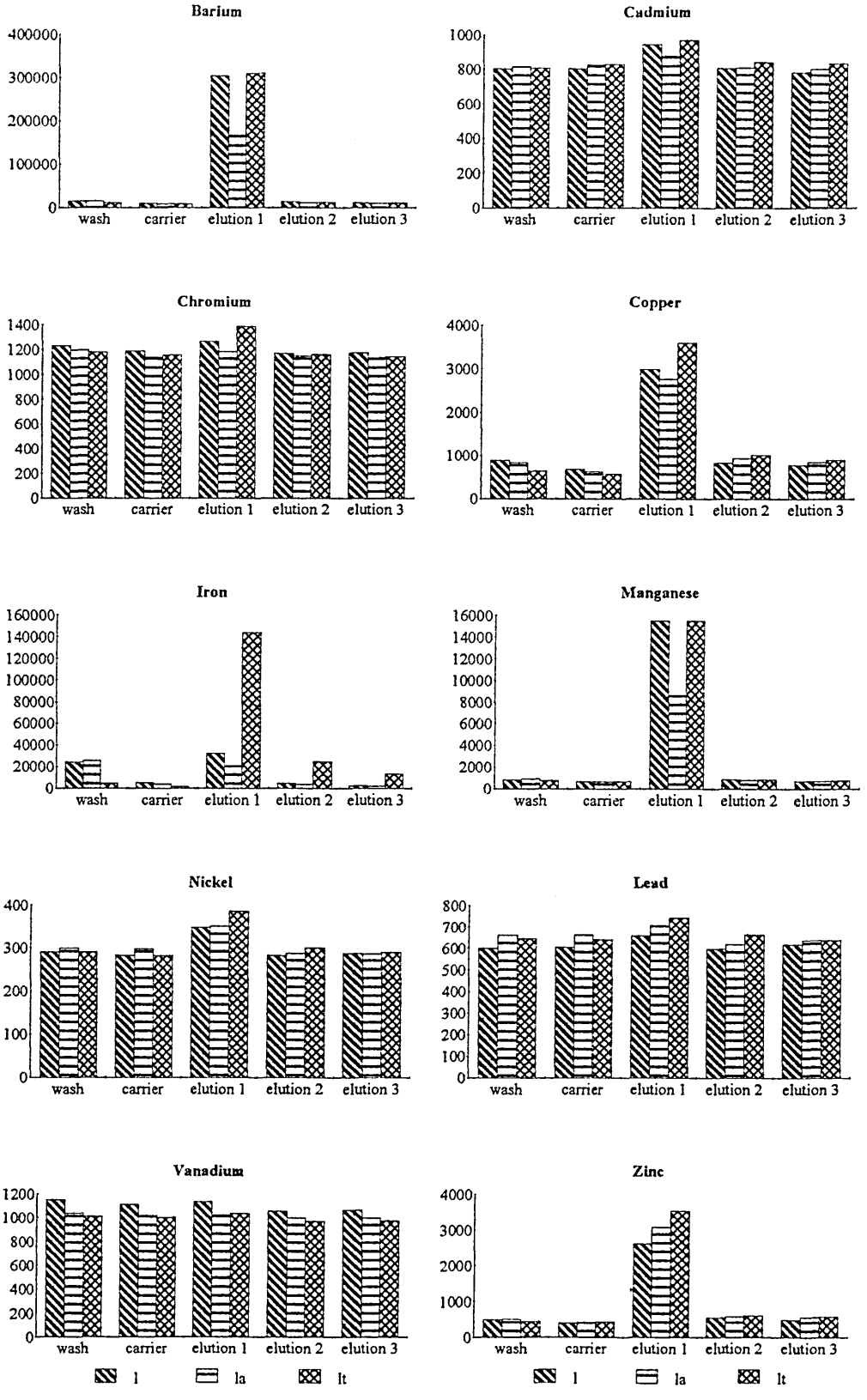


Fig.4.13 Bar chart illustrating the effect of complexing agent on the retention/elution of trace analytes present in Langsett Reservoir. l = Langsett; la = Langsett + acetic acid; lt = Langsett + tartaric acid.

formed are stronger as complete elution is not achieved with one injection of nitric acid.

In summary:

1. The addition of acetic acid to both Redmires and Langsett Reservoir Waters reduces retention of almost every analyte by activated alumina, compared to these samples without complexing agent addition. This suggests that acetic acid is not a suitable complexing agent to use for the trace analysis of Redmires and Langsett Reservoirs.
2. The addition of tartrate to both Redmires and Langsett Reservoir Waters improves retention of almost every analyte by activated alumina, compared to these samples without complexing agent addition. Hence, tartaric acid is a suitable complexing agent to use for the trace analysis of Redmires and Langsett Reservoir Waters
3. Almost all the analytes retained in the presence of the reservoir waters containing tartaric acid, experience inferior elution behaviour, compared with the analytes retained in the presence of the reservoir waters without tartaric acid addition.

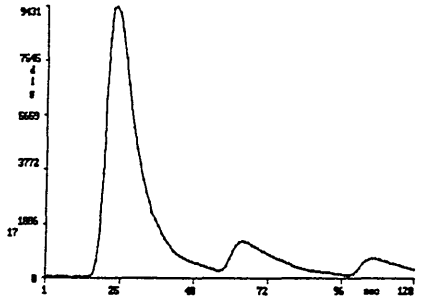
4.2.2 The Effect of Eluent Strength on Analyte Elution

The investigation in section 4.2.1, indicated that complete elution of the analytes could not be achieved with one 250 µl injection of 2 M nitric acid. This is in contrast to the investigations reported in the literature (135, 136, 138, 139) which have suggested that 1-2 M nitric acid is sufficient for complete elution. Therefore the eluent parameters of nature, strength and/or volume needed further investigation to improve elution of the analytes. The effect of eluent strength on analyte elution was thus studied.

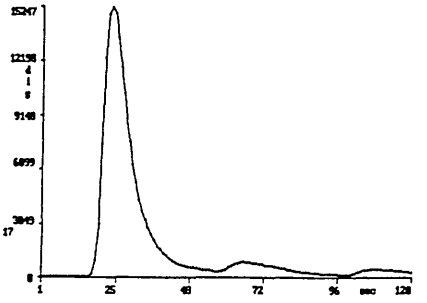
Using the procedure detailed in section 2.3.2, a 10 ml volume of the sample (Redmires or Langsett Reservoir Water, tartaric acid, 0.025 M) adjusted to pH 8, was processed in the FI system. The sample was eluted on three consecutive occasions with either 2, 3 or 5 M nitric acid. Typical examples of the time/elution profiles produced are displayed in Fig.4.14 and 4.15, for Fe and Mn respectively. The plots indicate that analyte elution improves significantly, with the increase in eluent strength from 2-5 M. Taller, narrower peaks are obtained for 5 M nitric acid and virtually complete elution is ensured for one, 250 µl injection. Therefore 5 M HNO_3 was utilised for further

IRON

Redmires Reservoir Water

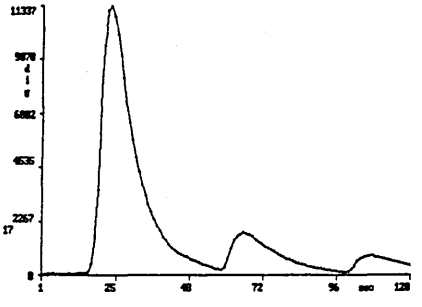


2 M HNO_3

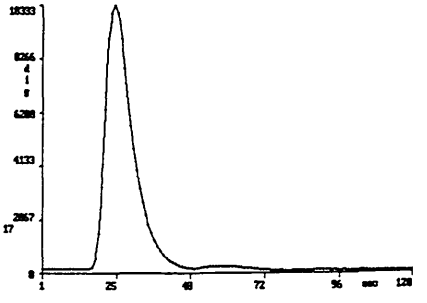


5 M HNO_3

Langsett Reservoir Water



2 M HNO_3

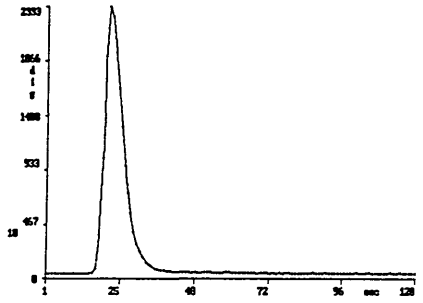


5 M HNO_3

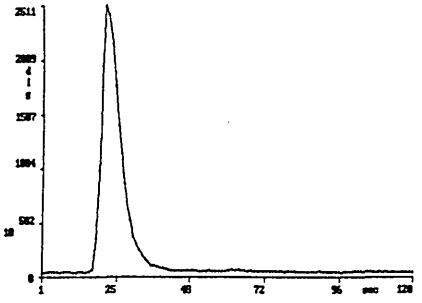
Fig.4.14 The effect of eluent strength on the elution of Iron. The sample volume is 10 ml. The eluent volume is 250 µl. The samples are Redmires and Langsett Reservoir Waters.

MANGANESE

Redmires Reservoir Water

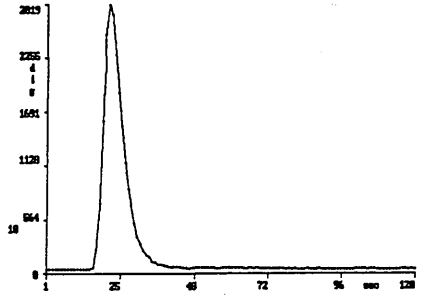


2 M HNO_3

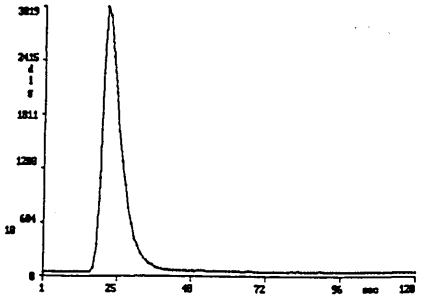


5 M HNO_3

Langsett Reservoir Water



2 M HNO_3



5 M HNO_3

Fig.4.15 The effect of eluent strength on the elution of Manganese. The sample volume is 10 ml. The eluent volume is 250 µl. The samples are Redmires and Langsett Reservoir Waters.

investigations.

In summary:

1. An increase in the strength of eluent (HNO_3), from 2 to 5 M ensures that virtually complete elution is achieved in one injection (250 µl).

4.2.3 Analytical Performance

The limit of detection for each analyte was calculated, using the developed microcolumn enrichment procedure with ICP-ES detection. The results were compared to those obtained by conventional ICP-ES analysis. The relative standard deviation was calculated for each analyte, by both techniques. Hence, a standard solution (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 50 µg l^{-1}) was prepared and adjusted to pH 8. The solution (10 ml), was processed in the FI system ten times. De-ionised water was processed similarly and used as the blank. A multi-element standard solution (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V, Zn, 10 mg l^{-1}) was analysed by conventional ICP-ES. De-ionised water was analysed using the same procedure and utilised as the blank. The calculations and procedures used are detailed in sections 2.4 and 2.5. The values are displayed in Table 4.6 a) and b).

Analyte	ICP-ES LD / µg/l	FI-ICP-ES LD / µg/l
Ba	0.4	0.087
Cd	6.2	0.18
Co	17	0.18
Cr	4.1	0.31
Cu	1.2	0.13
Fe	4	1.2
Mn	3.7	0.038
Ni	13	0.25
Pb	63	1.6
V	2.4	0.052
Zn	6.8	0.31

Analyte	ICP-ES % RSD	FI-ICP-ES % RSD
Ba	0.03	0.26
Cd	0.3	0.49
Co	0.58	0.32
Cr	0.34	0.94
Cu	0.31	0.27
Fe	0.27	0.27
Mn	0.4	0.29
Ni	0.6	0.55
Pb	0.88	0.77
V	0.29	0.62
Zn	0.3	0.46

Table 4.6 a) Limits of Detection (LD) and b) precision (% RSD) for conventional ICP-ES and microcolumn preconcentration with ICP-ES detection.

Utilising the optimum experimental conditions, the retention and elution efficiencies were calculated for each analyte, for the developed microcolumn enrichment

procedure. Maximum retention (100 %) of the analytes is achieved if the entire proportion of the analytes present in solution is completely retained in the retention step. Maximum elution (100 %) of the analytes is achieved if the entire proportion of the analytes retained is completely removed in the first elution. Using the procedure detailed in section 2.3.2, a 250 µl volume of a multi-element standard (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 500 µg l^{-1}, tartaric acid, 0.025 M), adjusted to pH 8 was processed in the FI system. The time/elution profile for each analyte was recorded for the retention step and three consecutive elutions. A 250 µl volume of the standard (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 500 µg l^{-1}, nitric acid, 5 M, tartaric acid, 0.025 M) was also processed in the FI system, without the alumina microcolumn in place. The time/intensity profile for each analyte was recorded. The calculations and procedures used are detailed in sections 2.4 and 2.5. The retention and elution efficiencies are displayed in Table 4.7.

Analyte	Retention Efficiency/%	Elution Efficiency/%
Ba	> 95	96
Cd	> 95	96
Co	> 95	99
Cr	93	94
Cu	> 95	95
Fe	> 95	85
Mn	> 95	100
Ni	> 95	98
Pb	> 95	99
V	95	90
Zn	> 95	95

Table 4.7 Retention and elution efficiencies calculated for the microcolumn enrichment technique. A 250 µl volume of the multi-element standard (Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn, 500 µg/l, tartaric acid, 0.025 M) was utilised.

If only background levels of the analytes are detected following the injection of sample, > 95 % retention efficiency is reported. If incomplete retention is observed following the injection of sample, the area of the peak produced during the retention step is calculated. This area is compared to the area of the transient peak produced following elution, to

determine the retention efficiency. The area of the transient peak produced following the injection of eluent, is compared to the area of the peak produced without the microcolumn in place, to determine the elution efficiency. Peaks may be produced following the second and third elutions, which may account for poor elution efficiency.

4.2.4 Recommendations for Analysis

The operational conditions recommended for analysis are:-
a pH of 8, a 10 ml sample volume, the addition of tartaric acid (0.025 M), a 1 ml min^{-1} sample and elution flow rate, a 250 µl eluent volume (5 M nitric acid) and the carrier solution 0.02 M ammonium hydroxide.

The recommended procedure was applied to the standard reference material SLRS-1. This is a river water sample gathered at a 2 to 3 metre level in the St. Lawrence River, upstream from Quebec City. The water was filtered through 0.45 µm porosity filters, acidified immediately to pH 1.6 and later re-filtered through 0.2 µm porosity filters. The sample was also gamma irradiated. The certified values given are based on the results of determinations by at least two independent methods of analysis. If the concentration of the analytes can be determined successfully in this sample, the viability of the microcolumn enrichment technique with ICP-ES detection will be recognised. Utilising the procedure detailed in section 2.3.2, a volume of 10 ml of the sample (SLRS-1, tartaric acid, 0.025 M) adjusted to pH 8, was processed through activated alumina microcolumns. A series of multi-element standard solutions (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, tartaric acid, 0.025 M) at concentrations of 0, 0.1, 1, 10 and 50 µg l^{-1}, adjusted to pH 8 were processed similarly. The columns were incorporated into the FI system. The analyte species retained were eluted and determined. The data generated were represented graphically, plotting concentration against emission intensity (transient signal area) for each analyte present in the standard solutions. The graph obtained for each analyte was linear. The correlation coefficients determined were: Ba - 0.9999; Cd - 0.9991; Co - 0.9996; Cr - 0.9994; Cu - 0.9999; Fe - 0.9998; Mn - 0.9992; Ni - 0.9983; Pb - 0.9964 and Zn - 0.9967. The concentrations of

the analytes present in SLRS-1, were interpolated from the appropriate graphs. The results are given in Table 4.8, along with the certified values.

The sub $\mu g\ l^{-1}$ concentrations of the analytes Cd, Co and Pb precluded their determination by this technique, using a 10 ml sample volume. Hence the use of a larger sample volume or alternatively ICP-MS detection, may result in their successful determination. The results obtained for the remaining analytes were in good agreement with the certified values. Hence, the concentration of the analytes Ba, Cr, Cu, Fe, Mn, Ni and Zn present in this sample has been successfully determined. Thus activated alumina has been shown to retain the total content of these analytes present in the river water sample SLRS-1. It should be noted however that this sample had been acidified with nitric acid to pH 1.6 immediately after collection. This ensures sample preservation, but may have released trace analytes from stable complexes, such as Cu-fulvate and those adsorbed on colloids (Pb-MnO_2) for example. Hence the determination of the total content of these analytes in real samples collected in the field, may prove more difficult.

Analyte	SLRS-1 Concentration µg/l	SLRS-1 Certified Value µg/l
Ba	21 ± 0.7	22.2 ± 1.7
Cd	n.d.	0.015 ± 0.002
Co	n.d.	0.043 ± 0.001
Cr	0.38 ± 0.08	0.36 ± 0.04
Cu	3.74 ± 0.3	3.58 ± 0.3
Fe	33.3 ± 2.4	31.5 ± 2.1
Mn	1.64 ± 0.17	1.77 ± 0.23
Ni	1.1 ± 0.06	1.07 ± 0.06
Pb	n.d.	0.106 ± 0.011
Zn	1.23 ± 0.3	1.34 ± 0.2

Table 4.8 Results obtained for SLRS-1. The experimental conditions used are detailed in the text. The certified concentrations are also given for this reference sample. (n.d. = not detected). The uncertainties represent n=5 determinations.

4.3 Conclusions

1. A technique for the determination of the trace analytes Ba, Cd, Co, Cr, Cu, Fe Mn, Ni, Pb, V and Zn present in Buxton Mineral Water and Redmires and Langsett Reservoir

Waters, using a microcolumn of activated alumina in a FI-ICP-ES system has been developed.

2. The key experimental parameters sample pH, nature of complexing agent and eluent strength were investigated and optimised.

3. The capability of the technique for on-line enrichment of the analytes was demonstrated. The limit of detection determined for Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn was 0.087, 0.18, 0.18, 0.31, 0.13, 1.2, 0.037, 0.25, 1.6, 0.052 and 0.31 μg l^{-1} respectively, for a 10 ml sample volume. The precision (RSD) was less than 1 % at the 50 μg l^{-1} level.

4. The technique was successfully applied to the determination of these analytes present in a certified reference material (SLRS-1).

5 Microcolumn Field Sampling

5.1 Introduction

The basic objective of sampling is the collection of a sample whose composition accurately represents the composition of the bulk water from which it is taken. This is achieved from careful consideration of the appropriate factors at each stage of the sampling process. Hence, in order that a sample has a composition which reflects temporal and spatial variations within a water body, the location, the times and the frequency of sampling must be taken into account. In order that a sample, analysed subsequent to sample collection, maintains its integrity, during transportation and storage, procedures and conditions should be appropriately selected. These general features have been considered previously (21,165-167), and are discussed in greater detail below.

5.1.1 Defining the Required Information

The quality parameters required must be precisely defined so that appropriate sampling and analytical techniques can be selected. Many analytes in water can exist as a variety of different chemical and physical species. For example chromium may be present as Cr(III) as the species $Cr(OH)_4^-$, and Cr(VI) as the species CrO_4^{2-}. Hence, whenever the possibility of different species of the same analyte arises, the species of interest must be precisely defined so that suitable methods of analysis can be selected.

5.1.2 Sampling Procedure

An exhaustive sampling procedure is essential in water analysis, due to potential variations in the water to be sampled. For example, spatial variations due to vertical thermal stratification are encountered in lake, reservoir waters and open ocean seawater. Hence, the depth at which a sample is taken, could have a significant effect on the sample composition. Undissolved materials are distributed according to their density in water and chemical/biological activity may be different at particular locations of the water system, changing the composition. Tributary inputs into rivers can have a significant

effect. The river may not be completely mixed until many miles downstream. A variation in the flow of the river, may change the results obtained on subsequent sampling occasions. Hence, the sampling location, frequency of sampling and number of samples taken should reflect the information required.

5.1.3 Sample Pre-treatment and Preservation

The samples are filtered in the field, generally through a membrane filter of pore size 0.45 μm, following their representative collection. This separates analytes present in the dissolved fraction, from analytes present in suspended matter. It is important to filter the sample immediately after collection, as changes can occur in the proportions of these analyte species (168). The total recoverable concentration can also be determined, usually following an appropriate digestion procedure. To ensure sample integrity is maintained, applicable preservation procedures must be implemented. The accepted method for preserving water samples with respect to trace analytes, involves the addition of 1% nitric acid. Acidification aids in the prevention of hydrolysis, oxidation, precipitation and coprecipitation of the analytes, reduces the possibility of chemisorption of the analytes to container walls, and inhibits biological activity. A schematic diagram summarising water sample preparation is shown in Fig.5.1.

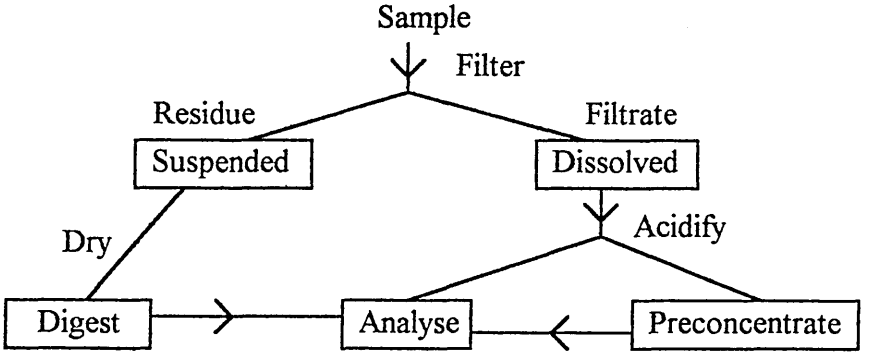


Fig.5.1 Schematic diagram for sample preparation. Reference 21.

5.1.4 Sample Storage and Transportation

The samples are transferred to pre-cleaned, inert containers, such as polyethylene or polypropylene, prior to transportation. It is essential to avoid extreme conditions

whilst transporting the samples, such as excessively high or low temperatures, to maintain sample integrity. Storage between 0-4 ^{o}C reduces the possibility of loss or change of labile analytes and deep freezing is also an option.

5.1.5 Sources of Contamination

Contamination is the addition of analyte into the sample, from other sources. Possible sources include: the sample collection apparatus, storage containers, chemical reagents, containers used for analysis, the laboratory environment and the analyst. It is imperative that contamination of the sample is avoided.

5.1.6 Water Analysis

The direct analysis of water appears to be the simplest application of ICP-ES. However, the concentration of the analytes of interest in these samples, often precludes their determination by this technique. It is frequently necessary to employ a preconcentration procedure to extend the capability of the analytical technique. Current methods utilised for enrichment are evaporation, solvent extraction, coprecipitation and ion exchange. Reduction in volume by evaporation is the primary non-selective method, however volatile analytes may be lost using this procedure. Solvent extraction, coprecipitation and ion exchange are particularly valuable, as they can be used to selectively concentrate the trace analytes in the sample, whilst rejecting the major constituents. The former techniques require more complicated sample handling procedures and greater reagent consumption than the latter.

In 1968, Riley and Taylor utilised the chelating resin Chelex-100 to preconcentrate the trace analytes Cd, Co, Cu, Ni and Zn from water samples (169). It was necessary to pass up to 10 L of water through the resin column, to adequately enrich the sample prior to determination. Experiments indicated that the analytes were quantitatively recovered. However, subsequent investigation by Florence and Batley (156), indicated that a significant proportion of the Cu, Pb, Cd and Zn, was present in a form that was not retained by Chelex-100. Trace analytes in water samples are not

entirely present in the free ionic form. Colloidal, suspended and/or complexed forms of the analytes may also be present. Hence, the use of standard solutions to determine recovery of the analytes from natural waters, may bear no relation to the analyte species actually present in the original sample. It was suggested that a major proportion of the trace analyte not retained, was adsorbed on, or occluded in, organic or inorganic colloidal particles. Batley and Florence proposed a scheme for the classification of trace analyte species in natural waters (170). The ability of Chelex-100 to retain labile fractions from bound fractions, was the basis for their classification. This is depicted in Fig.5.2. This scheme was utilised for the determination of Cd, Pb and Cu in natural water samples. Review articles concerning the determination of individual physico-chemical species of analyte in water samples, are available (163, 171). Sampling and analysis procedures, for the determination of trace analytes in natural waters are detailed (172-177).

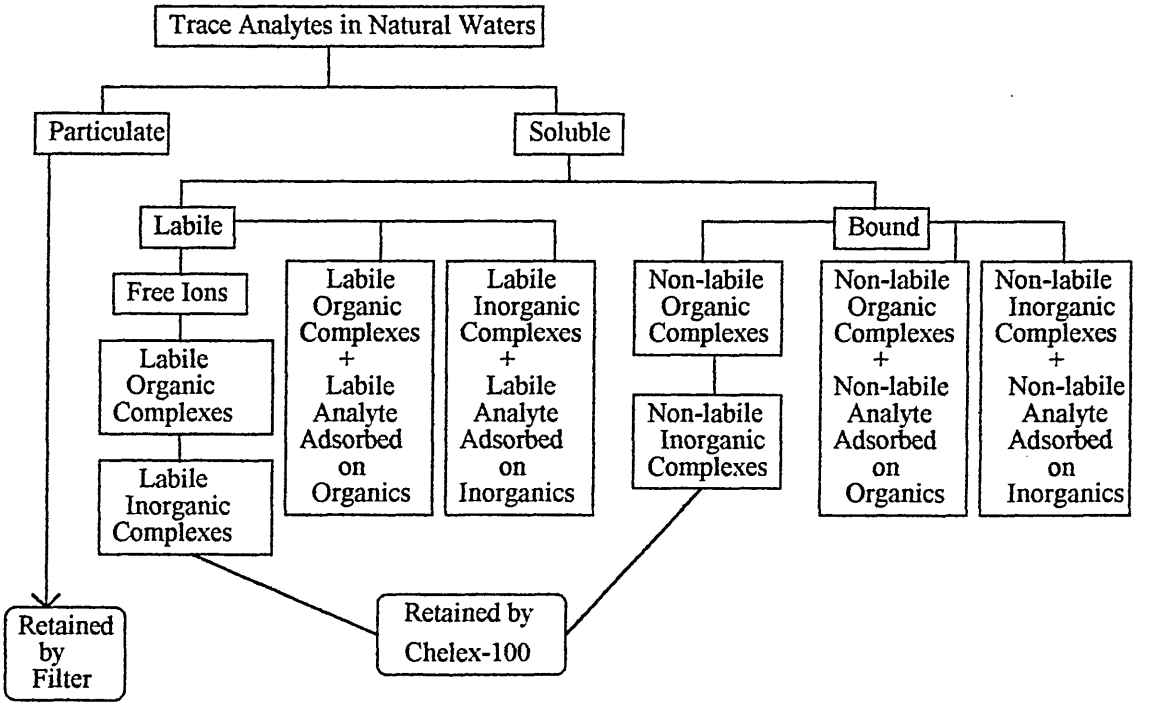


Fig.5.2 Classification of analyte species in natural waters. Reference 170.

In summary the sampling and analysis of water samples is an exacting task, which requires cautious consideration. Many analytes of interest are present at concentrations which preclude their direct determination by ICP-ES. Any preconcentration procedure selected prior to analysis, may also have limitations, which must be fully investigated before accurate results can be obtained. Hence, the conventional approach to sampling water, involves the collection and storage of relatively large volumes of sample. However, problems can occur when these samples are bottled, stored and transported. Changes in analyte concentration can arise with ease, as a result of sorption processes between the analytes, container walls and suspended particles. Chemical changes such as precipitation, oxidation and/or colloidal formation are possible and biological activity can contribute to changes in sample composition. Sample preservation techniques currently recommended for transportation and storage, involve the filtration of the sample in the field, through 0.45 μm membrane filters and acidification of the filtrate. This ensures the preservation of many trace analytes, but is only suitable for the determination of dissolved/filterable species of the analytes rather than suspended or total species (165-168). Suspended species are collected on the filter, digested and analysed by conventional ICP-ES. Total recoverable species are analysed by conventional ICP-ES without filtration of the sample, usually following an appropriate digestion procedure .

A field sampling technique is under development, which will provide preconcentration and high sample integrity. The microcolumns of activated alumina are utilised as new multi-element field sampling tools. Water samples are collected and processed at the sampling site by passage through alumina microcolumns, effectively immobilising desired analytes. The microcolumns are then returned to the laboratory and incorporated into a flow injection system. The retained species are eluted and determined by ICP-ES. This field sampling technique has been successfully utilised for speciation measurements by Wei and McLeod (178) for the determination of inorganic and methylmercury, and by Cox and McLeod (179) for the determination of Cr(III) and Cr(VI), in natural waters.

Initial investigations utilise a simulated field sampling procedure based in the laboratory, which incorporates the microcolumn enrichment technique developed in Chapter 4. This investigation shows that the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in Buxton Mineral Water and Redmires and Langsett Reservoir Waters, can be successfully immobilised on activated alumina microcolumns and subsequently eluted and determined. For validity of measurement, recovery of these analytes from a spiked Buxton Mineral Water sample and analysis of Redmires and Langsett by conventional ICP-ES and ICP-MS will be performed. The successful determination of the total analyte content in the above samples will clarify that field sampling is viable.

Field sampling studies will then be performed at the field sampling site. Samples will be taken from Redmires and Langsett Reservoirs and immediately processed through activated alumina microcolumns to attempt to immobilise the total content of the analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in them. This will ensure sample integrity. The microcolumns will be returned to the laboratory and incorporated into a FI system. The analytes will be eluted and determined by ICP-ES. For validity of measurement a proportion of the samples will be preserved in 1 % nitric acid and analysed by conventional ICP-ES/ICP-MS. The successful determination of the total analyte content in these samples will indicate that activated alumina microcolumns can be used as new multi-element field sampling devices. The stability of the analytes retained on the column from the presence of Redmires and Langsett Reservoir Waters and a multi-element standard solution, over a one month time period will be investigated. The field sampling microcolumn enrichment technique utilising ICP-MS detection will be applied to the determination of Cr, Mo and U in seawater samples, to indicate further capabilities of this technique and possibilities for future work.

5.2 Simulated Field Sampling Applications

5.2.1 Buxton Mineral Water

The simulated field sampling microcolumn enrichment procedure with ICP-ES detection was applied to the determination of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn in Buxton Mineral Water. Recovery experiments were also carried out by spiking Buxton Mineral Water at the 5 $\mu g\ l^{-1}$ level with these trace analytes. This was carried out to ensure that measurements obtained by this procedure were valid. Hence, utilising the procedure detailed in section 2.6, a volume of 10 ml of the samples (Buxton Mineral Water, multi-element solution spike, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, 5 $\mu g\ l^{-1}$, tartaric acid, 0.025 M) and (Buxton Mineral Water, tartaric acid, 0.025 M), adjusted to pH 8, were processed through alumina microcolumns. This was carried out off-line, in the laboratory using a peristaltic pump. A series of standard solutions (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, tartaric acid, 0.025 M) at concentrations of 0, 1, 5 and 10 $\mu g\ l^{-1}$, were processed similarly. The columns were incorporated into the FI system. The retained analyte species were eluted and determined. The data generated were represented graphically, plotting concentration against emission intensity (transient signal area) for each analyte present in the standard solutions. The graph obtained for each analyte was linear. The correlation coefficients determined were: Cd - 0.9999; Co - 0.9966; Cr - 0.9999; Cu - 0.9999; Fe - 0.9998; Mn - 0.9995; Ni - 0.9999; Pb - 0.9968; V - 0.9994 and Zn - 0.9980. The concentrations of the analytes present in the samples, were interpolated from the appropriate graphs. The results obtained are displayed in Table 5.1. Good recoveries (94-106 %) were obtained for Cd, Cr, Cu, Mn, Ni, V and Zn. The recoveries for Co, Pb and Fe were lower (90, 88 and 84 % respectively). This could be due to one or more of the following possibilities. The concentration determined in this study (5 $\mu g\ l^{-1}$) was close to the detection capability of this technique for Pb which is 1 $\mu g\ l^{-1}$, hence the variability was poor and affected the recovery determined. The elution efficiency for the analyte Fe is 85 %, which accounts for the low recovery of this analyte. Poor instrument variability for low Co concentrations had a detrimental affect on the recovery of this analyte. However, it can be concluded that the

Analyte	Buxton Mineral Water µg/l	Buxton Mineral Water 5 µg/l spike	Recovery
Cd	1.9 ± 0.2	5.2 ± 0.2	104%
Co	2.7 ± 0.5	4.5 ± 0.4	90%
Cr	3.4 ± 0.1	5.3 ± 0.2	106%
Cu	4.6 ± 0.1	5.1 ± 0.1	102%
Fe	4.7 ± 0.1	4.2 ± 0.2	84%
Mn	0.6 ± 0.1	4.9 ± 0.2	98%
Ni	2.3 ± 0.1	4.7 ± 0.2	94%
Pb	n.d.	4.4 ± 0.8	88%
V	3.6 ± 0.3	5.0 ± 0.2	100%
Zn	5.6 ± 0.2	5.1 ± 0.1	102%

Table 5.1 Results for Buxton Mineral Water and Buxton Mineral Water spiked at the 5 µg/l level. See text for experimental conditions. (n.d. = not detected). The uncertainties represent n=5 determinations.

microcolumn enrichment technique with ICP-ES detection is able to determine the total content of the analytes Cd, Cr, Cu, Mn, Ni, V and Zn present in Buxton Mineral Water.

5.2.2 Redmires and Langsett Reservoir Waters

The simulated field sampling microcolumn enrichment procedure was applied to the determination of the trace analytes Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn present in Langsett and Redmires Reservoir Water. This sample was not filtered before analysis in an attempt to clarify whether or not activated alumina could retain the total concentration of these trace analytes in a real water sample. Utilising the procedure detailed in section 2.6, a 10 ml volume of the sample (Redmires or Langsett Reservoir Water, tartaric acid, 0.025 M), adjusted to pH 8 was processed through alumina microcolumns. This was carried out off-line, in the laboratory using a peristaltic pump. A series of multi-element standard solutions (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, tartaric acid, 0.025 M) at concentrations of 0, 1, 10, 50, 100, 1000 µg l^{-1}, were processed similarly. The microcolumns were incorporated into the FI system. The analyte species retained were eluted and determined. Calibration graphs were produced for the standard solutions, plotting concentration against emission intensity (transient signal area), for each analyte present. The graph obtained for each analyte was linear.

The correlation coefficients determined were: Ba - 0.9999; Cd - 0.9999; Co - 0.9966; Cr - 0.9999; Cu - 0.9997; Fe - 0.9983; Mn - 0.9999; Ni - 0.9999; Pb - 0.9995; V - 0.9999 and Zn - 0.9988. The analyte concentrations present in the samples were interpolated from the appropriate graphs. The analysis of the samples was also carried out by conventional ICP-ES and ICP-MS without the use of microcolumn preconcentration for validity of measurement. The results obtained are given in Table 5.2 and 5.3.

Analyte	Redmires ICP-ES µg/l	Redmires FI-ICP-ES µg/l	Redmires ICP-MS µg/l
Ba	43 ± 2	39 ± 1	39 ± 2.2
Cd	n.d.	0.81 ± 0.1	0.46 ± 0.24
Co	n.d.	1.5 ± 0.4	1.7 ± 0.2
Cr	n.d.	1.3 ± 0.1	0.92 ± 0.5
Cu	13 ± 2	13 ± 1	13 ± 1
Fe	710 ± 5	650 ± 3	
Mn	180 ± 4	190 ± 1	
Ni	n.d.	9.2 ± 0.2	11 ± 1
Pb	n.d.	9.2 ± 1.1	8.9 ± 0.4
V	n.d.	0.7 ± 0.1	1.1 ± 0.2
Zn	56 ± 3	55 ± 1	51 ± 1

Analyte	Langsett ICP-ES µg/l	Langsett FI-ICP-ES µg/l	Langsett ICP-MS µg/l
Ba	23 ± 1	21 ± 1	19 ± 2
Cd	n.d.	0.8 ± 0.1	0.3 ± 0.1
Co	n.d.	1.5 ± 0.3	1.6 ± 0.2
Cr	n.d.	2.7 ± 0.1	2 ± 0.4
Cu	29 ± 1	28 ± 1	23 ± 1
Fe	1020 ± 7	930 ± 1	
Mn	150 ± 2	150 ± 1	
Ni	n.d.	3.6 ± 0.1	4.3 ± 0.7
Pb	n.d.	6.8 ± 0.9	5.1 ± 0.3
V	n.d.	1.1 ± 0.1	1.4 ± 0.2
Zn	46 ± 2	43 ± 1	39 ± 2

Table 5.2 and 5.3 The results for Redmires and Langsett Reservoir Waters using the simulated field sampling microcolumn enrichment technique, conventional ICP-ES and ICP-MS. The experimental conditions used are detailed in the text. (n.d. = not detected.). The uncertainties represent n=5.

The results show reasonable agreement between the three techniques. For example the result for the analyte Cu in Redmires Reservoir Water, by FI-ICP-ES, ICP-ES and ICP-MS is 13 $\mu g\ l^{-1}$. The result showing the worst agreement is for the analyte Cd in Redmires, with values of 0.81 and 0.46 by FI-ICP-ES and ICP-MS respectively. Unfortunately the ICP-MS determinations were carried out after four weeks of sample storage at 4 ^{o}C with the samples acidified for preservation. This may have resulted in some changes, particularly for the two very low concentration analytes Cd and V. These two analytes show the worst agreement as might be expected. The remaining analytes show good agreement. However the experiments carried out with the field sampling microcolumn enrichment technique and ICP-ES detection, suggests that the total content of the analytes Ba, Cd, Co, Cr, Cu, Mn, Fe Ni, Pb, V and Zn present in Buxton Mineral, Redmires and Langsett Reservoir Water can be determined. This was achieved due to the successful immobilisation of the analytes on activated alumina and subsequent elution.

5.3 Field Sampling Applications

5.3.1 Redmires and Langsett Reservoir Waters

The results reported in section 5.2 have demonstrated the potential for using activated alumina microcolumns as tools for sample collection in the field. Field sampling studies were therefore performed in an attempt to immobilise the trace analytes present in reservoir water samples on activated alumina microcolumns at the sampling site. If the determination of the trace analytes in these samples, by the field sampling microcolumn enrichment technique with ICP-ES detection, indicates equivalence with conventional analysis, a new approach to the sampling waters has been developed.

Utilising the procedure detailed in section 2.6, a sample was collected at Redmires Reservoir. Tartaric acid was added to a concentration of 0.025 M and the pH was adjusted to 8. This sample was processed through alumina microcolumns off-line, at the sampling site using a peristaltic pump for the retention of desired analytes. The columns were returned to the laboratory and incorporated into a FI system. The retained

analytes were eluted with nitric acid and determined by ICP-ES. The calibration graphs for these analytes showed good linearity with correlation coefficients of: Ba - 0.9997; Cd - 0.9999; Co - 0.9997; Cr - 0.9998; Cu - 0.9999; Fe - 0.9999; Mn - 0.9999; Ni - 0.9998; Pb - 0.9999; V - 0.9998; and Zn - 0.9998 over the concentration range 0-1000 $\mu g\ l^{-1}$. A proportion of the sample was preserved by the addition of nitric acid and determined by conventional ICP-ES and ICP-MS for validity of measurement. The results given in Table 5.4 indicate reasonable equivalence between the analytes determined by the field sampling microcolumn FI-ICP-ES technique and direct analysis by ICP-ES and ICP-MS.

Analyte	ICP-ES µg/l	FI-ICP-ES µg/l	ICP-MS µg/l
Ba	36.3 ± 0.2	36.1 ± 0.7	33.6 ± 2.7
			32.8 ± 2.3
Cd	n.d.	0.41 ± 0.09	0.48 ± 0.29
Co	n.d.	1.8 ± 0.4	1.6 ± 0.1
Cr	n.d.	0.35 ± 0.02	0.9 ± 0.6
			0.9 ± 0.6
Cu	3.7 ± 0.2	4.1 ± 0.14	2.9 ± 0.6
			3.0 ± 0.4
Fe	437 ± 6	391 ± 6	
Mn	141 ± 3	139 ± 3	
Ni	n.d.	5.7 ± 0.4	7.3 ± 1.9
			6.9 ± 0.9
Pb	n.d.	4.9 ± 0.9	4.3 ± 0.4
			4.5 ± 0.3
			4.6 ± 0.3
V	n.d.	1.1 ± 0.25	1.9 ± 0.1
Zn	35.1 ± 2.3	34.2 ± 5.7	33.8 ± 2.6
			33.6 ± 1.4

Table 5.4 The concentrations are determined by conventional ICP-ES, ICP-MS and the field sampling microcolumn preconcentration technique. See text for experimental details. (n.d. = not detected). The uncertainties represent n=10 determinations.

The results for the analytes Ba, Cd, Co, Fe, Mn, Ni, Pb and Zn showed good agreement by the microcolumn enrichment technique with FI-ICP-ES detection, direct ICP-ES and direct ICP-MS. This indicates that the total content of these analytes present in Redmires Reservoir Water was determined using the field sampling microcolumn

enrichment technique with ICP-ES detection. The uncertainties (represented by 95 % confidence limits), for the analytes Cd, Cr, Cu and Ni were fairly large however in comparison to the result calculated by ICP-MS. It is therefore not clearly known if the total concentration of Cd, Cr, Cu and Ni has been determined by the microcolumn enrichment technique with FI-ICP-ES detection. However, Cu has been previously determined in Redmires Reservoir Water (see Table 5.3) and was found to be 13 $\mu g\ l^{-1}$ by this technique, direct ICP-ES and direct ICP-MS, and hence it is possible that the total concentration of Cu has been determined. Good recoveries were obtained for the remaining analytes from Buxton Mineral Water (see Table 5.2) and hence it is assumed that the total concentration of Cd, Cr and Ni has been determined in this sample. It appears that the total concentration of V can not be determined in Redmires Reservoir Water by the microcolumn enrichment technique with ICP-ES detection. This is most likely due to incomplete retention and elution of V (see Table 4.7).

The field sampling procedure was repeated on a separate occasion. A second sample was collected at Redmires Reservoir, and a sample from Langsett Reservoir was taken also. Tartaric acid was added to a concentration of 0.025M and the pH was adjusted to 8. This sample was processed through alumina microcolumns for the retention of desired analytes off-line at the field sampling site (see section 2.6). The columns were returned to the laboratory and incorporated into a FI system. The retained analytes were eluted with nitric acid and determined by ICP-ES. The certified reference material SLRS-2 was analysed utilising this procedure also. The calibration graphs for the analytes showed good linearity with correlation coefficients of: Ba - 0.9999; Cd - 0.9999; Co - 0.9998; Cr - 0.9997; Cu - 0.9999; Fe - 0.9999; Mn - 0.9999; Ni - 0.9999; Pb - 0.9999; V - 0.9995; and Zn - 0.9999 over the concentration range 0-1000 $\mu g\ l^{-1}$. A proportion of the sample was preserved by the addition of nitric acid and determined by conventional ICP-ES for validity of measurement. The results given in Table 5.5, 5.6 and 5.7 indicate reasonable equivalence between the analytes determined by the field sampling microcolumn FI-ICP-ES technique and direct analysis by ICP-ES.

The results obtained for Ba, Cr, Cu, Fe, Mn, Ni, V and Zn present in SLRS-2, by the field sampling microcolumn enrichment technique with FI-ICP-ES detection showed reasonable agreement with the certified values. This sample was utilised as another method of validity of measurement. The very low concentrations of Cd, Co, Pb present in SLRS-2, precluded their determination by the microcolumn enrichment FI-ICP-ES technique using a 10 ml sample volume. The use of a larger sample volume or ICP-MS detection may facilitate the successful determination of these analytes.

Analyte	ICP-ES SLRS-2 µg/l	FI-ICP-ES SLRS-2 µg/l	SLRS-2 Certified Value µg/l
Ba	13.8 ± 0.2	13.6 ± 0.1	13.8 ± 0.3
Cd	n.d	n.d.	0.028 ± 0.004
Co	n.d	n.d.	0.063 ± 0.012
Cr	n.d	0.53 ± 0.07	0.45 ± 0.07
Cu	2.65 ± 0.3	2.86 ± 0.06	2.76 ± 0.17
Fe	128 ± 2	146 ± 1	129 ± 7
Mn	9.37 ± 1.4	9.78 ± 0.36	10.1 ± 0.3
Ni	n.d.	1.2 ± 0.1	1.03 ± 0.1
Pb	n.d.	n.d.	0.129 ± 0.011
V	n.d.	0.22 ± 0.05	0.25 ± 0.06
Zn	3.15 ± 1.4	3.12 ± 0.09	3.33 ± 0.15

Analyte	ICP-ES Redmires µg/l	FI-ICP-ES Redmires µg/l
Ba	39 ± 1	38 ± 1
Cd	n.d	0.99 ± 0.06
Co	n.d	0.62 ± 0.22
Cr	n.d	0.56 ± 0.04
Cu	2.9 ± 0.3	2.8 ± 0.2
Fe	350 ± 3	320 ± 2
Mn	120 ± 2	120 ± 2
Ni	n.d	7.9 ± 0.2
Pb	n.d.	5.2 ± 0.4
V	n.d.	0.14 ± 0.01
Zn	33 ± 2	34 ± 1

Analyte	ICP-ES Langsett µg/l	FI-ICP-ES Langsett µg/l
Ba	18 ± 1	18 ± 1
Cd	n.d	1.2 ± 0.2
Co	n.d	0.23 ± 0.05
Cr	n.d	0.91 ± 0.08
Cu	12 ± 1	13 ± 1
Fe	620 ± 4	530 ± 2
Mn	110 ± 2	110 ± 1
Ni	n.d.	6.7 ± 0.1
Pb	n.d.	5.0 ± 0.3
V	n.d.	0.20 ± 0.03
Zn	33 ± 2	34 ± 1

Table 5.5, 5.6, and 5.7 Results for SLRS-2, Redmires and Langsett Reservoir. See Text for Experimental Conditions. (n.d. = not detected). The uncertainties represent n=5 determinations.

The analytes Ba, Cu, Mn, V and Zn were determined within the certified limits. Hence the total content of these analytes present in SLRS-2 was determined by the field sampling enrichment FI-ICP-ES technique. The exceptions were the analytes Cr, Ni and Fe. All three indicated concentrations greater than expected by this technique.

The very low concentrations of the analytes Cd, Co, Cr, Ni, Pb and V present in Redmires and Langsett Reservoir Waters precluded their determination by direct analysis. However, the results obtained by the microcolumn enrichment FI-ICP-ES technique and conventional ICP-ES, for the analytes Ba, Cu, Mn, Zn indicated reasonable agreement (92-100 % recovery). The exception was the analyte Fe. The concentrations determined by conventional ICP-ES were greater than those determined by the enrichment FI-ICP-ES technique. Activated alumina was able to recover 91 % of the Fe from the Redmires sample and 85 % from the Langsett sample. This was thought to be due to the low elution efficiency experienced for this analyte (85 %) and/or the possibility that certain species of Fe were not retained by activated alumina.

It is therefore concluded that activated alumina microcolumns can be utilised as new field sampling devices. The total content of the analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn present in Buxton, Redmires and Langsett water samples can be determined by the field sampling microcolumn enrichment technique with ICP-ES detection.

5.4 Stability Trial

It has been established, with the possible exceptions of Fe and V, that the total concentration of the analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn present in selected mineral, river and reservoir water samples, may be determined by the alumina microcolumn enrichment technique with FI-ICP-ES detection. Furthermore alumina microcolumns have been utilised in the field, to immediately immobilise and hence stabilise the trace analytes on collection of the sample. However the stability of the analytes, retained on activated alumina columns, on storage has yet to be determined. This is important, as it will enable a recommended time period to be suggested, between

sampling time and time of analysis. For example, if samples are taken from rivers and reservoirs around the country, and retained on alumina microcolumns over a week period, it will be useful to determine if the analytes can be successfully recovered the following week.

Utilising the procedure detailed in section 2.6, a 10 ml volume of sample (Redmires Reservoir Water, tartaric acid 0.025 M) adjusted to pH 8, was processed through twelve alumina microcolumns. This procedure was repeated for Langsett Reservoir Water and a multi-element standard solution (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, 10 $\mu g\ l^{-1}$, tartaric acid 0.025 M). Three columns of each sample type were eluted after 1 hour, three after 1 day, three following 1 week and three following 1 month. The microcolumns were stored during this time period at room temperature in the laboratory. A series of standard solutions were prepared (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn), at concentrations of 0, 1, 10, 100 and 1000 $\mu g\ l^{-1}$ and processed on each of the above occasions. Calibration graphs were plotted for each analyte present in the standard solutions. The calibration graphs for the analytes showed good linearity with correlation coefficients between 0.9990-0.9999 over the concentration range 0-1000 $\mu g\ l^{-1}$. The concentrations of the analytes present in the sample were interpolated from the appropriate graphs. The results are displayed in Figs. 5.3, 5.4 and 5.5. The diagrams indicate significant loss of the analytes Ba, Cd, Co, Cr, Fe, Mn, Pb, V and Zn, from all three matrices, during the 1 month time period. Hence it is concluded that further experimentation is required before a time period can be recommended between sampling time and time of analysis. The percentage losses are given in Table 5.8.

Analyte	Percentage Loss After 1 Day	Percentage Loss After 1 week	Percentage Loss After 1 Month
Ba	8-10 %	13-16 %	17-19 %
Cd	6-9 %	17-20 %	22-24 %
Co	10-12 %	21-23 %	24-27 %
Cr	27-28 %	34-36 %	39-40 %
Mn	10-13 %	19-20 %	21-23 %
Pb	1-2 %	10-13 %	15-18 %
Zn	12-14 %	19-22 %	42-45 %

Table 5.8 Stability Trial Losses.

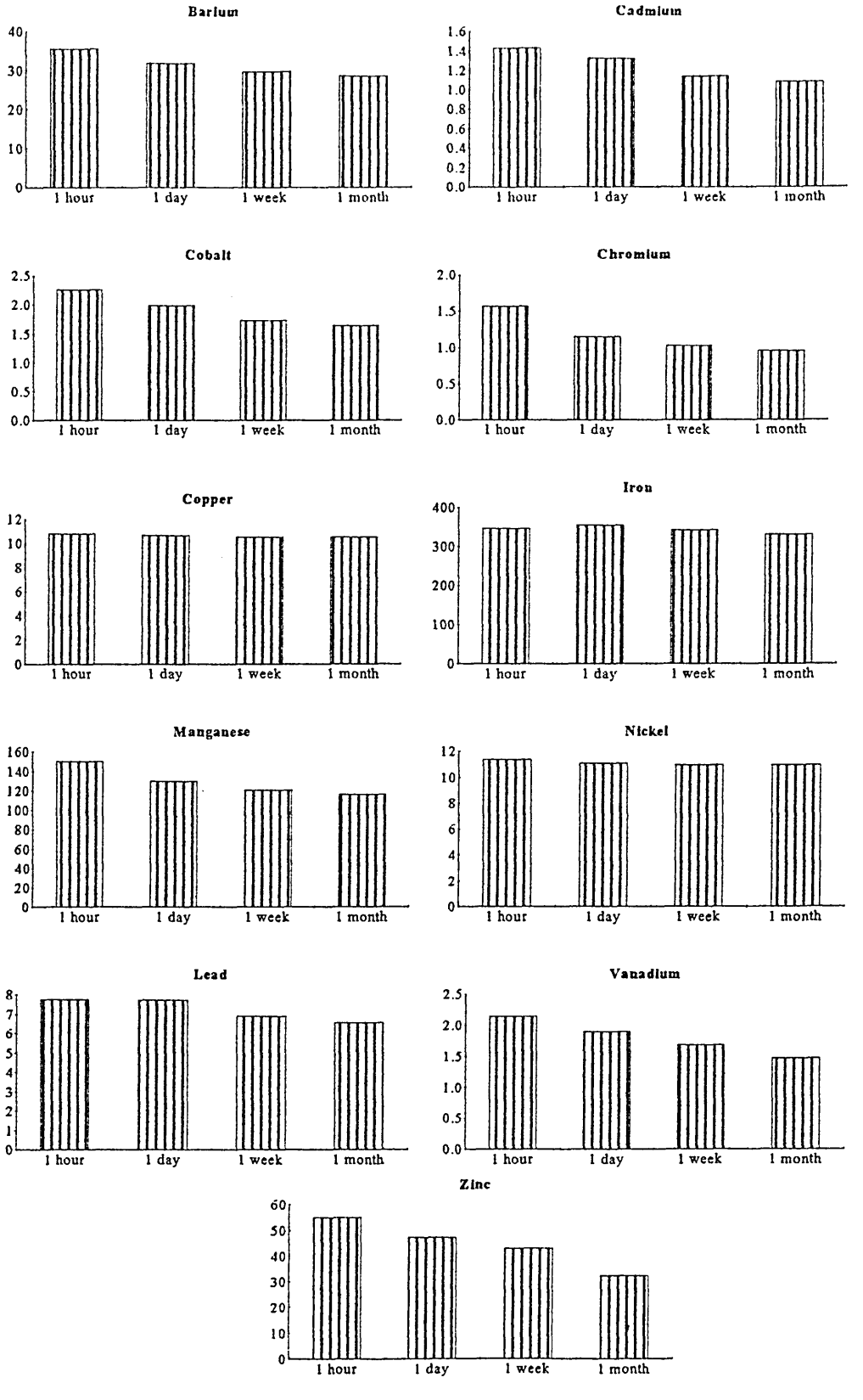


Fig. 5.3 The diagram represents the results observed for a stability trial. A sample collected from Redmires Reservoir was processed through alumina microcolumns. A proportion of these were eluted and the analyte concentrations determined in µg/l (y axis), following 1 hour, 1 day, 1 week and 1 month.

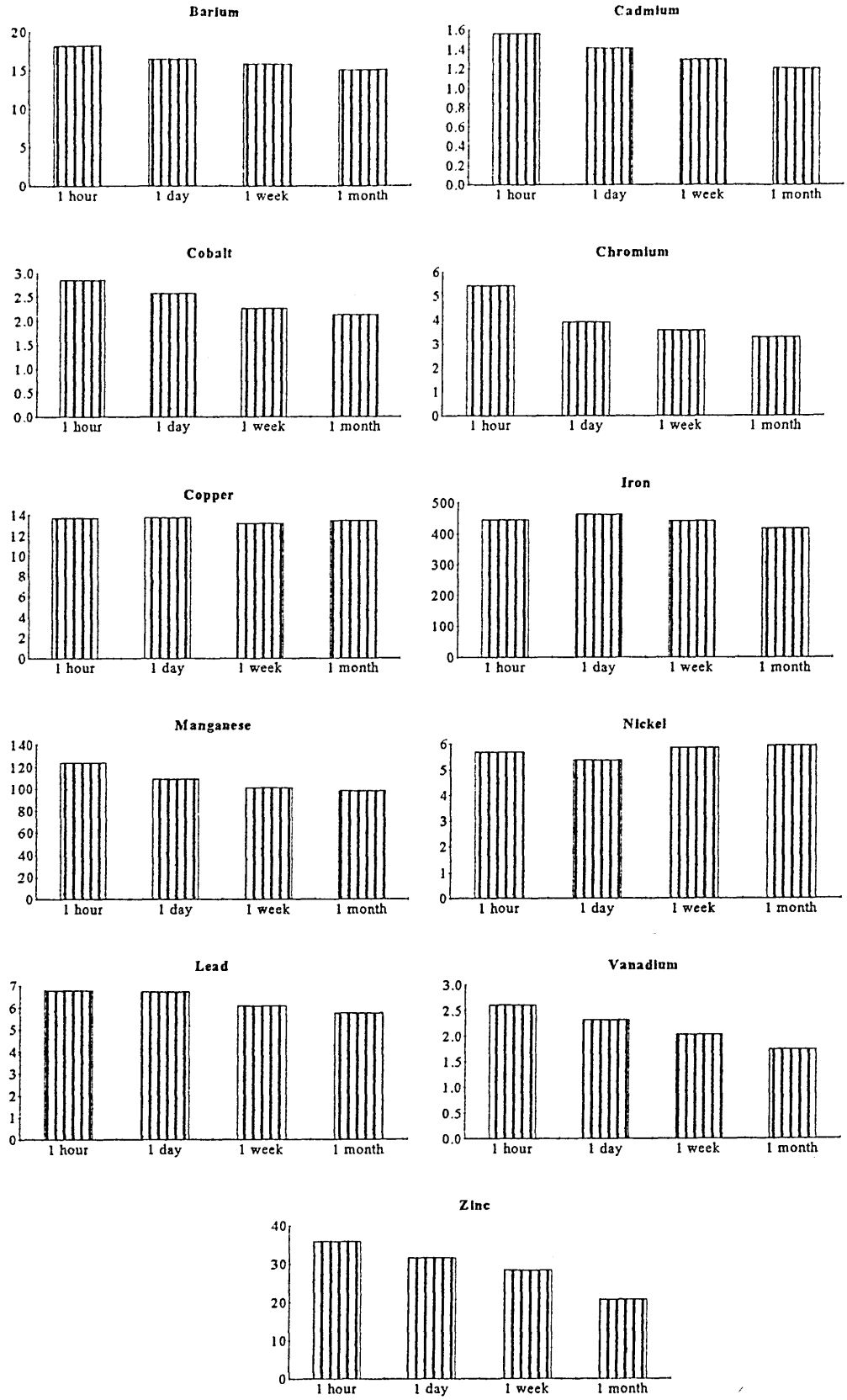


Fig. 5.4 The diagram represents the results observed for a stability trial. A sample collected from Langsett Reservoir was processed through alumina microcolumns. A proportion of these were eluted and the analyte concentrations determined in µg/l (y axis), following 1 hour, 1 day, 1 week and 1 month.

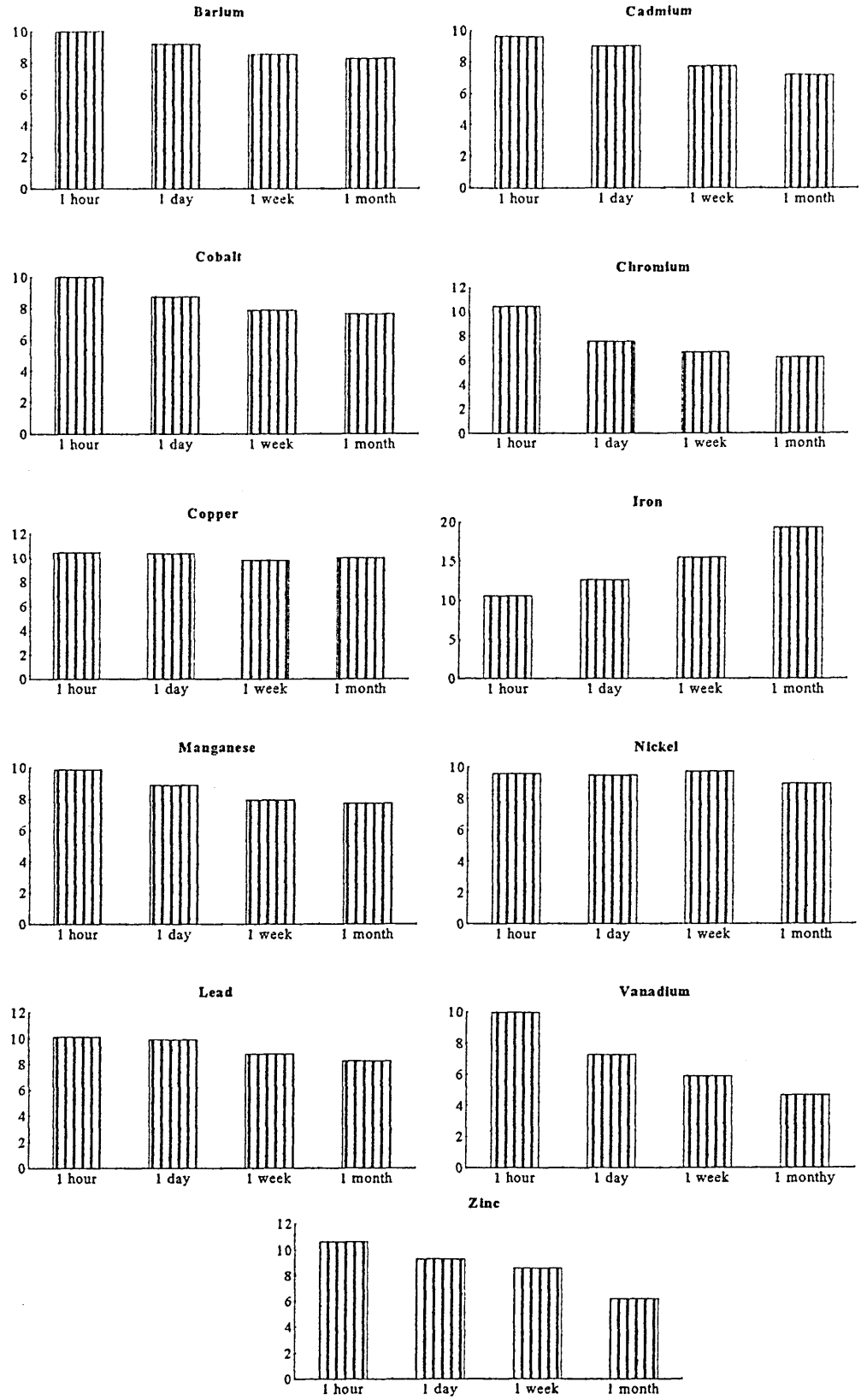


Fig. 5.5 The diagram represents the results observed for a stability trial. A multi-element standard solution (Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn, 10 µg/l) was processed through alumina microcolumns. A proportion of these were eluted and the analyte concentrations determined in µg/l (y axis), following 1 hour, 1 day, 1 week and 1 month.

It is possible that these analytes are either lost to the microcolumn tubing, or that the analytes become more strongly bound to alumina over the 1 month period, and cannot subsequently be recovered quantitatively with 5 M HNO_3. However, the loss is similar for all three matrices. Hence, appropriate standard solutions could be processed through alumina microcolumns in the field, with the sample. The concentrations subsequently determined for these analytes, within the 1 month time period, would be accurate. This would reduce the sensitivity of the technique however and is far from ideal. The exceptions were Ni, Cu, Fe and V. In the case of Fe, a loss between 6-9 % was experienced for this analytes present in the samples, but an increase of 45 % was observed for Fe in the standard solution. The analyte V experienced a loss between 33-35 % for the samples and 53 % for the standard solution. Hence, Fe and V can not be determined by the field sampling microcolumn enrichment technique with FI-ICP-ES detection. The analytes Cu and Ni retained on activated alumina were stable over the month storage period. This is encouraging as it may be possible to use different storage conditions to stabilise the analytes on the column. For example, storage of the microcolumns at 4 ^{o}C during the 1 month time period, or at elevated temperatures may produce improved recoveries. Alternatively the use of hot nitric acid as eluent may recover a greater proportion of the analytes. This requires investigation.

5.5 Additional Studies

The studies reported in chapters 4 and 5 have shown that the microcolumn enrichment technique can be utilised to determine the trace analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in selected mineral, river and reservoir water samples. Also that activated alumina microcolumns can be utilised as new field sampling tools. This is important for future work. Other water samples such as seawater and estuarine waters, which can not be directly analysed by ICP-ES, due to sensitivity limitations or ICP-MS, due to an intolerance for high dissolved solid content samples, will require pre-treatment and/or preconcentration procedures. Hence, the field sampling microcolumn enrichment technique, with ICP-MS detection, was applied to the determination of Cr, Mo and U in

seawater samples. Alumina microcolumns in the basic form were utilised for Cr and U enrichment, and alumina microcolumns in the acidic form were utilised for the enrichment of molybdate.

Alumina microcolumns were conditioned with 2 ml of 0.01 M ammonium hydroxide. The molarity of this solution was decreased to reduce the possibility of contamination from this conditioning step. A sample volume of 2 ml, collected in the Bay of Biscay, was processed through a column in duplicate This procedure was repeated for the Seawater Reference Material NASS-1, the pH of which was adjusted to 8. Each of the loaded columns was inserted into the FI system sequentially. The retained Cr was eluted with 3, 250 µl injections of 1 M nitric acid. Chromium was detected by ICP-MS (^{52}Cr), and the ion signal/time profiles are given in Fig.5.6. The certified concentration for chromium in NASS-1 is 0.184 µg l^{-1}. The concentration for chromium present in the Bay of Biscay sample is 0.4 µg l^{-1}.

Alumina microcolumns were conditioned using 2 ml of 0.01 M nitric acid, which reverted the alumina to its acidic form, ready for anionic preconcentration. A volume (2 ml) of an acidified sample collected in the Bay of Biscay, was processed through a conditioned column in duplicate. This process was repeated for the Seawater Reference Material NASS-1. The loaded microcolumns were inserted into the FI manifold (see section 2.3.1). The retained Mo was eluted with 3, 250 µl injections of 1 M ammonium hydroxide. The molybdate elutions were recorded by ICP-MS (^{98}Mo), and the ion signal/time profiles are shown in Fig.5.7. The molybdenum concentration appears to be similar in both the NASS-1 sample, an open ocean seawater reference material gathered in the North Atlantic and certified at 11.5 µg l^{-1}, and the open ocean seawater sample, collected in the Bay of Biscay.

The field sampling procedure was repeated for 10 ml volumes of sample, collected from the Irish Sea at various locations off the west coast of England. The processed basic alumina microcolumns were returned to the laboratory and incorporated into the FI system. The retained U was eluted with 1 M HNO_3. The concentration of ^{238}U was determined with the use of ^{238}U standards, processed in the same way as the

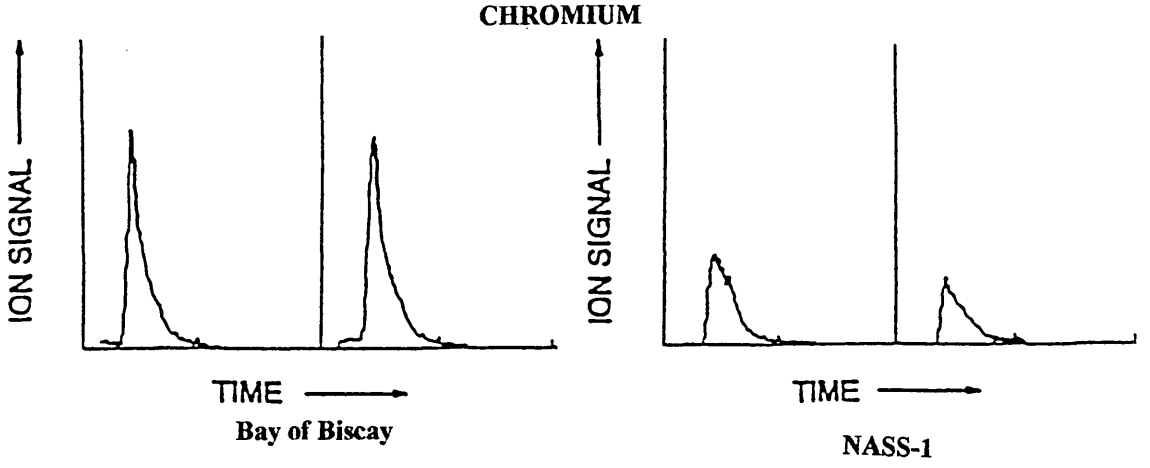


Fig.5.6 The signal/time response for elution (250 µl of 1 M nitric acid) of Cr, from seawater samples. 1:- Bay of Biscay (2 ml). 2:- NASS-1 (2 ml). The certified concentration of Cr in NASS-1 is 0.184 µg/l.

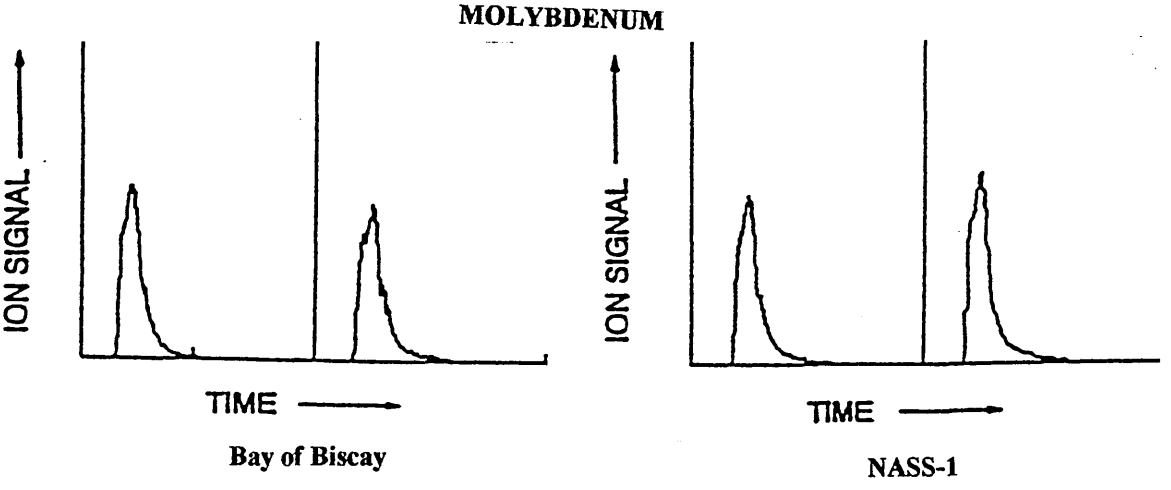


Fig.5.7 The signal/time response for elution (250 µl of 1 M ammonium hydroxide) of Mo, from seawater samples. 1:- Bay of Biscay (2 ml). 2:- NASS-1 (2 ml). The certified concentration of Mo in NASS-1 is 11.5 µg/l.

Analyte	Location deg min s	Concentration µg/l
U	N 53 26 83 W 3 01 55	2.1
U	N 53 42 718 W 3 19 46	2.4
U	N 54 07 55 W 3 22 02	1.7
U	N 54 24 37 W 3 32 85	1.3
U	N 54 23 72 W 3 32 79	1.5
U	N 54 24 09 W 3 32 35	1.9
U	N 54 24 29 W 3 32 72	2

Table 5.9 The concentrations were determinand by the field sampling microcolumn enrichment procedure, with ICP-MS detection. See text for experimental details.

samples. The results and the locations of sampling are given in Table 5.9. This study indicated the feasibility of the flow injection microcolumn preconcentration technique, with the use of seawater and ICP-MS detection. The experiment was able to show that the trace analytes chromium, uranium and molybdenum, could be retained on the alumina microcolumn, from a highly complexed material, such as seawater, and be subsequently eluted. It also demonstrates the versatility of alumina, in that it can function as both a cation and anion exchanger.

5.6 Conclusions

1. The total content of the analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn present in Buxton Mineral Water and Redmires and Langsett Reservoir Waters, can be determined by the field sampling microcolumn enrichment technique with ICP-ES detection. Due to poor retention/elution efficiencies, the total content present in the samples of the remaining analytes (Fe and V) cannot be determined by this technique.

2. The mechanisms by which activated alumina retains analyte species (dissolved, complexed, colloidal, particulate) present in natural water samples is not fully

understood. However, it is proposed that analyte-tartrate complexes are formed with dissolved and complexed analyte species, on the addition of tartaric acid to the sample (see Chapter 4). This maintains the analytes in solution in a form activated alumina can retain. Hence as the sample is processed through the column, the analytes are released from the tartrate complex and retained by activated alumina. It is also possible that Cr(III) and Fe(III) are retained by activated alumina as analyte-tartrate complexes (see Chapter 4). It is assumed that particulate analyte species are physically retained in the sponge, which is inserted into the ends of the microcolumn to keep the packing material in place. Hence on elution, the analytes are determined due to acid dissolution of the particulate matter. Analytes adsorbed on colloids may be retained in one of two ways. The colloidal matter may be physically retained in the sponge and/or by activated alumina due to its large size. Hence on elution, the analytes are determined due to acid dissolution of the colloidal matter. Alternatively, colloids such as humic acid may be retained by activated alumina (159-161) as detailed for tartaric acid in Chapter 4. This is feasible as activated alumina changes colour from white to yellow when a sample containing humic acid is processed.

3. Activated alumina microcolumns have been successfully utilised in the field, to immobilise the analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn present in reservoir water samples, at the time of collection. Hence, activated alumina microcolumns can be utilised as new multi-element sampling devices.

4. The analytes Ba, Cd, Co, Cr, Fe, Mn, Ni, Pb, V and Zn retained on activated alumina microcolumns, showed significant losses on storage of the columns over a 1 month time period. However, the use of different storage conditions may improve analyte stability on the columns, which requires investigation. The analytes Cu and Ni were stable over a one month period, using the storage condition of normal ambient temperature.

5. The field sampling microcolumn enrichment technique was combined with FI-ICP-MS detection for the determination of Cr, U and Mo in seawater. The results indicated that this technique is viable.

6 Conclusions and Future Work

New methodology for the ultratrace determination of nine analytes present in high purity alkali metal salts has been developed using microcolumns of activated alumina in a FI-ICP-ES system. The technique is robust, utilises limited sample handling and simultaneously preconcentrates and separates the analytes from matrix components. Hence possible matrix interferences are eliminated and limits of detection are significantly improved, in comparison to conventional ICP-ES analysis. A sample volume of 5 ml, at an optimum pH of 8 produced limits of detection for the analytes Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn of 0.25, 0.34, 0.72, 0.17, 2.1, 0.075, 0.50, 3.2 and 0.61 $\mu g\ l^{-1}$, respectively. A dual-valve FI system was employed to minimise matrix interferences and prevent nebuliser and tubing blockage. The technique was successfully applied to the determination of these analytes in a selection of the alkali metal salts (CsI, KBr, $LiNO_3$, NaCl, NaF, 1 % w/v). Typical concentration levels present in CsI ranged from 30 to 620 ng g^{-1} for Pb and Fe, respectively. For validity of measurement, the analytes were determined using two calibration techniques: A simple aqueous standard, and a standard addition calibration.

A technique for the determination of the total content of nine trace analytes present in Buxton Mineral Water and Redmires and Langsett Reservoir Waters, using microcolumns of activated alumina in a FI-ICP-ES system has been developed. This was achieved with the use of the complexing agent tartaric acid, which has shown to be effective in improving analyte retention. A sample volume of 10 ml, at an optimum pH of 8 and utilising 5 M HNO_3 as eluent, produced limits of detection for Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn of 0.087, 0.18, 0.18, 0.31, 0.13, 1.2, 0.037, 0.25, 1.6, 0.052 and 0.31 $\mu g\ l^{-1}$, respectively. The precision (RSD) was less than 1 % at the 50 $\mu g\ l^{-1}$ level. The procedure was successfully applied to determination of these analytes in a certified river water reference material (SLRS-1). Due to low retention and elution efficiencies, the total content of the analytes Fe and V present in Buxton, Redmires and Langsett samples was not determined by this technique.

Activated alumina microcolumns have been successfully utilised in the field to preconcentrate and immobilise the total content of the analytes Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn present in reservoir water samples, at the time of collection. Hence a new multi-element field sampling device, which gives high sample integrity has been developed. However the analytes Ba, Cd, Co, Cr, Fe, Mn, Pb, V and Zn present in reservoir water samples and retained on activated alumina microcolumns in the field, showed significant losses on storage of the columns over a 1 month time period. The analytes Cu and Ni were stable over the month period, using the storage condition of normal ambient temperature. It is therefore necessary under the present evaluated conditions, to elute the retained analytes from the microcolumns for determination on the same day as the sample collection.

The results generated in this thesis have indicated that the total content of nine trace analytes present in selected mineral and reservoir water samples, can be retained by activated alumina and subsequently eluted and determined. It is known that analytes are present in natural waters as a variety of different species, including dissolved, complexed, colloidal and particulate forms (163). It is therefore suggested that systematic studies are carried out in an attempt to clarify retention processes on activated alumina and the uptake of certain analyte species, in order to substantiate the results generated. Hence ethylenediaminetetraacetic acid (EDTA) and humic/fulvic acids may be added to standard solutions, to generate strong analyte complexed solutions and colloidally associated analyte solutions, respectively. The effective recovery of the analytes, following elution and determination will validate the results generated for natural waters in this thesis.

The applications demonstrated have been limited to a mineral water and two reservoir water samples. Hence, it would be appropriate to apply the microcolumn preconcentration technique with FI-ICP-ES detection to numerous samples in these water categories, such as lake, river, stream, reservoir, mineral and tap, to completely assess the capability of activated alumina to retain the total content of selected analytes present in these water systems.

Future investigations are proposed to apply the microcolumn enrichment technique with FI-ICP-MS detection to the retention of trace analyte species present in more complex water samples, such as sea and estuarine waters. These water samples cannot be directly analysed by ICP-ES, due to sensitivity limitations, or ICP-MS due to an intolerance for high dissolved solid content samples. The viability of this application has been demonstrated in the determination of Cr, Mo and U in chapter 5, but requires further investigation.

The results obtained for the stability trial were not satisfactory. The analytes retained, by processing samples though activated alumina microcolumns in the field, are effectively immobilised and stabilised at the time of collection. However, complete recovery of the analytes can only be achieved if the retained species are eluted and determined on the same day as sampling. Further investigations need to be carried out to determine if the stability period can be extended. This is essential if alumina microcolumns are to be used as field sampling tools in the future. It may be necessary to store the columns frozen, at 4 ^{o}C or at other temperatures to extend the stability time of the analytes retained. It may also be of interest to utilise alternative column packing materials with different chemistries, such as iminodiacetic acid based resins, which have been successfully utilised in laboratory based analysis, to resolve the problem of analyte instability on the microcolumns.

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Colette Gail Holmes, October, 1996.

POSTGRADUATE STUDIES

1. Lecture Courses

i) Selected Lectures from weekly School of Science Seminars

ii) Lectures Organised by the Chemistry Society at Sheffield Hallam University

iii) Short Courses: Laboratory Based Course in ICP Spectrochemical Analysis - Waters and Environmental Materials

Sample Presentation in Inductively Coupled Plasma Mass Spectrometry

2. Meetings

i) The Analytical Division of the Royal Society of Chemistry, R&D Topics

ii) School of Science Research Colloquia

3. Presentations

i) Oral Presentations given at Chemistry Research Meetings at Sheffield Hallam University

4. Posters

i) " From Field Sampling to Laboratory Measurement : An Integrated Approach to Trace Element Analysis ", Royal Society of Chemistry R&D Topics Conference, Aberdeen, July 1991.