DETERMINATION OF CHROMIUM IN NATURAL WATERS BY FLOW INJECTION INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY

by

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ABSTRACT

A successful approach for the accurate determination of chromium species in river waters is developed in this thesis. This is based on the use of alumina micro columns for in situ sampling and storage, followed by a simple introduction of the in situ samples to an inductively coupled plasma emission spectrometer using a flow injection manifold.

The approaches to speciation determination have been reviewed in Chapter 1. The need for in situ sampling and separation together with storage stability is evident, as is the limited success reported for many elements including chromium. Alumina is shown to be a material with promising characteristics for sampling and separation, and its properties as an ion exchanger are described.

Chapters 3 and 4 deal in turn with the investigation of the properties and application of the acidic and basic form of activated alumina for the determination of chromium species. The results provide the basic knowledge for the subsequent development of the methodology for in situ river sampling and analysis reported in Chapter 5.

Very successful results are reported. For the first time river water samples have been obtained for chromium species and transferred to the laboratory without any significant change in speciation. The methodology is simple and effective for the two river waters investigated. The concentration ranges found in the River Rother were 1.7 to 3.1 μg/l chromium (VI) and 8.6 to 19.5 μg/l for chromium (III). Similar results are reported for the River Don.

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CHAPTER FOUR

THE CHARACTERISATION OF BASIC ALUMINA AS A CHROMIUM (III) CATION EXCHANGE MATERIAL 68

1.1 Significance of chromium in the environment

Over the past number of years, the genetic and toxicological effects of chromium have been widely studied and as such are of scientific and public health concern. This interest centres around the fact that chromium has a dual biological role. In 1959, Schwartz and Mertz (1) observed impaired glucose tolerance in rats fed various diets, the cause being traced to chromium deficiency.

Later studies on chromium nutrition confirmed these findings (2) and it is now accepted that chromium is essential for the normal glucose tolerance factor (GTF) in man (3). GTF is essential for insulin activity and chromium is prescribed as a dietary supplement where impaired glucose tolerance is diagnosed. This is administered as a natural complex of chromium (III) with nicotinic acid, glycine, glutamic acid and cystiene (4). Animal protein is the best and most reliable source of this chromium complex, and such, the stable trivalent chromium (III) form is considered to be non toxic.

Toxicological hazards are associated with the hexavalent chromium (VI) form. In a recent paper De Flora et al. (5) reviewed 700 results reported on 32 chromium compounds, the majority of results obtained for chromium (VI) compounds showed that they were toxic as a function of solubility and bio-availability to target cells. The proposed mechanism suggests that chromium (VI), as the chromate CrO_4^{2-}

anion, is taken up by cells via the general protein anion channel. Having penetrated the cell, a variety of cytoplasmic electron donors reduce the chromium (VI) to chromium (III) which then forms chromium - DNA adducts to produce the genetic damage.

Chromium (III) compounds do not induce these genotoxic effects. The toxicological effects of industrial exposure to chromium (VI) are well known (6) and include allergic dermatitis, skin ulcers, perforation of the nasal septum and increased incidence of bronchocarcinoma. This was illustrated in a report by Morris et al. (7), who showed evidence of chromium toxicity in a group of stainless steel welders. The International Agency for Research on Cancer (I.A.R.C.) have found sufficient evidence to grade chromium (VI) compounds as Group 1, i.e. compounds which cause carcinogenicity in humans. Metallic chromium and chromium (III) compounds have been graded by the I.A.R.C. as Group 3, i.e. compounds for which there is inadequate evidence of carcinogenicity in humans (8, 9, 10).

With reference to this dual role played by chromium, attention in natural waters has centred around the distribution of the chromium (III) and (VI) oxidation states. However, little is known about the fate of the different chromium species in the aquatic environment and further studies are needed to investigate the environmental impact of chromium (III) and (VI) discharges.

1.2 Sources of chromium in the environment.

In the natural environment chromium occurs principally as the mineral chromite ($FeO.Cr_2O_3$ / $FeCr_2O_4$) which is an extremely stable trivalent state. Using chromium (III) stability data, Hem (11) suggested that the mineral chromite would limit dissolved chromium concentrations, caused by weathering processes, to 0.0052 µg/l in natural waters. The majority of the chromium would be co-precipitated with iron hydroxides. All reported total chromium levels in rivers and esturine waters are significantly in excess of the natural mobilisation figure, and where speciation levels have been determined significant fractions of chromium (VI) have been found. This suggests that environmental pollution by chromium occurs as a result of mans activities (12, 13, 14, 15, 16). In the majority of industrial atmospheric emissions chromium is in the trivalent state. Liquid emissions, resulting from the electroplating industry, the manufacture of alloys, the leather tanning industry and its use as a corrosion inhibitor in water pipes results mainly in hexavalent chromium species. It is interesting to note that the world wide consumption of chromium by the leather tanning industry alone has been estimated at 65,000 tons per year (17).

1.3 Chromium chemistry in natural waters.

In 1970 Elderfield (18) used equilibrium data to predict that chromium (III) and chromium (VI) should be the only significant oxidation states in natural waters, the most probable species being : $Cr(OH)_2^+ . 4H_2O$ and CrO_4^{2-}, respectively.

The redox equilibrium was assumed to be represented by the reaction:

$$Cr(OH)_2^+ . 4H_2O \rightleftharpoons CrO_4^{2-} + 6H^+ + 2H_2O + 3e^- \qquad (1.1)$$

This was confirmed by the work of Baes et al. (19) in 1976 and Hem (11) in 1977 who used thermodynamic data to show that the dominant dissolved chromium oxidation states and species in the pH range 5 - 9 would be :

(III): $Cr(OH)_2^+$ and $Cr(OH)^{2+}$. (VI): $HCrO_4^-$ and CrO_4^{2-}

Using electric potential (pE) versus pH data, Nriagu et al. (20) showed that above pH 4.0, due to hydrolysis, the hydrated $Cr(H_2O)_6^{3+}$ ion cannot exist. They also showed that in the absence of chelating agents $Cr(OH)_2^+$ and $Cr(OH)^{2+}$ are the predominant species in the pH range 6 to 7. This means that at pH values between 4 and 9 the only chromium species in natural waters will be in the (III) and (VI) oxidation states and they will form cations and anions respectively.

Studies of ^{51}Cr transport in natural waters have shown that in well aerated river waters under slightly alkaline conditions, chromium (III) will tend to be re-oxidised to chromium (VI) (21). In polluted river systems the low oxygen concentrations will favour reduction of chromium (VI) to

chromium (III) which in turn is readily adsorbed by suspended particles, aquatic plants or bottom sediments (22, 23, 24). Release of this adsorbed chromium is slow with the chromium in the trivalent form. Chromium (VI) is only weakly adsorbed on these media, and adsorption often involves a reduction process to chromium (III). This is also the same for organic matter associated with soils and sediments. Localised reduction of chromium (VI) can also occur in any natural water where the oxygen concentration is depleted as in anoxic basins (12). For these reasons the valency distribution of dissolved chromium in natural waters depends upon the oxygen content and redox potential of the water, the presence of dissolved or particulate organic matter, and the presence of suspended particulate matter.

This means that where the natural chromium levels in river waters are disturbed by either atmospheric or direct aqueous inputs, the level of pollution, the distance from the input, the flow of the river and time allowed for mixing will be significant factors in determining the chromium (III) and (VI) ratio.

1.4 Separation procedures for the speciation of chromium (III) and chromium (VI)

1.4.1 Ion chromatography

Urasa and Nam (25) used two columns, one a strong base anion exchange resin (HPIC-AS-7) and a strong acid cation exchange resin (HPIC-CS-2) to separate the chromium (III) and (VI) species. The ion chromatograph was coupled to a direct current plasma (DCP) for detection of the species. Preconcentration of the species was achieved by multiple injections of the sample on to the columns prior to elution, and detection limits were reduced to less than 1.0 μg/l for both species. Analysis of certified reference materials was performed and satisfactory results obtained. Analysis time without using preconcentration was approximately 8 minutes.

Orvini et al. (26) used ion chromatography with neutron activation analysis (NAA) as the means of detection. Sample solutions were passed through quartz tubes filled with resins (AG 50 WX4 and AG 1X8) to separate and retain the chromium (III) and (VI) species. The quartz tubes were then heat sealed, irradiated for 30 hours, left to cool for one week and then counted.

Neither workers addressed the issue of species stability nor applied their work to sampling natural waters.

1.4.2 High performance liquid chromatography (HPLC)

Krull et al. have made many contributions in this field (27, 28, 29, 30, 31) using HPLC coupled with inductively coupled plasma (ICP) and direct current plasma (DCP). They used a paired ion reverse phase column in a HPLC system coupled to a DCP, and obtained limits of detection of 5 to 10 µg/l for chromium (III) and (VI). Spiked water samples and NBS reference water 1634a were analysed. Results for the reference water were inconclusive with concentrations in the region of the limit of detection (L.O.D.). Water samples were collected and spiked with chromium (VI), but none was detected by HPLC - DCP, although the added chromium (VI) did contribute to the total chromium levels observed.

Syty et al. (32) used HPLC coupled to atomic absorption spectrometry (AAS). Preconcentration of chromium (VI) was achieved using a C-18 bonded silica column with a sampling time of 5 min. The limit of detection was 0.8 µg/l chromium (VI). Pond waters spiked with chromium (VI) were analysed, and recovery immediately after spiking was 100%. When the spiked samples were left for 24 hours, recoveries in the range 81 - 85% were achieved. Typical analysis times were 12 minutes per determination. The poor stability of the chromium (VI) species severely limits the application of this methodology.

1.4.3 Classical extraction techniques

Unlike the chromatographic ion exchange separation techniques already discussed, classical extraction only facilitates the determination of one of the chromium species. A total chromium determination has then to be carried out and the remaining species determined by difference. Subramanian (33, 34) used an ammonium pyrrolidinecarbodithioate - methyl isobutyl ketone (APCD - MIBK) extraction system with graphite furnace atomic absorption spectrometry (GFAAS) for determination of chromium (III) and (VI). Optimisation of phthalate and APCD concentrations, pH and extraction time enabled the APCD - MIBK system to selectively separate chromium (VI) from chromium (III) and simultaneously extract both chromium (III) and (VI). Limits of detection of 0.3 μg/l were obtained for both chromium (III) and (VI), but the relative standard deviation (RSD) was 33% at five times the limit of detection.

Cranston and Murray (12, 13) used iron (II) and iron (III) co-precipitation to determine chromium (III) and (VI). Iron (III) hydroxide only precipitates the chromium (III) species while iron(II) precipitates both chromium species, therefore chromium (VI) can be determined by difference. The authors collected large numbers of river esturine and sea water samples, and to eliminate storage problems the precipitation and filtration steps were carried out on board ship. Chromium (III) and total chromium determination was carried out on the filtrates in the laboratory using GFAAS. Spiked river and esturine samples were also

studied and determinations carried out over a period of 100 hr from the time of spiking. It was found that very large analyte losses occurred. The average loss for chromium (III) over the time period was 78%, and for chromium (VI) 14%. It was assumed that this was due to adsorption on both the container walls and the filtration equipment.

1.5 Species stability and preservation

It is widely recognised that speciation changes occur during sampling, storage and manipulation (12, 13, 28, 32). Normal sampling procedures create many problems when related to the preservation and stability of the chromium species prior to analysis. It has been shown that sample acidification and increases in temperature cause reduction of chromium (VI) to chromium (III) (20). Sample filtration and the removal of humic substances lead to adsorption of chromium (III) to the sample container walls (21, 35, 36, 37, 38).

Hence any proposed method must be able to separate and immobilise the chromium species at the time of sampling in order to avoid these losses.

As early as 1974 Paulsen et al. (39) recognised that the problems in trace metal analysis were not necessarily in the quantitative analytical technique used to obtain the data, but in the methods used to obtain a representative sample free from errors introduced during sampling and

storage.

In an attempt to overcome these problems, Paulsen proposed that an in situ method of sampling should be used that would render the sample both chemically and physically inert at the time of sampling.
To illustrate this he used a glass bead immobilised chelate (8 - hydroxyquinoline), packed into a cartridge through which known volumes of sea water were passed (this being achieved at the sampling site). Copper, nickel and cobalt were effectively chelated onto the cartridge which was returned to the laboratory for the successful analysis by x - ray fluorescence spectrometry. The extension of this to other applications has not been reported.

It should also be recognised that to assist in the development of any proposed method, an aqueous chromium (III) and chromium (VI) reference material at a neutral pH is needed to asses the quality of measurement and obtain comparability (40, 41). There are in fact at present no available reference materials certified for the separate chromium species.

The Community Bureau of Reference (BCR), which has the task of improving the quality of measurements, recognised this difficulty and highlighted the need for an aqueous reference material. In 1989 a preliminary stability study was completed (42) and in 1990 the BCR initiated a project at the end of which it was hoped would provide such a reference material for waters.

1.6 Alumina as an ion exchange material

The properties of alumina as a stationary phase for adsorption and or partition chromatography have been studied for a long time. The ability to exhibit ion exchange characteristics has been widely recognised in the past. Schwab and co workers in 1937 (43, 44) and 1940 (45) carried out the first detailed studies of alumina as an ion exchanger when they examined the retention of inorganic cations and anions on a column of alumina. Subsequently batch equilibration (46), column (47) and thin layer (48) chromatographic experiments with alumina and alumina impregnated paper all indicated that ion exchange was the major factor in determining retention of inorganic cations and anions.

Alumina has a very complex surface which is dependent upon pretreatment and chemical environment. The ion exchange concept in an aqueous environment involves a surface charge appearing due to dissociation of surface AlOH groups and detachment of either hydrogen or hydroxide ions. As a result of the charge sites, ions of opposite charge are attracted from the solution with the resulting formation of two charged planes at the interface (49).

In simplest terms the proposed mechanism can be represented by dissociation equilibria (1.2) and (1.3), which yield positive and negative surfaces respectively.

$$Al - O - H \leftrightharpoons Al^{+} \; O - H^{-} \qquad (1.2)$$

$$Al - O - H \leftrightharpoons Al - O^{-} \; H^{+} \qquad (1.3)$$

Anion and cation exchange can then take place at these charge sites as shown in equation (1.4) and (1.5).

$$Al^{+} \; O - H^{-} + X^{-} \leftrightharpoons Al^{+} \; X^{-} + OH^{-} \qquad (1.4)$$

$$Al - O^{-} \; H^{+} + X^{+} \leftrightharpoons Al - O^{-} \; X^{+} + H^{+} \qquad (1.5)$$

Because alumina is amphoteric in nature its ion exchange properties will be strongly pH dependent (50). Upon hydration two distinct types of hydroxyl groups are present on the alumina surface (equation 1.2 and 1.3). When this hydrated alumina is washed with base (NaOH) the protons will be neutralised and replaced with more loosely bound sodium ions (see Figure 1.1). The sodium ion can exchange with other cations and are responsible for the cation exchange properties of basic alumina at high pH. Conversely when the basic alumina is washed with acid (HCl) the protons of the acid produce two effects. They desorb the hydroxyl groups, which are then replaced by chloride ions to give the anion exchange properties of acidic alumina, and replace the sodium cations attached to the oxygen atom.

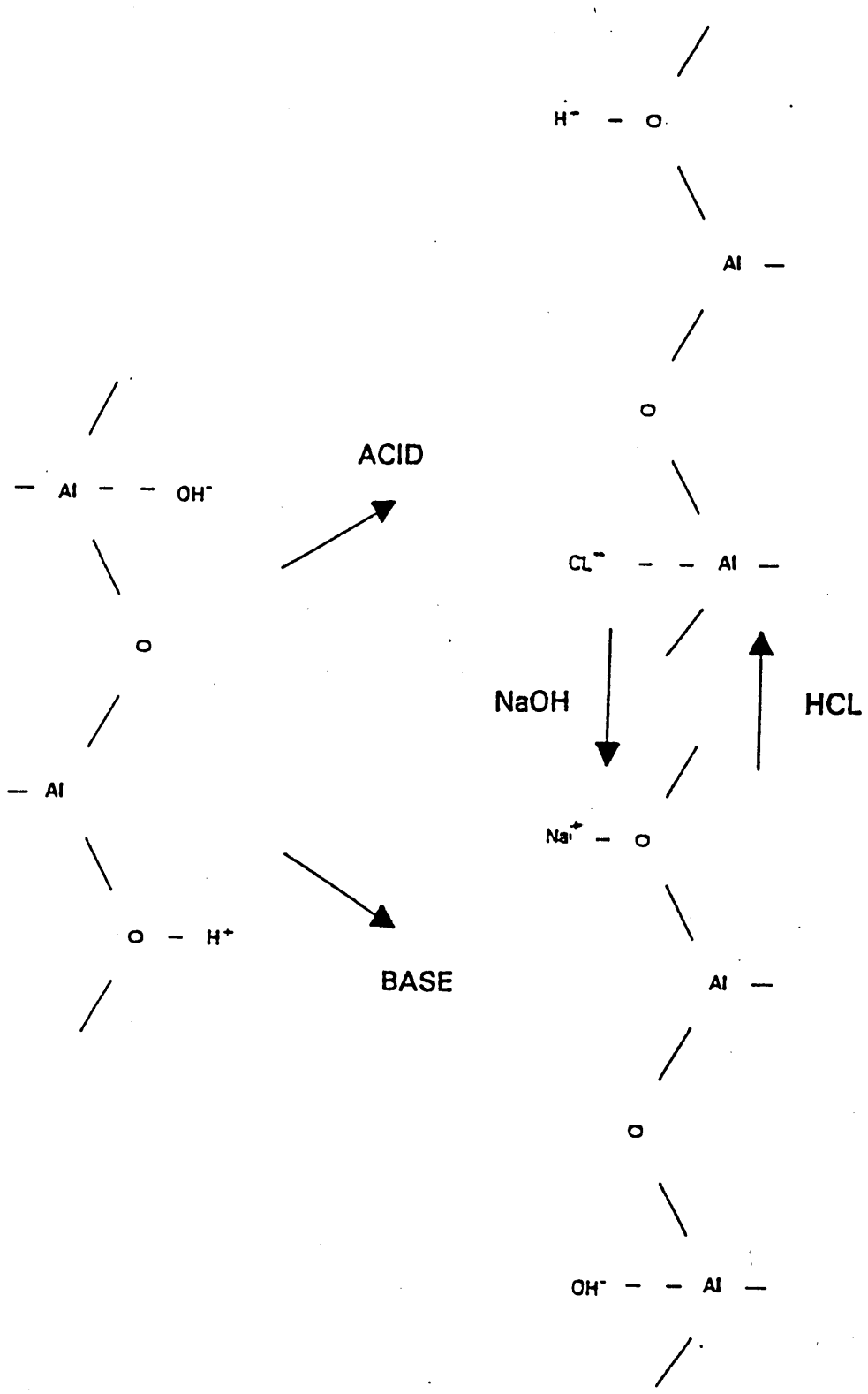

Figure 1.1 Alumina ion exchange in acidic and basic solutions.

Davis et al.(51) used a column of activated alumina (acidic form) to retain phosphate anions from an acidic sample solution, while potentially interfering cations such as iron were not retained. The phosphate ions were subsequently eluted from the column using sodium hydroxide solution and the phosphate determined colorimetrically. This work was adapted by McLeod et al. (52) with the application of a combined flow injection - inductively coupled plasma - emission spectroscopy system (FI - ICP - ES). The use of the FI - ICP - ES technique had until this time mainly concentrated on the advantages FI itself offered, as a highly precise, high sampling throughput (in the ul sample range) means of sample introduction into the ICP - ES (53).

The technique successfully used by McLeod et al. (52) linked ICP - ES with a FI manifold which incorporated a micro column of activated alumina. Rapid on line analyte enrichment and matrix removal enabled the successful determination of phosphorus in steels.

1.7 Aims and scope of this work

The work reported in this thesis is concerned with the selective speciation of chromium (III) and chromium (VI) in river waters.

The previous sections have shown that to acquire meaningful chromium speciation data certain points have to be met.

1. The separation material must be stable, easily handled and ideally retain both chromium species.

2. The separation stage must be rapid, selective and be accomplished on site.

3. Once separated the chromium species must be immobilised and rendered stable during storage, so that no losses occur prior to making analytical measurements away from the sampling site.

4. The detection system must be sensitive, element specific and free from interferences.

5. The measurement must be rapid and reproducible.

A micro column of activated alumina is to be investigated as the means of meeting the sampling, separation and stability requirements for

chromium (III) and chromium (VI). It is to be used as an integral part of the laboratory analysis equipment based on the flow injection - inductively coupled plasma - emission spectrometry technique successfully employed in our laboratories by McLeod et al. (52).

The flow injection manifold is also the interface between field sampling and laboratory analysis, by effecting the simple transfer of analyte from the alumina micro column to the ICP - ES. Analysis time in the laboratory is expected to be in the region of one or two minutes per column. The ICP - ES system has proved to be very sensitive (limit of detection for chromium, 5 ug/l) and free from spectral interferences (54). Hence it's use for all analytical measurements.

2.1 Reagents and materials

Chromium (III) and chromium (VI) stock solutions (1000 mg/l) were prepared from chromium (III) nitrate and potassium dichromate (BDH Chemicals, AnalaR grade), respectively. Standard solutions of chromium (III) and chromium (VI) (single or mixed) were prepared daily by appropriate dilutions of the stock solutions. Stock hydroxide solutions (2.0 M) were prepared from solid potassium hydroxide and concentrated ammonium hydroxide solution (BDH Chemicals, Aristar). Stock acid solutions (2.0 M) were prepared from concentrated nitric acid (BDH Chemicals, Aristar). Hydroxide and acid carrier solutions (0.01 and 0.02 M respectively) were prepared by appropriate dilution of the stock solutions. High purity water was used throughout and solutions were stored in high density polyethylene (Nalgene) containers. Activated alumina (BDH Chemicals, Brockmann grade 1) in the acidic and basic form (particle size range 120 - 150 μm) was used for column packing.

2.2 Apparatus and Instrumentation

2.2.1 The Flow injection manifold (FI)

The manifold (Figure 2.1) consisted of a peristaltic pump, rotary injection valve, a micro column of activated alumina and a crossflow nebuliser.

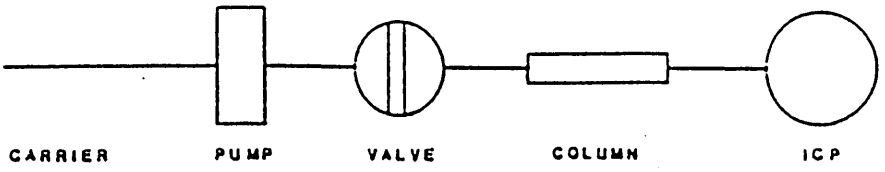

Figure 2.1 Flow Injection Manifold (FI)

The Gilson Minipulse peristaltic pump has a variable speed control to set flow rates, using the rotation speed of the roller head, rather than changing pump tube diameters. This accurate control means that very reproducible flow rates were achieved on a day - to - day basis. The rotary injection valve used in the first part of the acidic alumina micro

column study, was a custom made Teflon valve with sample and elution loops in one unit. This was changed when leaks between the Teflon faces, causing contamination between the two loops, became apparent. All further work was carried out using a Rheodyne (low pressure) Teflon rotary injection valve. The Rheodyne is a six port valve with an external loop which is readily interchangeable. Figure 2.2 shows the valve operating procedure. The "load" position (Figure 2.2.a) allows the loop to be filled without interruption of the flowing carrier stream. Rotating the valve to the "inject" position (Figure 2.2.b) allows the contents of the loop to be injected into the manifold.

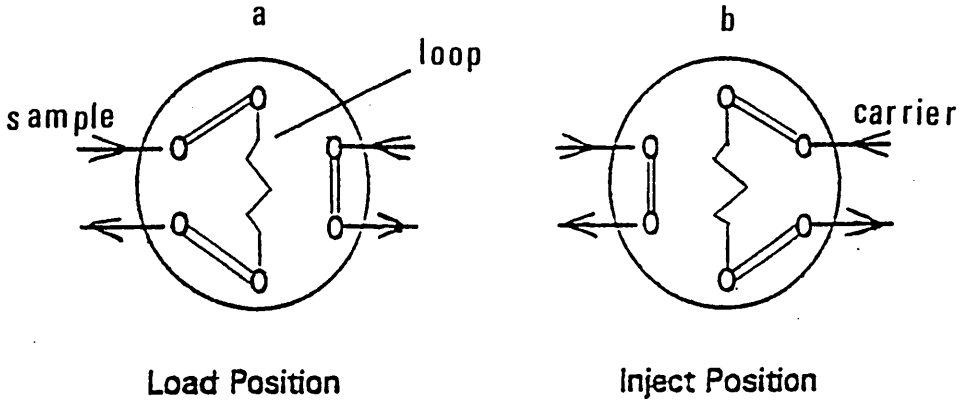

Figure 2.2 Schematic Diagram of Rheodyne Injection Valve

The alumina micro column was constructed using Teflon tubing (6 cm length, 1.5 mm i.d.) packed with sieved alumina (mesh size 120 - 150 μm). The micro column was dry packed (by hand) until approximately 3 cm of the Teflon tube was filled, small pieces of sponge were used to physically hold the alumina in place.

The micro column was connected between the valve and nebuliser using Teflon tubing (0.8 mm i.d., 1.5 mm o.d.), the outside diameter of this tubing and the inside diameter of the micro column tubing were such that a leak proof, push fit could be made. To minimise sample dispersion in the FI manifold, these tube lengths were kept to a practical minimum. The crossflow nebuliser was used as a means of sample introduction into the spectrometer.

2.2.2 Inductively Coupled Plasma Emission Spectrometer (ICP - ES)

A Jarrell - Ash (model ICAP 9000) simultaneous spectrometer (30 channels) equipped with an Apple II micro computer was used. The ICP source is formed by the coupling of a flowing stream of ionised argon gas with a 2.5 kW crystal controlled Radio Frequency (R.F) generator operating at 27.12 MHz. Sample is introduced to the high temperature plasma as an aerosol mist and the particles undergo desolvation, decomposition, atomisation / excitation and ionisation / excitation. The atomic and ionic emission characteristic of the analyte elements is received by the spectrometer and the signals processed by the computer.

The quartz torch (based on a design by Fassel (55)), surrounded at the top end by a water cooled copper induction coil, is coupled to a spray chamber and nebuliser. The torch consists of two concentric tubes (outer and intermediate) which supply the coolant and auxiliary argon gas

and an inner smaller diameter axial tube (nebuliser) used to introduce the aerosol through the plasma.

To initiate the plasma a tesla coil is used to ionise the non - conducting argon gas and provide a seed of electrons which become thermally excited in the alternating R.F. field provided to the coil. A rapid rise in electron energy promotes further ionisation of the argon and the collision / excitation processes develop and maintain the plasma. Once the plasma has formed a hole is punched through the flattened base (creating a torroidal structure) by the introduction, through the nebuliser tube, of the sample aerosol.

The aerosol is produced by a fixed crossflow nebuliser, this consists of a liquid - carrying capillary tube at a right angle to a capillary tube carrying the high velocity argon nebuliser gas stream set in a Teflon body. A pressure differential created across the sample capillary orifice draws the sample solution through the capillary where collision with the nebuliser gas stream creates an aerosol. The aerosol passes to a spray chamber, where large droplets are removed to waste, then to the plasma.

Data acquisition, via the Apple II micro computer, is controlled by a user defined software method. The method details the elements chosen from the polychromator, the delay time and the integration time. The number of integrations (1 - 10), the output mode (concentration or intensity) and in what form the output is printed (individual integrations, average and

standard deviation) are chosen by the operator, using a command sequence, at the time of acquisition.Emission time profiles are accomplished using a separate piece of software (Time Study) which measures signal intensity as a function of time (seconds) for all the elements defined in the method used.

2.2.3 Operating parameters

Details of instrumentation and operating parameters are given in Table 2.1.

Forward Power	1.1 kW
Observation Height	15 mm
Coolant Argon	18 lpm
Nebuliser Argon	0.5 lpm
Carrier Stream Flow Rate	1.0 ml / min
Pump Tubing	1.42 mm i.d.
Delay Time	9 s
Integration Time	30 s
Output Mode	Intensity Data
Analytical Wavelengths	
Chromium	267.72 nm
Aluminium	308.22 nm
Calcium	317.90 nm
Magnesium	279.50 nm

Table 2.1 ICP Operating Parameters

2.3 Operating and sampling procedures

The FI manifold was set up (Figure 2.1) and measurements started after the ICP - ES had been allowed to stabilise (15 - 30 minutes)

2.3.1 On - line sampling

With the alumina micro column in the FI manifold (acidic or basic) the peak integration method was initiated on the micro computer. The carrier stream intensity signal for the elements (Cr, Al, Ca and Mg) was obtained using the software command sequence, this was repeated until the intensities were stable. With the injection valve in the "load" position the loop (200 - 5000 µl) was filled with the sample using a disposable polyethylene syringe. Immediately coincident with turning the valve to the "inject" position the software procedure was started, by keyboard command, to record and output the intensity data of the elements (Cr, Al, Ca and Mg). This recorded signal was due to sample not retained on the alumina micro column. With the injection valve returned to the "load" position, the loop (200 µl) was filled with eluant solution and again on turning the valve to the "inject" position the data acquisition immediately started. The recorded intensity signal was now due to analyte eluted from the alumina micro column. The eluant injection and data acquisition cycle was repeated until the eluant baseline signal was reached.

To obtain emission time profiles the "Time Study" software routine was

called up, the method to be used and the time scale (60 - 100 seconds) entered. Using this software allowed the delay and the integration times, needed for the peak integration method, to be calculated. After loading the chromium sample on to the alumina micro column the eluant was injected and at the same time data acquisition commenced. From the "graphics printout" the delay and integrations times were measured. Graphical representation of the separation of chromium (III) and (VI) and the preconcentration capability of the alumina micro column using the "Time Study" software was also obtained. Software manipulation enabled the profiles of the same element but from different runs to be overlaid and printed out.

2.3.2 Off - line sampling

The FI manifold (acidic or basic), without the alumina micro column in place, was set up. The alumina micro column was conditioned (made acidic or basic), off - line, by passing through nitric acid or ammonia solutions (0.02 M, 2.0 ml) respectively, using a 2.0 ml disposable polyethylene syringe as shown in Figure 2.3. Chromium (III) and (VI) solutions (2.0 - 8.0 ml) were drawn through the conditioned micro column into the syringe, then passed back through the column out to waste. The sampled alumina micro column was then inserted into the FI manifold and the retained chromium species eluted and measured as detailed earlier.

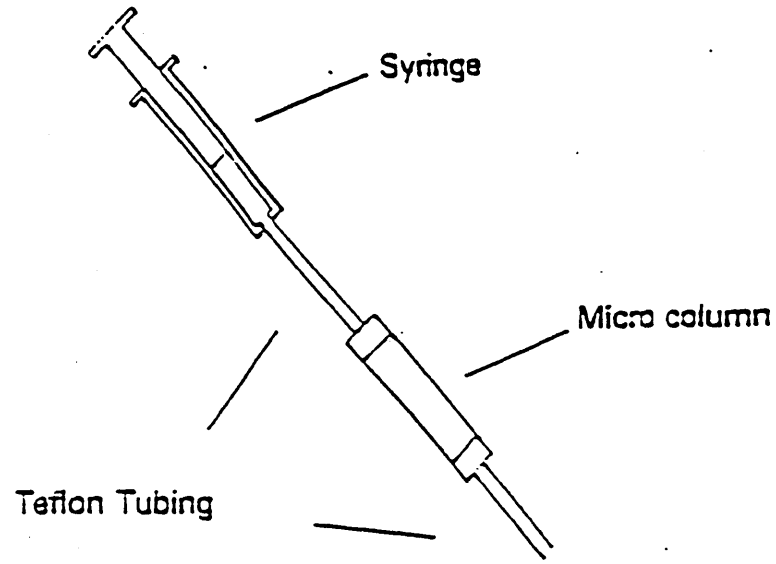

Figure 2.3 Off - Line Sampling Apparatus

2.3.3 Field sampling

At the field sampling site (Figures 2.4, 2.5) a river water sample was obtained using a pre-cleaned polyethylene container (2.5 l). Columns were then conditioned (Fig. 2.6) using one of two methods, first as already detailed by passing nitric acid or ammonium hydroxide (0.02 M, 2.0 ml) through the micro column using a syringe or by having stored the micro columns in either nitric acid or ammonium hydroxide solutions (0.02 M).

The river water sample (2.0 - 8.0 ml) was then drawn through the micro column, using a syringe, and passed back out to waste. The micro columns were returned to the laboratory inserted into the appropriate FI manifold and the retained chromium species eluted and measured as

detailed earlier.

A river water sample was also taken from the container into a pre-cleaned polyethylene bottle, acidified to less than pH 2 using concentrated nitric acid (BDH Chemicals, Aristar) and returned to the laboratory for measurement of total chromium.

Figure 2.4 River Don Field Sampling Site

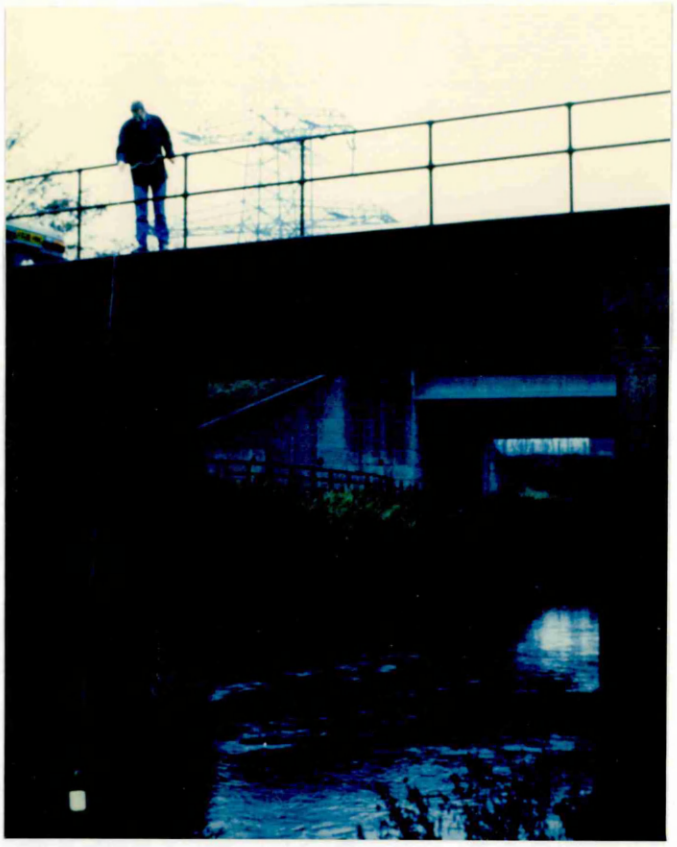

Figure 2.5 River Rother Field Sampling Site

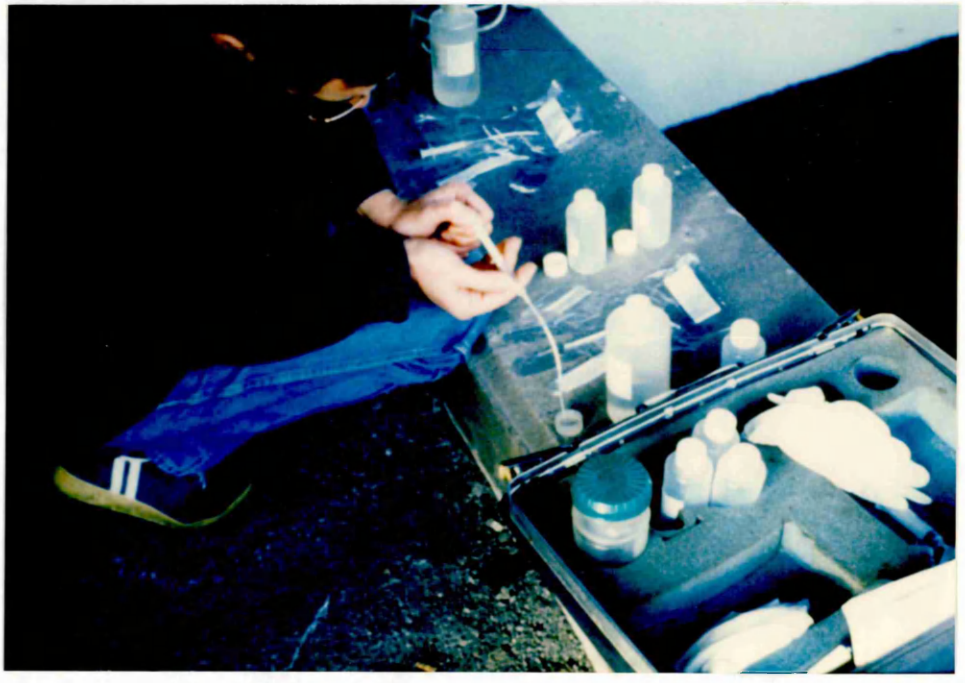

Figure 2.6 On site field sampling

CHAPTER THREE

THE CHARACTERISATION OF ACIDIC ALUMINA AS A CHROMIUM (VI) ANION EXCHANGE MATERIAL

3.1 Introduction

The need for obtaining chromium speciation data has been discussed in Chapter One. This Chapter examines the potential of the alumina micro column incorporated into a FI - ICP - ES system for the determination of the chromium (VI) species. Preconcentration of chromium (VI) is particularly important because expected concentrations in natural waters may be at or below the LOD of the ICP - ES technique.

The anion exchange characteristics of activated alumina (acidic form) for the separation and determination of the chromium (VI) species are investigated; first with synthetic solutions and then with reference waters. The process (50) by which the proposed anion exchange takes place is illustrated in Figure 3.1.

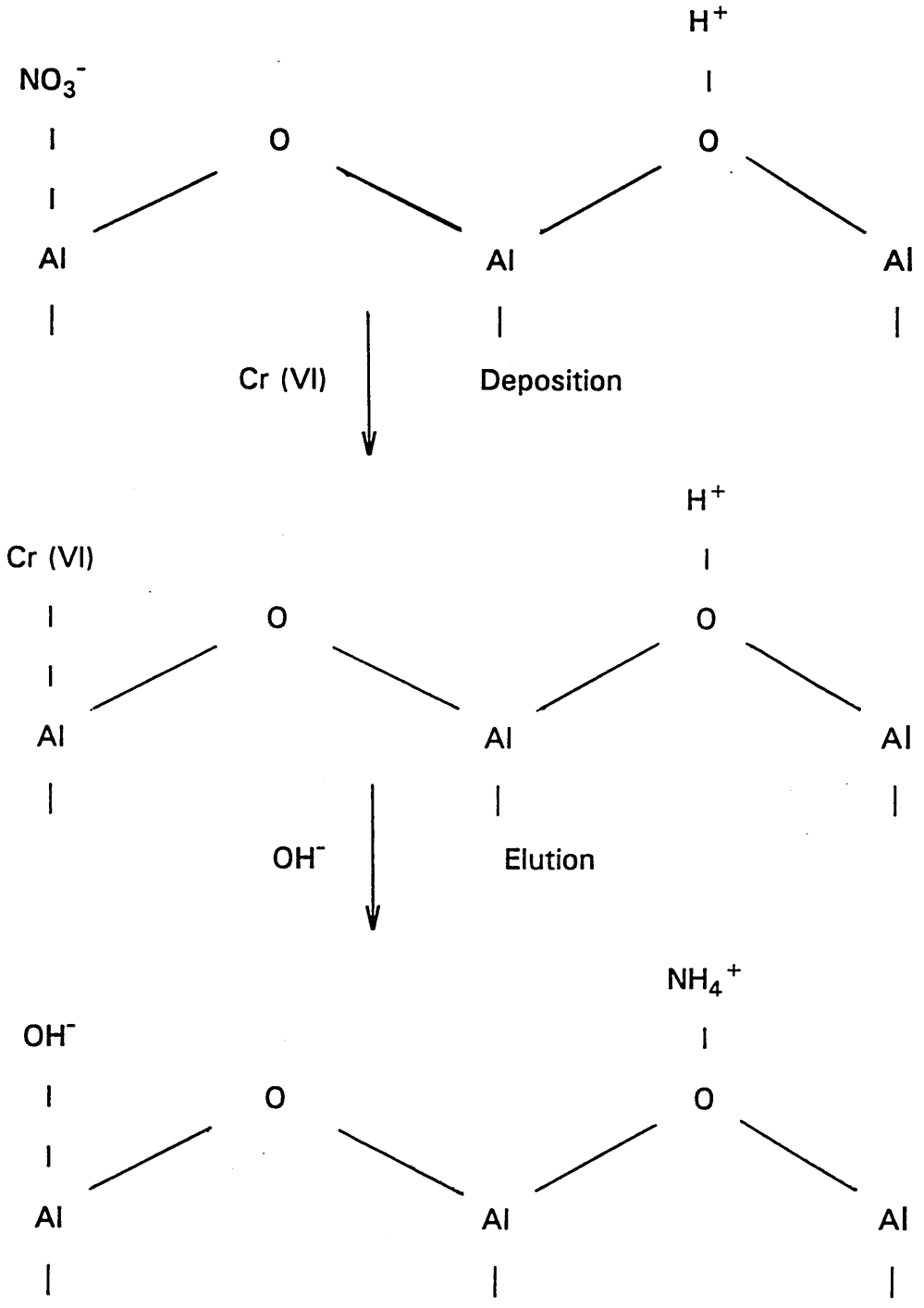

Figure 3.1 Anion Exchange Mechanism

3.2 Initial Characterisation

In the phosphate procedure McLeod et al. (52) investigated the effects of sample acid concentration and the nature and concentration of the eluant on the retention and elution of phosphate in the FI manifold. These parameters were also investigated to ensure efficient deposition onto and elution of the chromium (VI) from the activated alumina micro column, whilst at the same time ensuring that chromium (III) is separated on line. An analyte enrichment route is also needed for samples of low concentration to increase method sensitivity.

There are five key parameters that need to be examined if characterisation of the FI - ICP - ES system for chromium (VI) is to be accomplished. These are :-

1. **Nature and strength of the carrier stream.**
   In the phosphate system, water was used as the carrier stream and the acidic alumina micro column was regenerated by:
   (a) the passage of the acidic sample
   (b) the injection of acid solution after each sampling cycle.
   A better arrangement would result if the carrier stream was acidic, and used to maintain the alumina micro column in the acidic form, rather than the injection of acid solution after each sampling cycle.

2. **Degradation of the alumina micro column.**

   The effect the acid and the base have on the alumina during their passage through the micro column needs to be examined to ensure maximum possible micro column life.

3. **Nature and strength of the eluant.**

   The type and concentration of the base needed to ensure quantitative removal of the retained chromium (VI) species from the alumina micro column.

4. **Separation of chromium (III) species.**

   Once optimised for chromium (VI) retention and elution, the system must allow the chromium (III) cation species to pass through (unaltered) the micro column for determination.

5. **Chromium (VI) preconcentration capability.**

   The limit of detection for chromium by ICP - ES, based upon twice the standard deviation of the background signal, is 5 µg/l (conventional nebulisation). This FI manifold design offers the opportunity to concentrate chromium (VI) on the alumina micro column by the passage of large sample volumes through the system. If accomplished this would extend the ICP - ES detection capability. Experiments were designed to examine the above parameters.

3.2.1 Nature and strength of the carrier stream.

An acidic carrier stream was used in order to maintain the alumina in the acidic form, in an attempt to dispense with the injection of acid (used in the phosphate study) after the injections of base.

For the acid to be effective it must :-

a) Maintain the alumina in the acidic form so that only anionic chromium (VI) species are retained.

b) Allow the base to efficiently remove (elute) the retained chromium (VI) species from the alumina micro column.

c) Be able to quickly reconvert the alumina back to the acidic form, after the injections of base, ready for the next sample cycle.

Carrier stream flow rates were fixed at 1 ml/min, since previous work (56) had shown this was the optimum flow rate for the crossflow nebuliser fitted to the Jarrell Ash ICAP 9000. Previously published anion exchange selectivity orders have shown nitrate as one of the most weakly absorbed anions (only perchlorate is weaker). This means that the chromium (VI) anion species should easily replace the nitrate ion in the proposed ion exchange process. For this reason, and that it is easily obtained in the pure (BDH, Aristar) form, nitric acid was chosen as the carrier stream.

The eluant chosen, aqueous potassium hydroxide (0.5 M, 200 µl), was initially used at the same concentration as for the phosphate determination (52). Optimisation was considered later.

The FI - ICP - ES system was set up (as detailed in Chapter Two) and studies carried out on six different nitric acid concentrations (0.8, 0.4, 0.1, 0.05, 0.01 and 0.005 M).

In practice the system was allowed to stabilise with each nitric acid carrier stream concentration and a chromium (VI) solution (1 mg/l, 200 µl) was injected into the manifold. The retained chromium (VI) was then eluted by an injection of potassium hydroxide (0.5 M, 200 µl) for determination by ICP - ES, (Table 3.1). The signal due to the chromium (VI) sample injection was also determined

Nitric Acid Carrier Concentration (M)	Signal Intensity		
	Carrier	Sample Cr (VI)	Elution Cr (VI)
0.8	2065	2070	6100
0.4	2068	2074	6549
0.1	2072	2078	6900
0.05	2078	2078	7342
0.01	2083	2085	7502
0.005	2088	2094	7553

Note: Each result is the average of three replicates.

Table 3.1 Effect of nitric acid carrier concentration upon deposition (1 mg/l, 200 µl) of Cr(VI) solution with elution by potassium hydroxide (0.5 M, 200 µl)

Immediately after each chromium (VI) sampling and elution cycle, a chromium (III) solution (1 mg/l, 200 µl) was injected into the manifold for each of the six nitric acid concentrations and the results are shown in Table 3.2.

Nitric Acid Carrier Concentration (M)	Signal Intensity Cr (III)
0.8	15010
0.4	15052
0.1	15034
0.05	15048
0.01	15024
0.005	12730

Note: Each result is the average of three replicates.

Table 3.2 Effect of nitric acid carrier concentration upon deposition (1 mg/l, 200 µl)of Cr (III) solution

The results in Table 3.1 show a steady increase in the eluted chromium (VI) signal as the nitric acid carrier stream concentration decreases. This means that the base, potassium hydroxide (0.5 M, 200 µl), is increasingly more able to convert the acidic alumina micro column to the basic form and so remove the retained chromium (VI) anion species. Comparison of the carrier stream and chromium (VI) sample signals, for each nitric acid concentration used, shows no difference between the two signals. This indicates that every nitric acid concentration used is capable of maintaining the alumina in the acidic form. Breakthrough of the chromium (VI) species would otherwise occur and result in an increase in the sample chromium signal.

What is not apparent, but is shown in Table 3.2, is the ability of the carrier stream to reconvert the alumina back to the acidic form after the basic elution injections. If the alumina was acidic the cationic chromium (III) species would not be retained on the micro column but pass straight through for determination. The 0.005 M nitric acid carrier stream shows some retention of the chromium (III) species, indicating that the alumina micro column was not totally reconverted to the acidic form in the same time span as the other acid concentrations used. The results show that a continuous sample - elution cycle of injections is possible with nitric acid carrier stream concentrations greater than 0.005 M. The results also indicate that the retained chromium (VI) species is efficiently removed from the alumina micro column with nitric acid concentrations less than 0.05 M.

3.2.2 Degradation of the alumina micro column.

With the alumina micro column being subjected to a continual flow of dilute nitric acid there could possibly be chemical attack on the alumina.

To study this the aluminium line (308.22 nm) was simultaneously monitored on the ICP - ES during the sampling cycle. Results for the aluminium signal due to the nitric acid carrier streams as well as distilled water are shown in Table 3.3.

Nitric Acid Carrier Concentration (M)	Signal Intensity Aluminium
0.8	17875
0.4	10632
0.1	4527
0.05	3642
0.01	2477
0.005	2401
Distilled Water	2223

Note: Each result is the average of three replicates

Table 3.3 Effect of nitric acid carrier concentration upon removal of aluminium from micro column

These results show that there is significant chemical attack on the alumina micro column using nitric acid carrier streams greater than 0.05 M. The results for 0.005 and 0.01 M nitric acid show only a slight increase in signal intensities over the distilled water background signal (2,477 against 2,223).

These results together with the conclusions reached in section 3.2.1 show that 0.01 M nitric is the optimum carrier stream, and this concentration was used in all further work.

3.2.3 Nature and strength of the eluant.

The eluant used up to this point had been based upon the findings of the phosphate study. To optimise elution efficiency, 200 µl injections of potassium hydroxide solutions (2.0, 1.5, 1.0, 0.5 and 0.1 M) and ammonium hydroxide solutions (3.0, 2.0, 1.0, 0.5 and 0.1 M) were studied. All results are based upon the chromium signal obtained from the elution of a chromium (VI) solution (1.0 mg/l, 200 µl) deposited on the alumina micro column using a 0.01 M nitric acid carrier stream. The results using potassium hydroxide as the eluant are given in Table 3.4, and for ammonium hydroxide as eluant are given in Table 3.5. The ICP - ES software was used to obtain corresponding emission time profiles (detailed in chapter two) and are shown in Figure 3.2 and 3.3 for potassium hydroxide and ammonium hydroxide respectively.

Potassium Hydroxide Concentration (M)	Signal Intensity Chromium (VI)
2.0	ICP Extinguished
1.5	10104
1.0	9603
0.5	8641
0.1	4950

Note: Each result is the average of three replicates

Table 3.4 Effect of potassium hydroxide on elution (200 µl) of Cr (VI) solution (1.0 mg/l, 200 µl)

Ammonium Hydroxide Concentration (M)	Signal Intensity Chromium (VI)
3.0	13175
2.0	13105
1.0	13197
0.5	12128
0.1	7979

Note: Each result is the average of three replicates

Table 3.5 Effect of ammonium hydroxide (200 µl) on elution of Cr (VI) solution (1.0 mg/l, 200 µl)

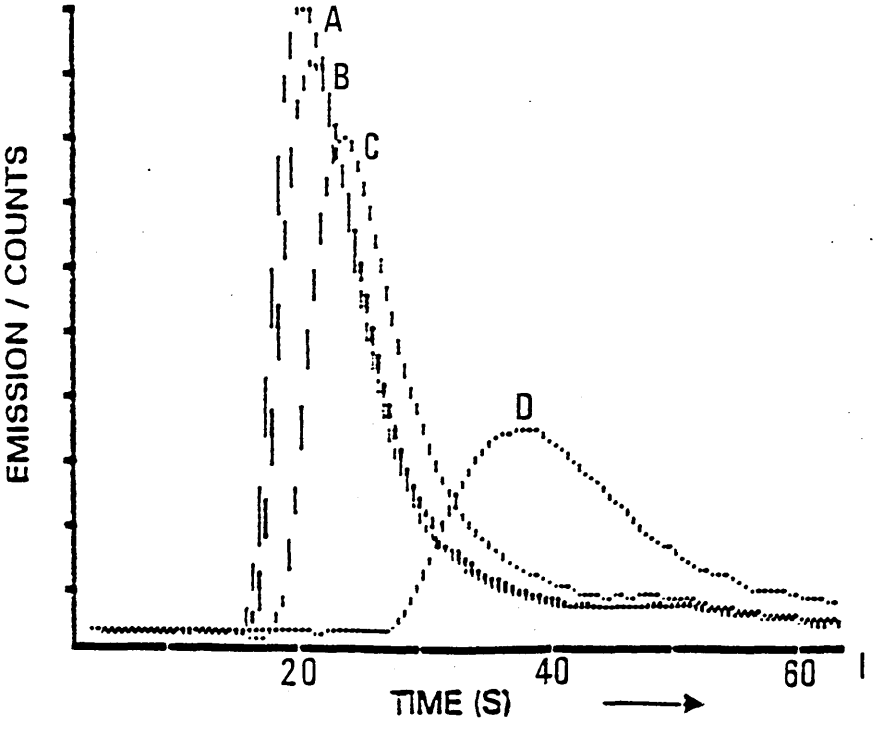

Figure 3.2 Emission (267.72 nm) - time response for elution of Cr (VI) (1.0 mg/l , 200 µl) using potassium hydroxide (200 µl) (A, 1.5 M; B,1.0 M; C, 0.5 M; D, 0.1 M)

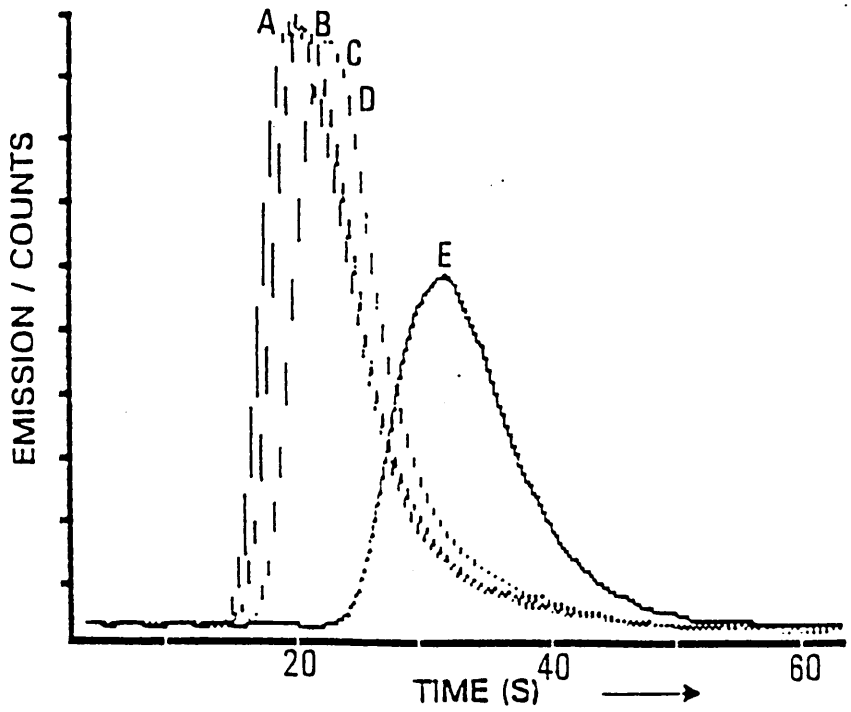

Figure 3.3 Emission (267.72 nm) - time response for elution of Cr (VI) (1.0 mg/l, 200 µl) using ammonium hydroxide (200 µl) (A, 3.0 M; B, 2.0 M; C, 1.0 M; D, 0.5 M; E, 0.1 M)

From a comparison of Tables 3.4 and 3.5, it would seem that ammonium hydroxide is more efficient at removing the retained chromium (VI) species than potassium hydroxide. However experiments revealed that chromium emission intensity was supressed in the presence of high concencentrations of potassium hydroxide in contrast to that for ammonium hydroxide. For example; signal intensities for chromium standard solutions containing potassium hydroxide (1.0 M) were approximately 30% lower than for simple aqueous standards or standards prepared in ammonium hydroxide (1.0 M)

The emission time profiles also show differences in peak shape for the eluted chromium signal against the concentration of the eluant used. As the concentration of the eluant increases so the eluted chromium reaches the plasma sooner and the peak becomes sharper (the signal reaches maximum emission intensity virtually straight away) then tails off to the background signal (a reduced dispersion peak(53)). This indicates that the frontal zone of the eluant plug removed the retained chromium (VI) species as the eluant passed through the column. The chromium signal due to the least concentrated of the eluents gives a typical limited dispersion peak (53) and is some 10 seconds slower in reaching the ICP - ES indicating that mixing of the eluant and chromium occurred during the passage through the column. The results (Table 3.5) show that ammonium hydroxide solutions (200 µl) of concentrations greater than 0.5 M were the most efficient at removing the retained chromium (VI) species. As in the carrier stream study (3.2.1) no further conclusions were reached before a study was carried out on the degradation of the alumina by both eluents.

3.2.4 Degradation of the alumina micro column.

To study the possible degradation of the alumina in the micro column injections of potassium hydroxide and ammonium hydroxide solutions were made. The aluminium line (308.22 nm) was monitored during the elution cycle, and emission time profiles were obtained (Figure 3.4 and 3.5 respectively).

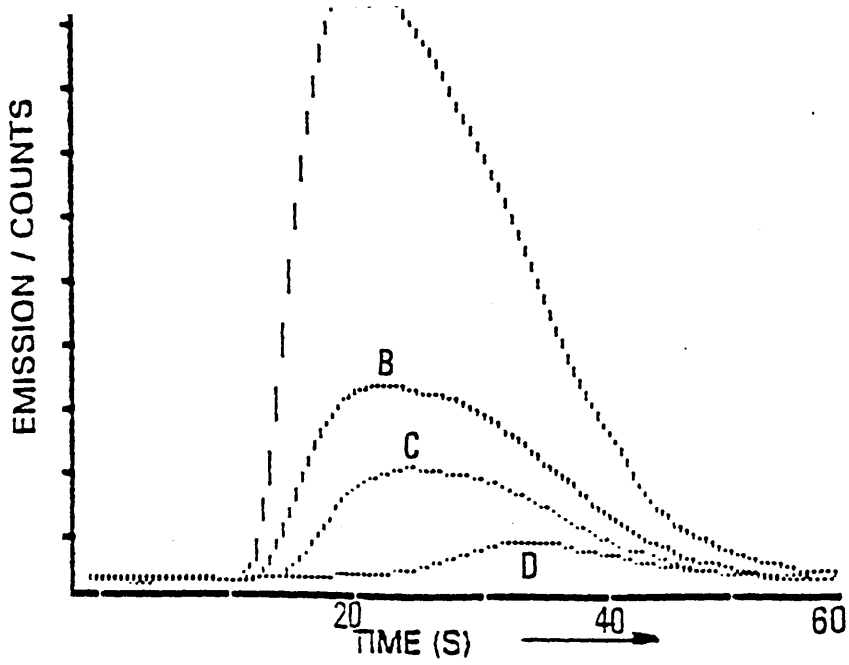

Figure 3.4 Emission (308.22 nm) - time response for aluminium using potassium hydroxide (200 µl) as eluent (A, 1.5 M; B, 1.0 M; C, 0.5 M; D, 0.1 M)

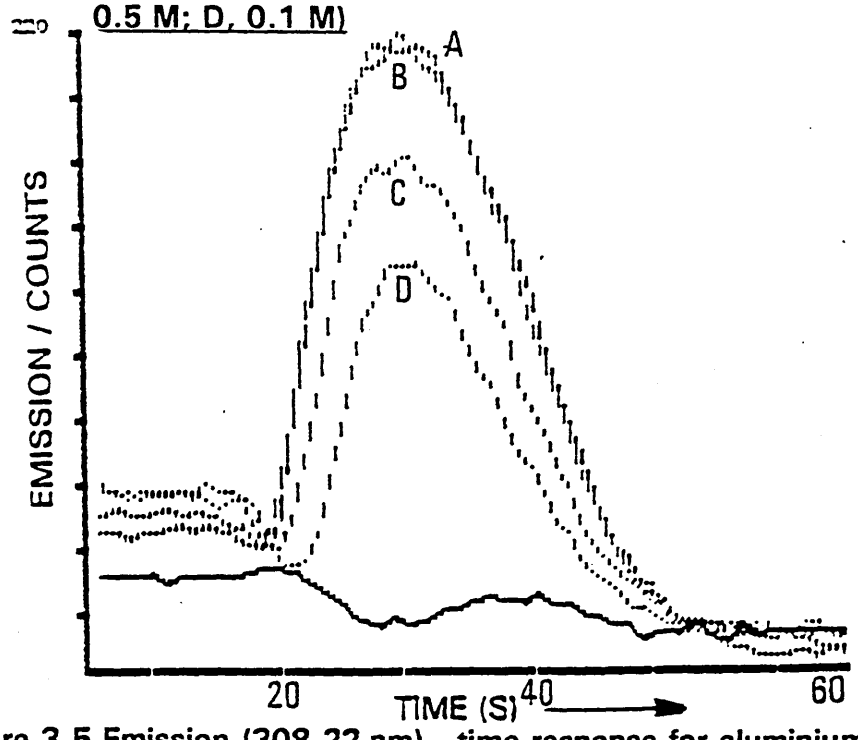

Figure 3.5 Emission (308.22 nm) - time response for aluminium using ammonium hydroxide (200 µl) as eluent (A, 3.0 M; B, 2.0 M; C, 1.0 M; D, 0.5 M; E, 0.1 M)

The profiles show that both potassium hydroxide and ammonium hydroxide solutions remove aluminium from the column during the elution cycle. There was a considerable difference though between the amounts. The aluminium concentrations were approximately 30 times greater with potassium hydroxide (60 versus 2 ug/ml) reflecting significant chemical attack on the alumina by potassium hydroxide. Again, with the potassium hydroxide solution (1.5 M), a frontal zone effect can be seen (a reduced dispersion peak (53)). The least concentrated potassium hydroxide solution produced a typical limited dispersion peak (53) which reached the ICP - ES some 10 seconds later than the 1.5 M potassium hydroxide peak.

Taking into account the results from the previous study and to minimise any possible changes in column performance over extended periods of time, all further work was carried out using 1.0 M (200 µl) ammonium hydroxide as eluant.

3.2.5 Retained chromium (VI) recovery.

Having optimised the concentration and nature of the carrier and eluant it was necessary to study whether one injection of the eluant quantitatively removed the retained chromium (VI) species from the alumina micro column, or if not whether the percentage removed was a reproducible amount for a number of sample / elution cycles.
This was achieved using two different methods:

Emission time profiles, Peak integrations.

An emission time profile was obtained for a chromium (VI) solution (1.0 mg/l, 200 µl), using the FI manifold, without the column in place. This produced a typical limited dispersion peak that enabled the calculation of the 100% peak area measurement to be made. The column was then replaced in the FI manifold and the same chromium (VI) solution (1.0 mg/l, 200 µl) injected onto the column and an emission time profile obtained for the eluted chromium signal and the area calculated. From these two peak areas the % recovery is calculated.

A chromium (VI) solution (1.0 mg/l, 200 µl) was injected on to the column using the FI manifold and the chromium (VI) signal due to the first injection of eluant measured using the integration software of the ICP- ES. The chromium (VI) signal due to the second injection of the eluant was then measured and this subtracted from the first eluted signal, the whole being divided by the first eluted signal minus the background signal due to the eluant.

Ten sample - elution cycles selected at random for a chromium (VI) solution (1.0 mg/l, 200 µl) over a three week period were used to calculate % recovery.

The overlaid emission time profiles are shown in Figure 3.6

$$\% \text{ Recovery} = \frac{\text{Area under eluted peak}}{\text{Area under peak (no column)}} \times 100$$

The areas under the peaks were calculated from the profiles using a planometer.

$$\% \text{ Recovery} = \frac{0.250}{0.290} \times 100$$

% Recovery = 86

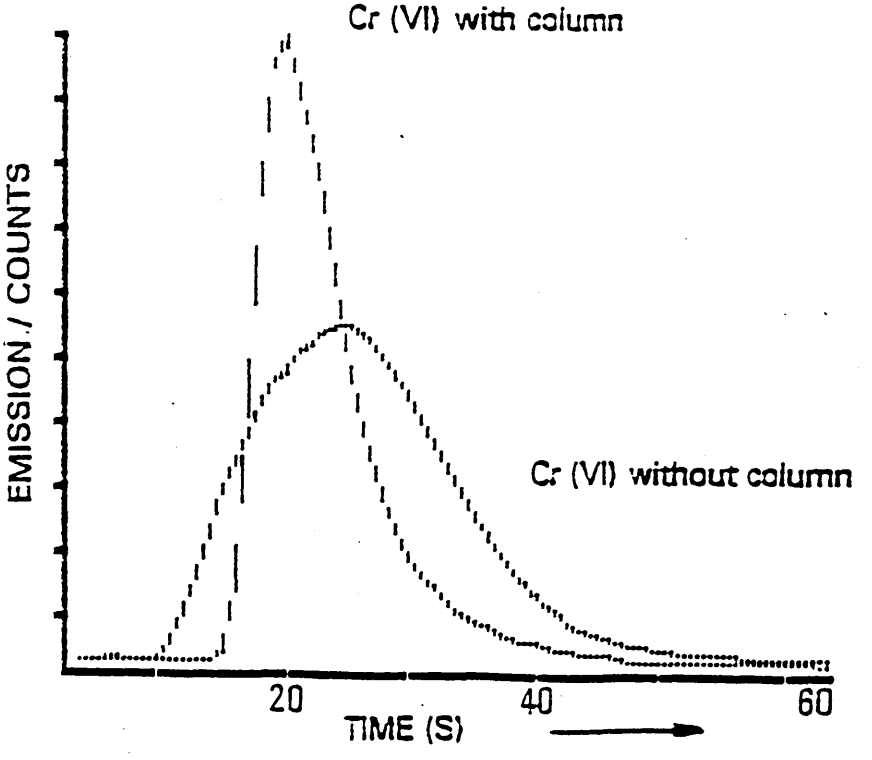

Figure 3.6 Emission (267.72 nm) - time response for Cr (VI) solution (1.0 mg/l, 200 µl) with / without the alumina micro column

For the peak integrations a sample calculation is given below :-

$$\% \text{ Recovery} = \frac{\text{First eluant Cr signal - Second eluant Cr signal}}{\text{First eluant Cr signal - Background eluant signal}} \times 100$$

$$\% \text{ Recovery} = \frac{14{,}951 - 4{,}816}{14{,}951 - 3071} \times 100$$

$$\% \text{ Recovery} = 85.3$$

The ten random sample / elution cycles gave an average recovery of 85.9% (relative standard deviation 2.0%). The excellent precision obtained from these results, over the three week period, shows the reliability of the FI manifold incorporating the alumina micro column. Both methods, emission time profiles and peak integrations, also produced the same % recovery and give confidence in the results obtained.

The results also show that quantitative recovery was not obtained with one injection of the eluant and that several injections of the eluant were needed to return to the baseline eluant signal. As the column must be clean, i.e. have no deposited chromium (VI) solution remaining before the next sample / elution cycle, the number of eluant injections (ammonium hydroxide, I.0 M, 200 µl) needed was studied. A range of chromium (VI) solutions (0.1, 0.5, 1.0, 5.0, 10.0 mg/l) were deposited

one at a time upon the alumina micro column and eluted. For all the chromium concentrations used, 3 injections of the eluant (ammonium hydroxide, 1.0 M, 200 µl) were needed to clear the column and return to the base line eluant signal.

The emission time profile of the elution signal for chromium (VI), (fig 3.6) gives information about the delay time (time taken for the eluted chromium signal to reach the plasma) and the signal integration time (time the chromium signal was resident in the plasma). These values were measured using the time scale axis (delay time 9 seconds and integration time 30 seconds) and incorporated into the data acquisition software.

3.2.6 Effect of FI Manifold on Cr III species.

In order to ensure that on line separation of chromium (III) and (VI) takes place, cationic chromium (III) must pass through the micro column unhindered under the experimental conditions optimised for anionic chromium (VI). To test this requirement a chromium (III) solution (0.1 mg/l, 200 µl) was injected into the system and an emission time profile obtained. The alumina micro column was then removed from the FI manifold and replaced with a piece of tubing of the same length and a repeat injection of the chromium (III) solution (0.1 mg/l, 200 µl) carried out and the emission time profile obtained. These two profiles overlaid, are shown in Figure 3.7.

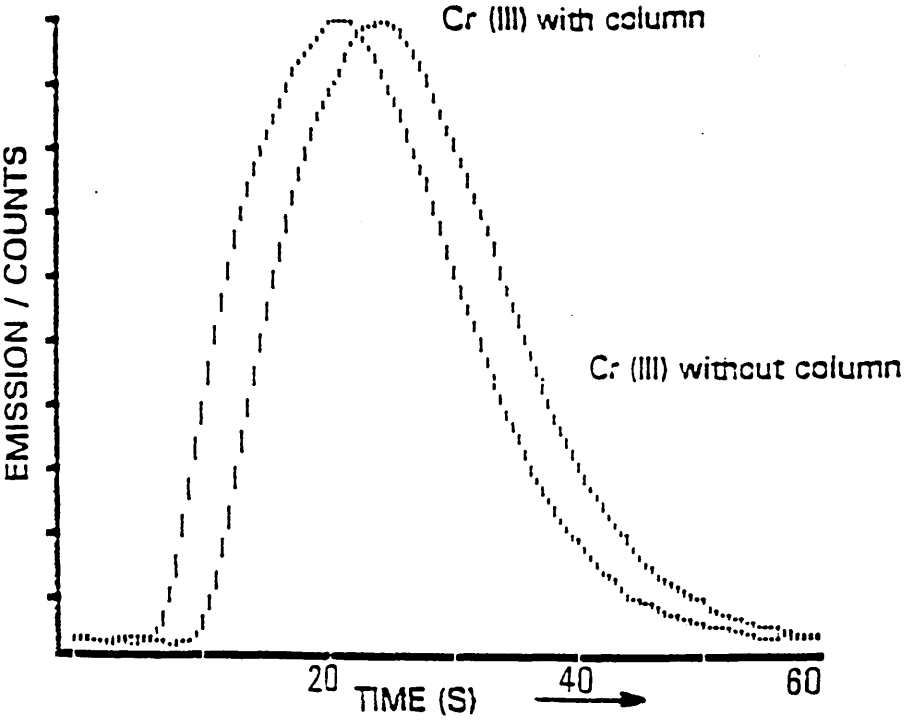

Figure 3.7 Emission (267.72 nm) - time response for Cr (III) solution (0.1 mg/l, 200µl) with / without the alumina micro column

The profiles show that both peaks are identical in shape and area and both give typical limited dispersion peak profiles (53). This means that the chromium (III) solution was not retained and the acidic alumina micro column has no effect on the chromium (III) species, and is totally selective for chromium (VI). The profile shows that the chromium (III) signal without the column in place reaches the plasma first. This is because no compensation was made for any difference in flow rate

there might be having removed the alumina micro column from the FI manifold. That there is a difference is due to back pressure produced by the column in the FI manifold.

There are two further points from this emission time profile. First the delay time (time taken for the Cr (III) signal to reach the plasma) is virtually identical (l0 seconds) to that for the eluted chromium (VI) signal (9 seconds), reinforcing the point that a frontal zone of the eluant plug was responsible for removing the retained chromium (VI) species. Second the residence time in the plasma for the chromium (III) signal is 40 seconds against 30 seconds for the chromium (VI) signal. This means that measurements for chromium (III), if the integration time is left at 30 seconds, would not include the whole peak, but as the FI manifold is known to be highly precise (53) the same portion of the signal will be measured every time, and reproducible results will be obtained. To alter the integration time from 30 to 40 seconds between injections would involve a large amount of software manipulation, and rather than include a large portion of the background for the measurement of the eluted chromium (VI) signal, the integration time was left at 30 seconds

3.2.7 Separation of chromium (III) and (VI).

The system has so far been optimised using single chromium solutions. Chromium (VI) has been retained on the alumina micro column prior to elution / quantitation and chromium (III) was unaffected by the passage

through the alumina micro column. To show whether or not on line separation of chromium (III) and (VI) is possible, a mixed chromium (III) and (VI) solution (0.1 mg/l) was injected (200 µl) into the FI system followed by the injection of ammonium hydroxide (l.0 M, 200 µl) and the emission time response recorded. This is given in Figure 3.8 .

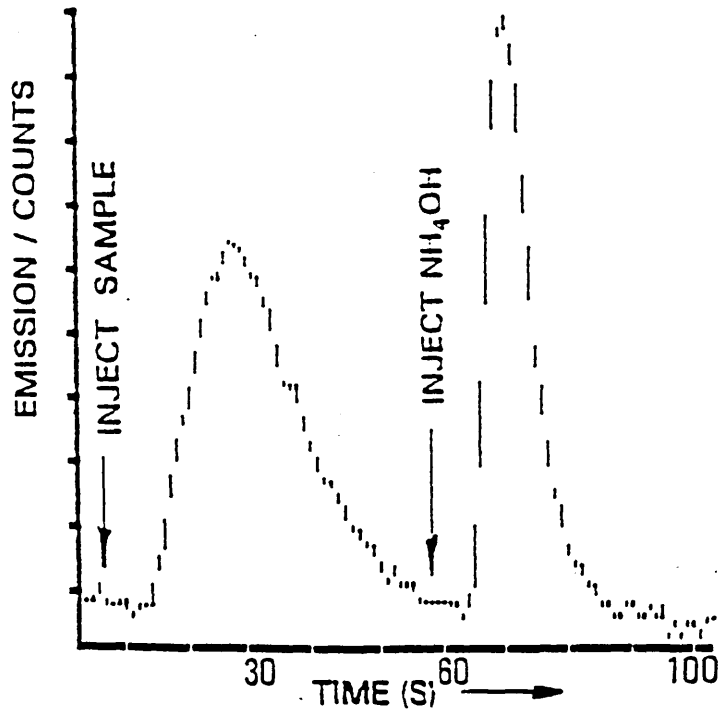

Figure 3.8 Emission (267.72 nm) - time response for a 200 µl injection of Cr (III) - Cr(VI) solution (0.1 mg/l) and a 200 µl injection of 1.0 M ammonium hydroxide

The emission time response (Figure 3.8) starts at the time the mixed chromium solution was injected, and after l0 seconds the signal due to the chromium (III) species appears. At time = 50 seconds ammonium

hydroxide (I.0 M, 200 µl) was injected and the signal due to the chromium (VI) species appears after a further 9 seconds. The peaks due to the chromium (III) and (VI) species are identical to those seen before but from the respective single species solutions (Figure 3.7 and 3.6 respectively). Hence time - resolved separation of chromium (III) and chromium (VI) has been achieved using the FI - ICP - ES procedure.

3.2.8 Chromium (VI) preconcentration capability.

As already noted the limit of detection for chromium by conventional nebulisation into the ICP - ES is 5 µg/l (55). The acidic alumina micro column, incorporated into the FI manifold, offers the capability to preconcentrate chromium (VI) by the passage of large sample volumes through the system prior to elution. The subsequent elution / quantitation of this preconcentrated chromium (VI) signal would extend the ICP - ES detection capability. The proposed ion exchange mechanism means that there are two linked limiting factors to the alumina preconcentration capability : pH, and the number of available exchange sites. If the acidity of the alumina is altered towards the isoelectric point, by the passage of large sample volumes, then there will be a reduction in the available exchange sites for the chromium (VI) anion species and breakthrough will occur. The volume of alumina used has a finite number of exchange sites (capacity) available for the chromium (VI) species and again if this point was reached by using large sample volumes breakthrough might occur. Until either of these two conditions is experienced it should be possible to preconcentrate

chromium (VI) on the acidic alumina micro column. To study this, sample volumes of 200 µl, 1.0 ml and 2.0 ml of a chromium (VI) solution (20 µg/l) were separately processed. The corresponding emission time profiles are shown in Figure 3.9. It should be noted that only the sample volume was changed, the elution volume was kept constant at 200 µl.

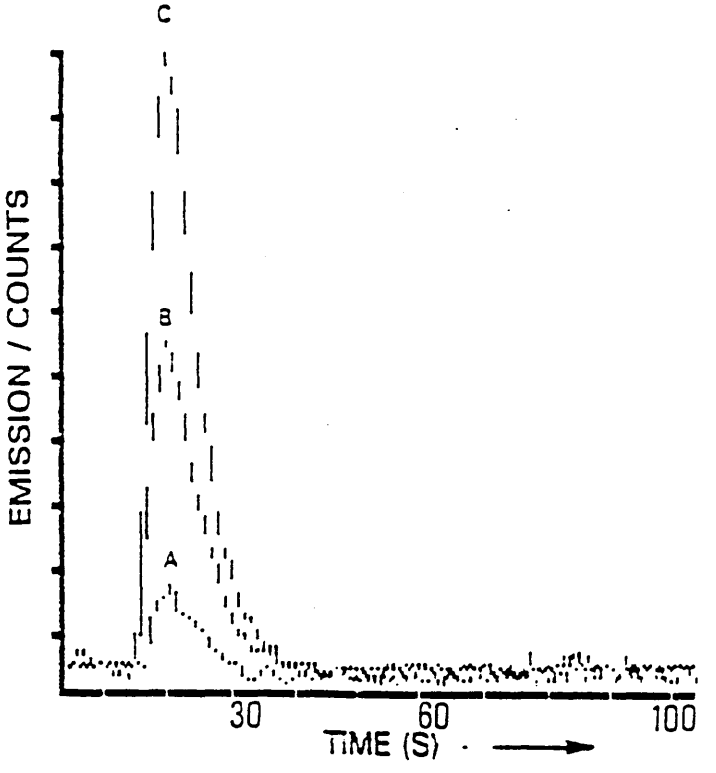

Figure 3.9 Emission (267.72 nm) - time response for elution (200 µl of 1.0 M ammonium hydroxide) of Cr (VI) for various injection volumes of Cr (VI) solution : A, 0.2 ml; B, 1.0 ml; C, 2.0 ml

The eluted signal responses for the three different sample volumes of the same solution (20 µg/l), clearly show that preconcentration was achieved. A separate study of the chromium emission intensities during sample loading showed that breakthrough of chromium (VI) did not occur. This means that the capacity of the alumina micro column was not reached nor the acidity of the alumina altered significantly. What these profiles do indicate is the capability of the FI manifold to improve the detection limits of the ICP - ES for chromium (VI).

3.3 Analytical performance

With the initial characterisation completed and the system configured for optimum performance the full analytical potential was studied by the analysis of reference materials.

3.3.1 Chromium (III) and (VI) calibration graphs.

Freshly prepared mixed standard chromium (III) and (VI) solutions (10, 50, 10, 500 and 1000 µg/l) were separately injected (200 µl) into the FI manifold for elution / quantitation in triplicate. The sample / elution and data acquisition followed a set procedure, using the timings written in the software. For each standard, the signal due to chromium (III) was obtained by subtracting the carrier stream signal from the sample injection signal and the signal due to chromium (VI) obtained by subtracting the baseline eluant signal from the first eluant signal. The

signals for chromium (III) and (VI) were then plotted on separate graphs against concentration (μg/l). For both chromium (III) and chromium (VI) the calibration graphs gave good linearity with correlation coefficients of 0.99998 and 0.99997 respectively. At the 10 μg/l level the relative standard deviations (based upon ten injections) were 10% for chromium (III) and 12% for chromium (VI). This indicates that precision for chromium (VI) was not significantly impaired by the deposition / elution cycle. Limits of detection calculated as twice the standard deviation of the background noise signal were 1.0 μg/l for chromium (III) and 1.4 μg/l for chromium (VI). This indicates the FI manifold did not impair performance and the longer integration times needed, resulted in a more stable signal giving the lower than expected limit of detection (1.0 ug/l against 5.0 ug/l).

3.3.2 Calibration using the preconcentration technique.

To extend the detection range of the ICP - ES for chromium (VI) (1.4 μg/l) the preconcentration capability of the acidic alumina micro column was used. Freshly prepared mixed chromium (III) and (VI) standard solutions (5, 10, 20 and 50 μg/l) were prepared and three sample volumes chosen (200 μl, 1.0 and 2.0 ml). These samples were injected using the appropriate size sample loops. The elution volume in every case was kept constant at 200 μl. Data acquisition was as previously detailed apart from the time between the sample injection and the first elution. This was extended according to the sample volume

injected i.e. for the 2.0 ml sample, a two minute delay was left between sample injection and the first elution. The calibration results for triplicate injections of each standard and each volume are shown in Figure 3.10.

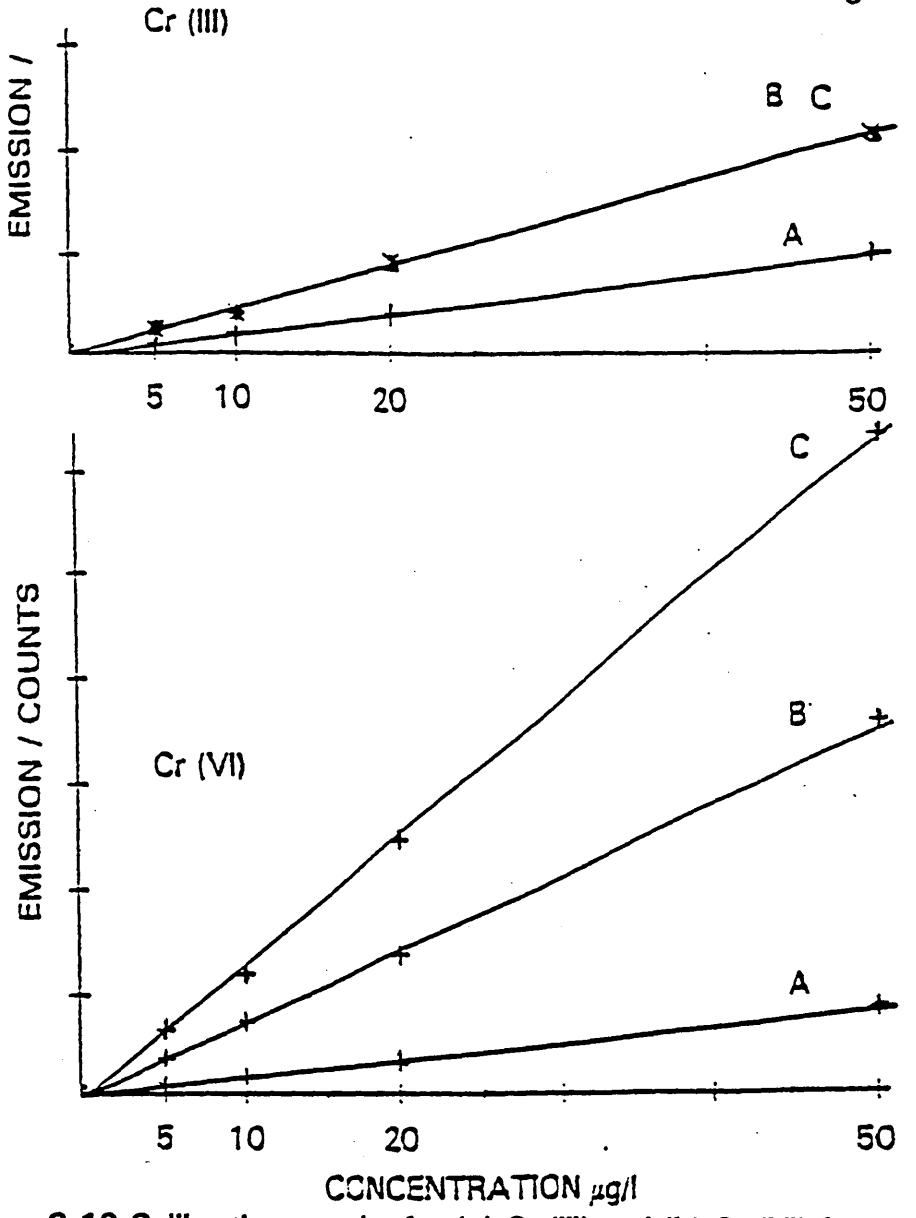

Figure 3.10 Calibration graphs for (a) Cr (III) and (b) Cr (VI) for various injection volumes of Cr (III) - Cr (VI) solution : A, 0.2 ml; B, 1.0 ml; C, 2.0 ml. Elution 200 µl of 1 M ammonium hydroxide

The calibration graphs for chromium (III) show that the 1.0 ml and 2.0 ml sample injection volumes give an identical line. This means that the chromium (III) species was not amenable to preconcentration and the signals for the 1.0 ml and 2.0 ml sample volumes are equivalent to those for conventional nebulisation. So improved sensitivity for chromium (III) using large sample volumes was not possible. Chromium (VI) on the other hand was preconcentrated on the alumina micro column and improved sensitivity thereby realised. The limits of detection based upon the above results for the 2.0 ml sample volume were calculated as 1.4 μg/l for chromium (III) (the same as for the previous calibration graph) and 0.2 μg/l for chromium (VI) a seven fold improvement over the 200 μl sample volume. The relative standard deviation based upon ten injections of a 10 μg/l mixed chromium standard (2.0 ml) were 2.2% for chromium (III) and 1.1% for chromium (VI) which is a significant increase in precision over the previous results obtained without preconcentration.

3.4 Determination of chromium (III) and (VI) in reference waters.

The FI - ICP - ES system was applied to the determination of chromium (III) and (VI) in two reference waters :- NIST Trace Elements in Water (CRM 1643a) and British Geological Survey Reference Water (C2) There are very few reference waters available with certified values for chromium in the low μg/l range and none at all with certified values

for separate chromium species. The certified value of NIST CRM 1643a for total chromium is 17 ± 2 ng/g, (value for the B.G.S sample not available).

3.4.1 Emission time profile for NIST CRM 1643a.

Before analytical work was started an initial emission time profile of each reference water was obtained for a 200 µl sample injection volume and this was overlaid with an injection of a mixed chromium (III) and (VI) standard solution (0.1 mg/l, 200 µl). The profile for the NIST CRM 1643a is shown in Figure 3.11.

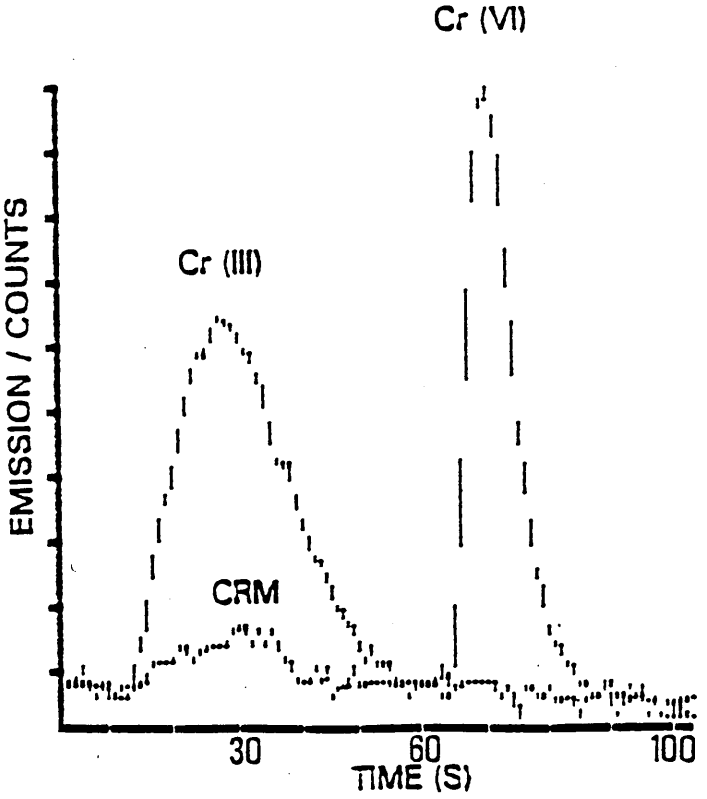

Figure 3.11 Emission (267.72 nm) - time response for 200µl injection of Cr (III) - Cr(VI) solution (0.1 mg/l) and NIST CRM1643a. Elution, 200µl of 1 M ammonium hydroxide

Inspection of the figure reveals that the predominant chromium oxidation state for the NIST CRM 1643a is chromium (III), this was also true for the BGS C2 reference water. This means preconcentration of chromium (VI) is required to obtain meaningful analytical data for both reference waters.

3.4.2 Analytical data for reference waters.

Freshly prepared mixed chromium (III) and (VI) standard solutions (10, 20 and 50 µg/l) were used to obtain chromium (III) and (VI) calibration graphs for two sample volumes (200 µl and 2.0 ml). The two reference waters were then separately injected, using the same sample volumes, and results determined from the calibration graphs. Each reference water was injected seven times for each sample volume to obtain precision data and the results are given in Table 3.6.

Sample	Concentration / µg/l			
Injection	NIST 1643a *		BGS C2	
Volume	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
200 µl	15.0 ± 2.1	N.D.	13.5 ± 1.8	N.D.
2.0 ml	14.8 ± 1.0	1.96 ± .32	13.5 ± 1.4	0.51± 0.22

Note: Number of Injections for each measurement, 7

Uncertainty Limits, ± 2σ

Not Detected, N.D.

* Certified chromium value 17 ± 2 ng/g

Table 3.6 Determination of Cr (III) and Cr (VI) in Reference Waters

The data obtained confirms that the predominant oxidation state, for both samples, was chromium (III) and preconcentration was needed to detect chromium (VI). The results also show that certainly for the NIST reference water, the chromium (III) and chromium (VI) additive results (16.76 ± 1.32 µg/g) are in very good agreement with the certified value (17 ± 2 µg/g). These results were later confirmed by Subramanian (33) who analysed the same NIST CRM 1643a reference water and found substantially the same results for the speciated data (Cr (III) 14.6 + 0.5 and Cr (VI) 2.1 + 0.3 ug/l).

3.5 Conclusion

A technique for the rapid sequential determination of chromium (III) and chromium (VI) using a micro column of activated alumina (acidic form) in a FI - ICP - ES system has been developed. Key operating parameters, nature and strength of carrier and eluent, were investigated and optimised. The capability of the technique for on-line preconcentration of the chromium (VI) species was demonstrated, and the limit of detection was 0.33 µg/l with a 2 ml sample volume.

The long term reliability of the alumina micro column was successfully shown, the same micro column being used for the duration of the study.

The analytical performance of the technique was demonstrated, and the application to the determination of chromium (VI) in reference waters was successfully accomplished.

The rapid measurement time (approximately 20 samples per hour) and the achieved detection limit (chromium (VI) 0.33 µg/l) are seen to be a significant advance over procedures currently available.

This work formed the basis of a publication (57).

CHAPTER FOUR

THE CHARACTERISATION OF BASIC ALUMINA AS A CHROMIUM (III) CATION EXCHANGE MATERIAL

4.1 Introduction

The potential of the acidic micro column linked with the FI - ICP - ES system has been demonstrated. The ability to extend the detection capability of the ICP - ES by preconcentration is important particularly so for chromium (VI).

This enrichment procedure, using an acidic alumina micro column was successful for chromium (VI) but not for not chromium (III). However, alumina is amphoteric by nature and its ion exchange properties are strongly pH dependent (50), its anion exchange capacity increases as the acidic pH decreases and cation exchange capacity increases as the basic pH increases (49). If the alumina used in the micro column is in the basic form then it is expected to function as a cation exchanger.

This chapter examines the cation exchange characteristics of activated alumina (basic form) in the separation and determination of chromium (III) species, first in synthetic solutions and then applied to reference waters.

The process (50) by which the proposed cation exchange takes place is illustrated in Figure 4.1.

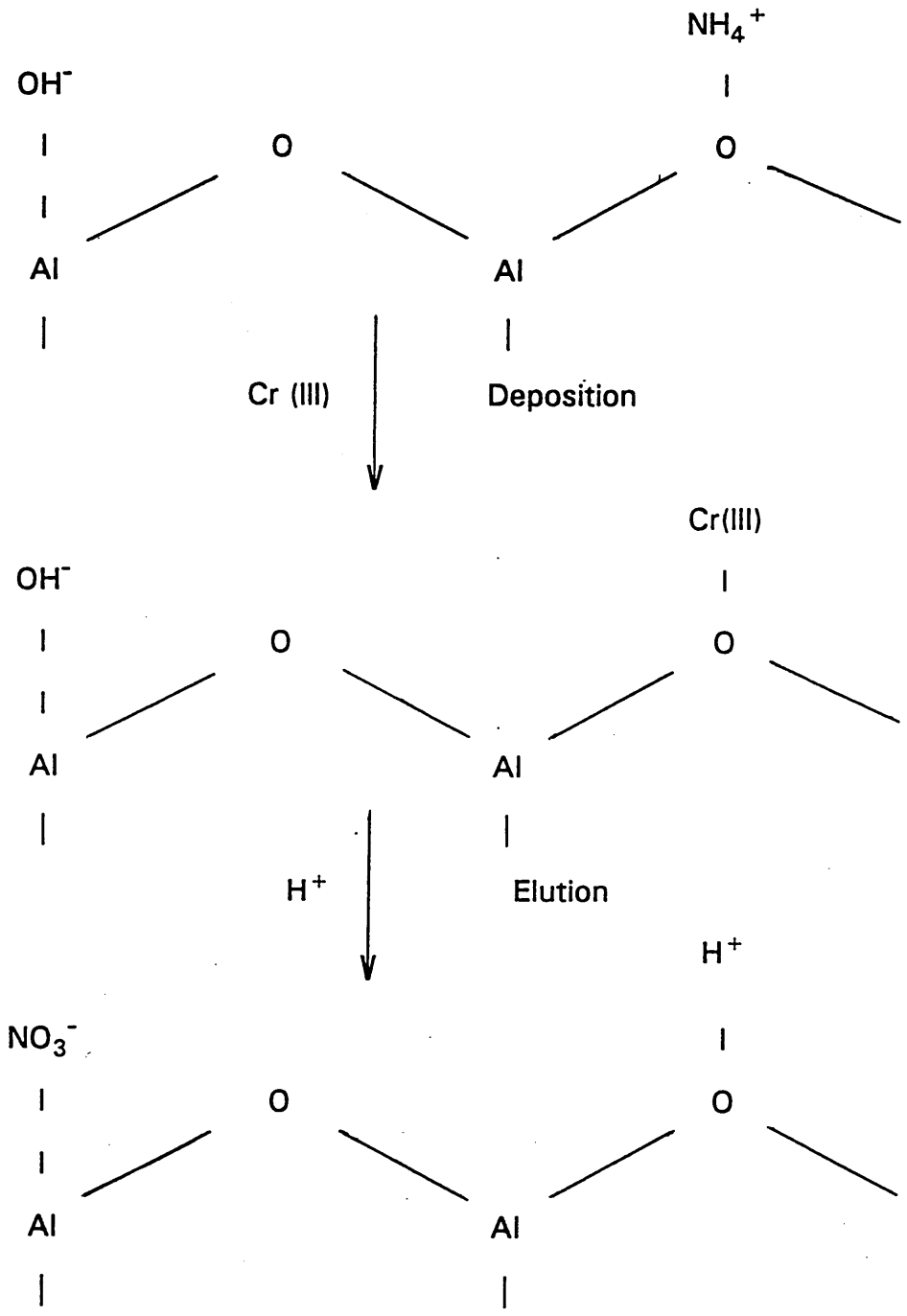

Figure 4.1 Cation exchange process

4.2 Initial characterisation.

As in the characterisation of the acidic alumina FI - ICP - ES system there are five key factors that need to be investigated to ensure optimum performance. These are :

1. Nature and strength of the carrier stream. The proposed ion exchange process means that the alumina must be kept in the basic form for it to retain the cationic chromium (III) species. As already demonstrated the optimum method to achieve this is to have a carrier stream continually generating the required alumina form. This means that for this system the carrier must be basic.
2. Nature and strength of the eluant. The acidic eluant must be able to quantitatively remove the retained chromium (III) species from the alumina micro column.
3. Degradation of the alumina micro column. The effects of the basic carrier stream and the acidic eluant on the alumina micro column need to be examined in order to maximise micro column life.
4. Separation of chromium (VI). The optimised conditions for the retention and elution of chromium (III) must not affect the passage of chromium (VI) through the system so that on line separation can be achieved.
5. Chromium (III) preconcentration capability. The capability to extend the detection range of the ICP - ES, for the chromium (III) species using the alumina micro column as a means of sample enrichment prior to chromium (III) elution / quantitation . Experiments were

designed to examine the above parameters.

4.2.1 Nature and strength of the carrier stream.

Potassium hydroxide and ammonium hydroxide solutions have already been used as eluents in the acidic system and the adverse effect potassium hydroxide has on the alumina micro column noted. Even the use of very dilute potassium hydroxide solutions as the carrier would greatly reduce the effective life of the alumina. For this reason the carrier stream study was limited to the use of ammonium hydroxide solutions, which have been shown to have a less damaging effect. For the ammonium hydroxide carrier stream to be effective it must :

Maintain the alumina in the basic form so that only chromium (III) cation species are retained.

Allow the acid to efficiently remove (elute) the retained chromium (III) from the alumina micro column.

Be able to quickly reconvert the alumina back to the basic form, after the injections of the acid, ready for the next sample cycle.

The FI - ICP - ES system was set up as previously detailed (Chapter Two) and studies were carried out on four different ammonium hydroxide concentrations (0.10, 0.05, 0.02 and 0.01 M). In practice the system was allowed to stabilise with each ammonium hydroxide carrier stream concentration, and a chromium (III) solution (0.5 mg/l, 200 µl) was then injected onto the column. The retained chromium (III) was then eluted with nitric acid (0.5 M, 200 µl) (nitric acid was used for

reasons which will be discussed later). The signal due to the injection of the chromium (III) solution and the eluted signal are shown in Table 4.1. Immediately after each chromium (III) sampling and elution cycle, a chromium (VI) solution (0.5 mg/l, 200 µl) was injected for each of the four ammonium hydroxide carrier streams and the results are shown in Table 4.2 .

Ammonium Hydroxide Carrier Concentration (M)	Signal Intensity		
	Carrier	Sample Cr (III)	Elution Cr(III)
0.1	1530	1532	2336
0.05	1525	1529	2488
0.02	1538	1540	2632
0.01	1534	1538	2646

Note: Each result is the average of three replicates.

Table 4.1 Effect of ammonium hydroxide carrier concentration upon deposition (0.5 mg/l, 200 µl) of Cr (III) solution with elution of nitric acid (0.5 M, 200 µl)

Table 4.1 shows an increase in the chromium (III) eluted signal as the ammonium hydroxide carrier stream concentration decreases. This means the acid eluant injection (0.5 M, 200 µl) is more able to convert the basic alumina to the acidic form and so release the retained

chromium (III). Comparison of the carrier stream signal and the signal obtained when the chromium (III) solution was injected shows no difference between them for any of the ammonium hydroxide concentrations used. This means that breakthrough of the chromium (III) did not occur and that each concentration of ammonium hydroxide used was capable of maintaining the alumina in the basic form.

Ammonium Hydroxide Carrier Concentration (M)	Signal Intensity Cr (VI)
0.1	7350
0.05	7310
0.02	7320
0.01	5012

Note: Each result is the average of three replicates.

Table 4.2 Effect of ammonium hydroxide carrier concentration upon deposition of Cr (VI) solution (0.5 mg/l, 200 µl)

The results in Table 4.2 show that when a carrier stream of 0.01 M ammonium hydroxide is used some retention of chromium (VI) takes place. Clearly the alumina micro column is not totally regenerated to the basic form in the same time span as the other carrier solutions used. In fact it took approximately 5 minutes to re- establish the column basicity. Any of the higher concentration solutions would be satisfactory subject to any possible degradation of the alumina.

4.2.2 Degradation of the alumina micro column

During the carrier stream study, the aluminium line (308.22 nm), was simultaneously monitored on the ICP - ES to determine whether or not the alumina was subjected to chemical attack by the ammonium hydroxide carrier stream. Results for the aluminium signal due to the continual passage of the ammonium hydroxide carrier streams through the alumina micro column and distilled water are shown in Table 4.3. These results show there was no significant attack on the alumina by any of the ammonium hydroxide carrier stream concentrations used. Hence the carrier stream concentration used in all further work was 0.02 M ammonium hydroxide solution. This enables rapid regeneration of the alumina to the basic form after the elution cycle and gives maximum elution efficiency.

Ammonium Hydroxide Carrier Concentration (M)	Signal Intensity Aluminium
0.1	1050
0.05	1010
0.02	993
0.01	990
Distilled Water	982

Note: Each result is the average of three replicates.

Table 4.3 Effect of ammonium hydroxide concentration upon removal of aluminium from micro column

4.2.3 Nature and strength of the eluant.

The proposed ion exchange mechanism shows the chromium (III) cations will attach to the oxygen of the dis - associated alumina hydroxyl group having displaced the weakly attached NH_4^+ group. Treating the alumina with acid (eluant) the protons of the acid (which are the most strongly absorbed cations (49)) replace the chromium (III) cations attached to the oxygen atom.

Of the acids available only hydrochloric and nitric are readily obtainable in a pure (BDH Aristar) form. This level of purity is needed to reduce the risk of possible chromium contamination when high concentrations of acid are injected to elute the retained chromium (III) species.
It is accepted that concentrated solutions of mineral acids affect the operation of the ICP - ES pneumatic nebuliser, changes in the physical properties of the acids particularly, density, viscosity and surface tension result in a reduction of the relative sensitivity of the analyte (58). Nitric and hydrochloric are the best of the mineral acids, in that they have the least effect, with nitric acid being the better of the two.

For these reasons and that nitric acid was successfully used as the carrier stream in the acidic system it was decided to optimise the basic system using only nitric acid as the eluant. Five concentrations of nitric acid were chosen (3.0, 2.0, 1.0, 0.5 and 0.1 M) and 200 µl injections of each were used as the eluant. All results (Table 4.4.) are based upon the chromium signal obtained from the elution of a chromium (III)

solution (0.5 mg/l, 200 µl) deposited upon the alumina micro column using a 0.02 M ammonia solution carrier stream. They show that the 2.0 M and 3.0 M nitric acid solutions were the most effective at removing the retained chromium (III) species.

Nitric Acid Concentration (M)	Signal Intensity Chromium (III)
3.0	6910
2.0	6950
1.0	6350
0.5	4650
0.1	2262

Note: Each result is the average of three replicates

Table 4.4 Effect of nitric acid on elution (200 µl) of Cr (III) solution (0.5 mg/l, 200 µl)

Emission time profiles of each of the eluted chromium signals were obtained and are shown overlaid in Figure 4.2. The peak shapes are identical to those obtained in the chromium (VI) study (section 3.2.3). When the eluant concentration increases so the eluted chromium signal reaches the plasma sooner and the peak becomes sharper (a reduced dispersion peak(53)). This means that a frontal zone of the eluant plug removed the retained chromium species as the eluant passed through the column.

As before (section 3.2.3), the injection of the least concentrated of the eluents gives rise to a chromium signal that has a typical limited dispersion peak (53) and is some 10 seconds slower reaching the plasma, indicating that mixing of the eluant and chromium occurred.

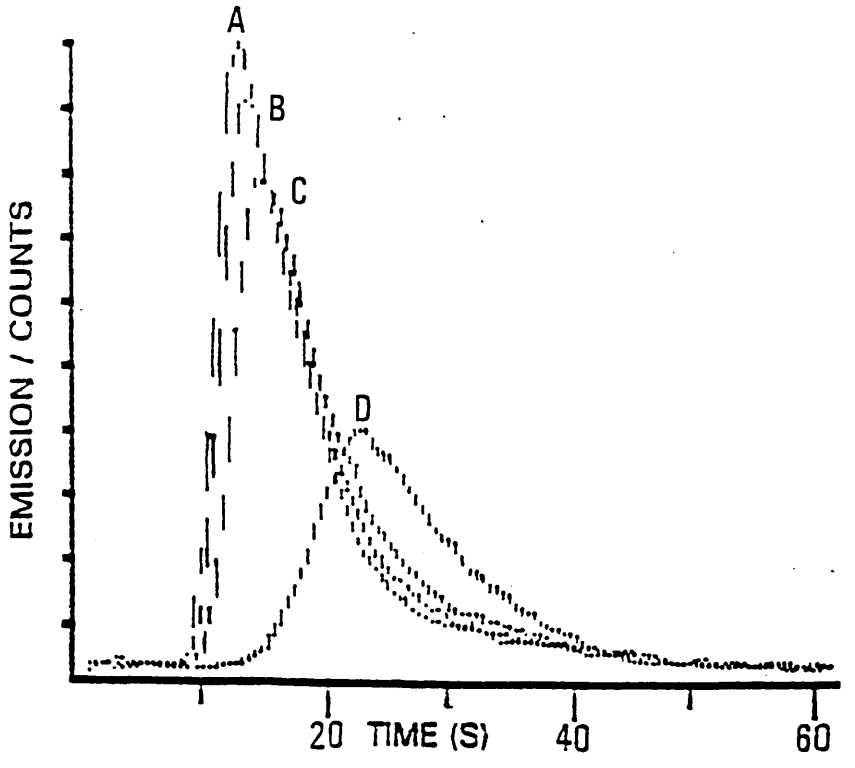

Figure 4.2 Emission (267.72 nm) - time response for elution of Cr (III) solution (0.5 mg/l, 200µl) using nitric acid (200 µl) : A, 2.0 M; B, 1.0 M; C, 0.5 M; D, 0.1 M.

4.2.4 Degradation of the alumina micro column.

To determine whether or not different nitric acid concentrations degraded the alumina micro column, the aluminium line (308.22 nm) was simultaneously monitored during the elution cycle. The results of this study are presented in Table 4.5.

Nitric Acid Concentration (M)	Signal Intensity Aluminium
3.0	5242
2.0	3212
1.0	2100
0.5	1672
0.1	1634

Note: Each result is the average of three replicates

Table 4.5 Effect of nitric acid concentration upon removal of aluminium from micro column

The results indicate that all concentrations of nitric acid remove aluminium from the column during the elution cycle. Even though 2.0 and 3.0 M nitric acid gave identical results for removal of the retained chromium (III) species there is a considerable difference in the aluminium figures.

The aluminium signal due to the injection of 3.0 M nitric acid (200 µl) was almost twice as high as the injection due to the 2.0 M nitric acid (200 µl) (5,242 against 3,212). Thus in order to minimise aluminium loss all further work was carried out using 2.0 M nitric acid (200 µl) as the eluant.

4.2.5 Retained chromium (III) recovery.

Having optimised the carrier and eluant concentrations, the amount of retained chromium (III) eluted with one injection of the nitric acid (2.0 M, 200 µl), i.e. % recovery, was determined.

If recovery was not quantitative with one injection of the eluant then further injections would be needed to clean the column before the next sample cycle could be started.

Recovery was calculated using two different methods :-

- Emission time profiles
- Peak integration

Emission time profiles were obtained for a chromium (III) solution (0.5 mg/l, 200 µl) using the FI manifold with and without the alumina micro column in place.

The areas under the peaks were measured (using a planometer) from the overlaid emission time profiles shown in Figure 4.3.

$$\% \text{ Recovery} = \frac{\text{area under eluted peak}}{\text{area under peak (no column)}} \times 100$$

$$\% \text{ Recovery} = \frac{0.278}{0.301} \times 100$$

Recovery = 92.4 %

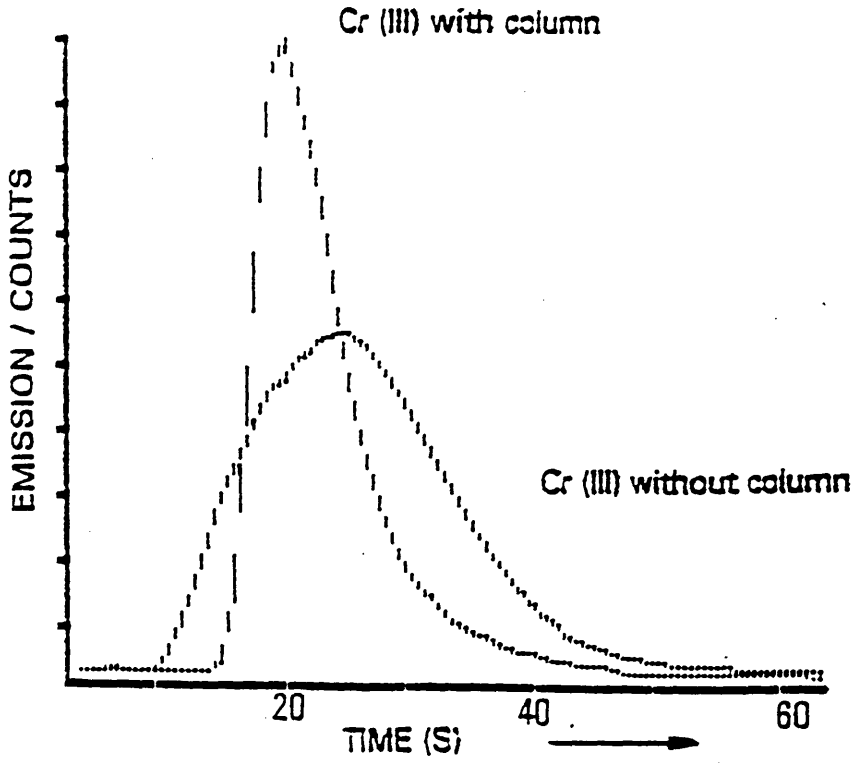

Figure 4.3 Emission (267.72 nm) - time response for Cr (III) solution (1.0 mg/l, 200 µl) with / without the alumina micro column

A chromium (III) solution (0.5 mg/l, 200 µl) was first injected onto the alumina micro column followed by three separate injections of eluant (nitric acid, 2.0 M, 200 µl) The chromium signals from each of the first two eluant injections were measured, and the signal corresponding to the third injection was taken as the background eluant signal.

$$\% \text{ Recovery} = \frac{\text{First eluted Cr signal - Second eluted Cr signal}}{\text{First eluted Cr signal - Background elution signal}} \times 100$$

$$\% \text{ Recovery} = \frac{8{,}010 - 1{,}500}{8{,}010 - 989} \times 100$$

Recovery = 92.7 %

Ten sample / elution cycles gave an average recovery of 92.8 % and a relative standard deviation of 2 %.

This excellent precision data mirrors that found in the chromium (VI) study (section 3.2.5) and reinforces the reliance of the FI manifold. The fact that both methods gave the same % recovery data also gives confidence to the results.

What must not be overlooked is that recovery was not quantitative for a single injection of the eluant, and the column must be clean of any retained chromium (III) before the next sample / elution cycle is commenced. It was found that three nitric acid injections (2.0 M, 200 µl) were needed to clean the column and re-establish the eluant baseline signal, for a variety of chromium (III) solutions (10.0, 5.0, 1.0 and 0.5 mg/l), (200 µl).

The emission time profile (4.3), for the eluted signal, was used to measure the delay time (time taken for the eluted chromium signal to reach the plasma) and the integration time (time the chromium signal was resident in the plasma). These values were measured using the X axis time scale (delay time 9 seconds and integration time 30 seconds) and incorporated into the data acquisition software.

4.2.6 Effect of the FI manifold on the chromium (VI) species

For the system to be effective there must be no effect on the passage of chromium (VI) anion species through the alumina micro column. This would ensure that on line separation of chromium (III) and (VI) takes place.

To study this a chromium (VI) solution (0.1 mg/l, 200 µl) was injected into the FI manifold and the emission time profile recorded. The alumina micro column was then replaced with a piece of tubing the same length, the carrier flow rate adjusted to 1 ml/min., the

chromium (VI) solution injection repeated and the emission time profile obtained.

These two profiles were overlaid and are shown in Figure 4.4.

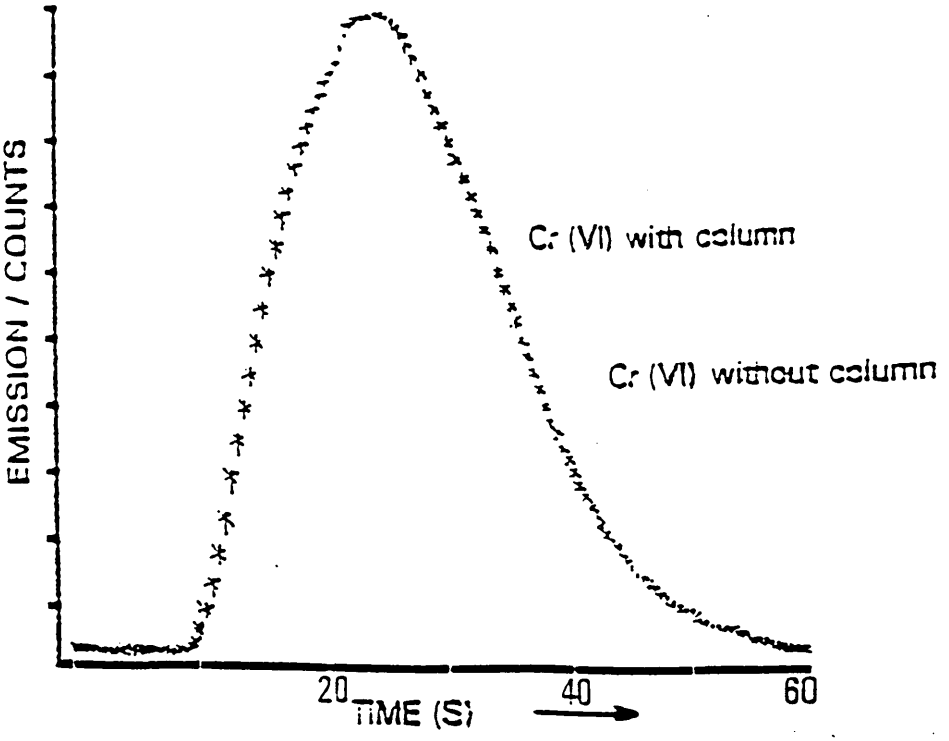

Figure 4.4 Emission (267.72 nm) - time response for Cr(VI) solution (0.1 mg/l, 200 µl) with / without the alumina micro column

The profiles show that both peaks were identical in shape and area and both gave typical FI limited dispersion shapes. This means the basic alumina micro column had no effect on the chromium (VI) solution and is totally selective for chromium (III). The emission time profiles also indicate two further points of information:

i) The delay time is the same for the chromium (VI) peak as the chromium (III) eluted peak, reinforcing the point that a frontal zone of the eluant plug is responsible for removing the retained chromium species.
ii) The residence time in the plasma is ten seconds longer for the chromium (VI) peak (40 seconds) against the chromium (III) eluted peak (30 seconds).

To avoid the large amount of software manipulation that would be required to alter the integration times needed for each different chromium species as it was measured, the integration time was left at 30 seconds. This means that measurements of chromium (VI) signal will not include the whole peak, as the FI manifold is known to be highly precise (53) the same portion of the signal will be measured every time.

4.2.7 Separation of chromium (III) and (VI)

It has been demonstrated that the basic alumina micro column is totally selective for chromium (III) using single chromium species solutions. To demonstrate on - line separation of chromium (III) and (VI) a mixed chromium solution (0.1 mg/l) was injected (200 µl) into the FI system, followed by injection of nitric acid (2.0 M, 200 µl) and the emission time response obtained Figure 4.5 .

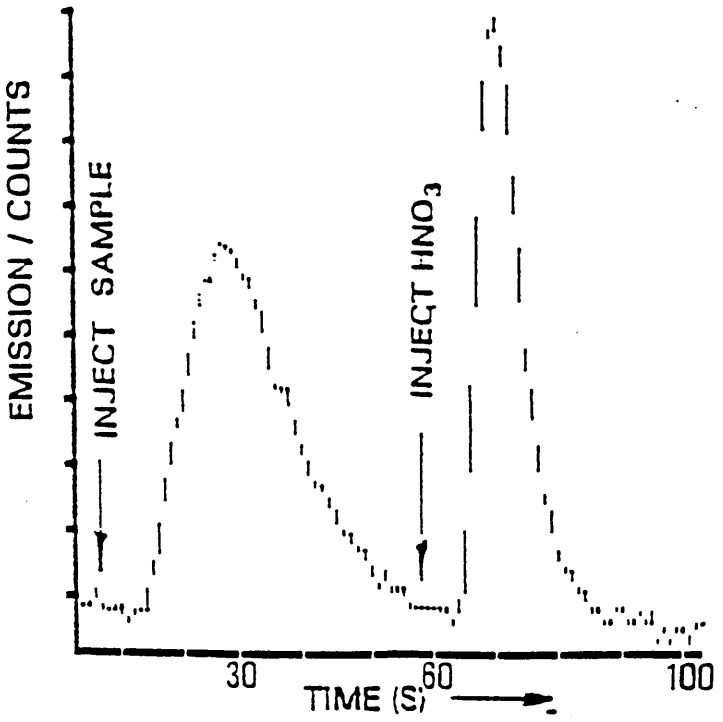

Figure 4.5 Emission (267.72 nm) - time response for a 200µl injection of Cr(III) - Cr(VI) solution (0.1 mg/l) and a 200 µl injection of 2.0 M nitric acid.

The emission time profile starts at the same time as the mixed chromium solution was injected, after 10 seconds the signal due to the chromium (VI) species appears, after 50 seconds nitric acid (2.0 M, 200 µl) was injected and after a further 9 seconds the signal due to the retained chromium (III) species appears.

The peak profiles for each chromium species are identical to those obtained from the respective single solutions. This means that real time / on - line separation of chromium (III) and chromium (VI) has been achieved using the FI - ICP - ES system.

4.2.8 Chromium (III) preconcentration capability

The limit of detection for chromium by conventional nebulisation into the ICP - ES is 5 µg/l (based on twice the standard deviation of the background signal). To be able to measure low µg/l concentrations the detection range of the ICP - ES must be extended. The acidic alumina micro column was very successful in this respect for chromium (VI) species (section 3.2.8), and hence a corresponding evaluation for the chromium (III) species was carried out on the basic alumina micro column. The two linked limiting factors to this preconcentration capability still apply : pH, and the number of available exchange sites.

If the basicity of the alumina is altered towards the isoelectric point (pH 7), by the passage, through the micro column, of large sample volumes at or near the isoelectric point, then there will be a reduction in the available exchange sites for the chromium (III) cation species and breakthrough will occur. The volume of alumina used has a finite number of exchange sites (capacity) available for the chromium (III) cation species and breakthrough would occur if large sample volumes were to be used. It should be possible therefore to preconcentrate chromium (III) cations on the basic alumina micro column until either of these two conditions are met.

To study this three sample volumes (1.0, 2.0 and 5.0 ml) of a chromium (III) solution (4 µg/l) were separately injected into the FI manifold. The overlaid emission time profiles for the corresponding

eluted signals are given in Figure 4.6. It should be noted that although the sample volume was changed the elution volume was kept constant at 200 µl.

The eluted signal responses clearly show that preconcentration was achieved. A separate study of the chromium emission intensities during sample loading, indicated that breakthrough of chromium (III) did not occur meaning that the capacity of the column was not reached or the basicity of the alumina altered for sample volumes up to 5.0 ml.

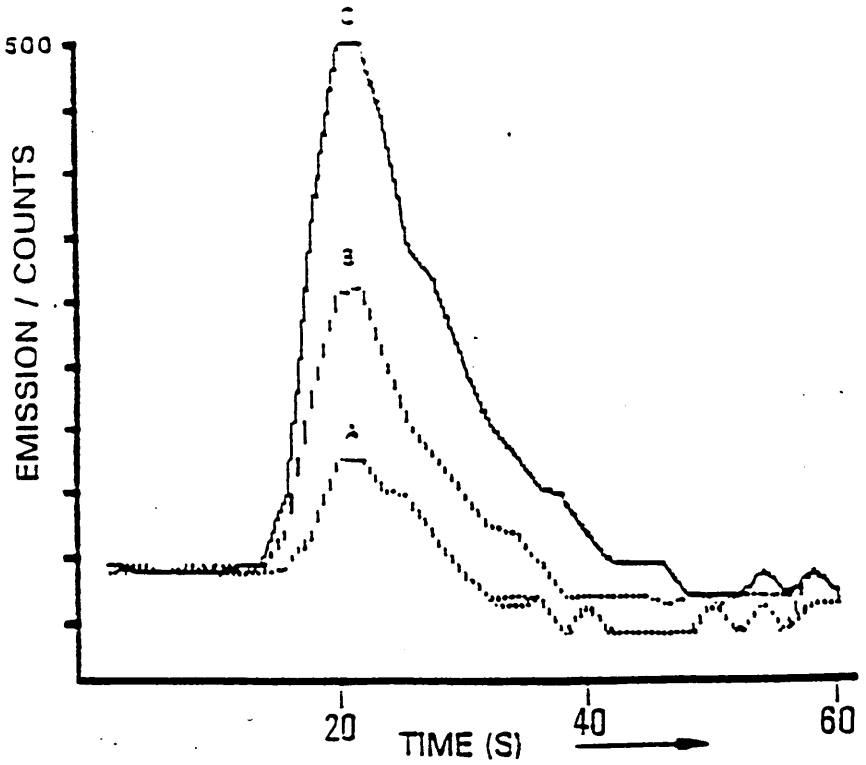

Figure 4.6 Emission (267.72 nm) - time response for elution (200 ul of 2 M nitric acid) of Cr (III) for various injection volumes of Cr (III) solution : A, 0.2 ml; B, 1.0 ml; C, 2.0 ml.

4.3 Analytical performance

With the initial characterisation completed and the system configured for optimum performance, the analytical potential of the system was investigated by the analysis of reference materials.

4.3.1 Chromium (III) calibration graph

Freshly prepared mixed standard chromium (III) and (VI) solutions (10, 20, 50, 100, 250, 500 and 1000 μg/l) were separately injected (200 μl) into the system.

The data acquisition routine using the sample and elution injections has been detailed in Section 3.3.2. As the acidic and basic alumina micro column systems have now been characterised, the preferred method for the quantification of chromium (VI) in solution would be using the acidic alumina micro column. For this reason, only the chromium (III) calibration graph will be commented on.

The chromium (III) graph gave good linearity with a correlation coefficient of 0.99997. The limit of detection calculated as twice the standard deviation of the background noise signal was 0.92 μg/l. At the 10 μg/l level the relative standard deviation (based upon ten injections) was 12 %.

These results are identical to those obtained for chromium (VI) using the acidic alumina micro column at the 200 µl sample volume and again point to the stability and precision of the FI - ICP - ES system.

4.3.2 Chromium (III) calibration using the preconcentration technique

To extend the detection range of the ICP - ES for chromium (III) the preconcentration capability of the basic alumina column was investigated.

Freshly prepared chromium (III) standard solutions (5, 10, 15 and 20 µg/l) were prepared and three sample volumes chosen (2.0, 4.0 and 8.0 ml). These samples were injected using the appropriate sample loops, the elution volume in each case being kept constant at 200 µl. The results for triplicate injections of each standard and each volume are shown in Figure 4.7.

The limits of detection based upon the above results for the 8.0 ml sample volume were calculated as 0.063 µg/l (a 15 fold improvement over the 200 µl sample volume, 0.92 ug/l).

The relative standard deviation based on ten injections of a 10 µg/l chromium (III) standard was 1.2 % which is a significant improvement in precision over the previous results.

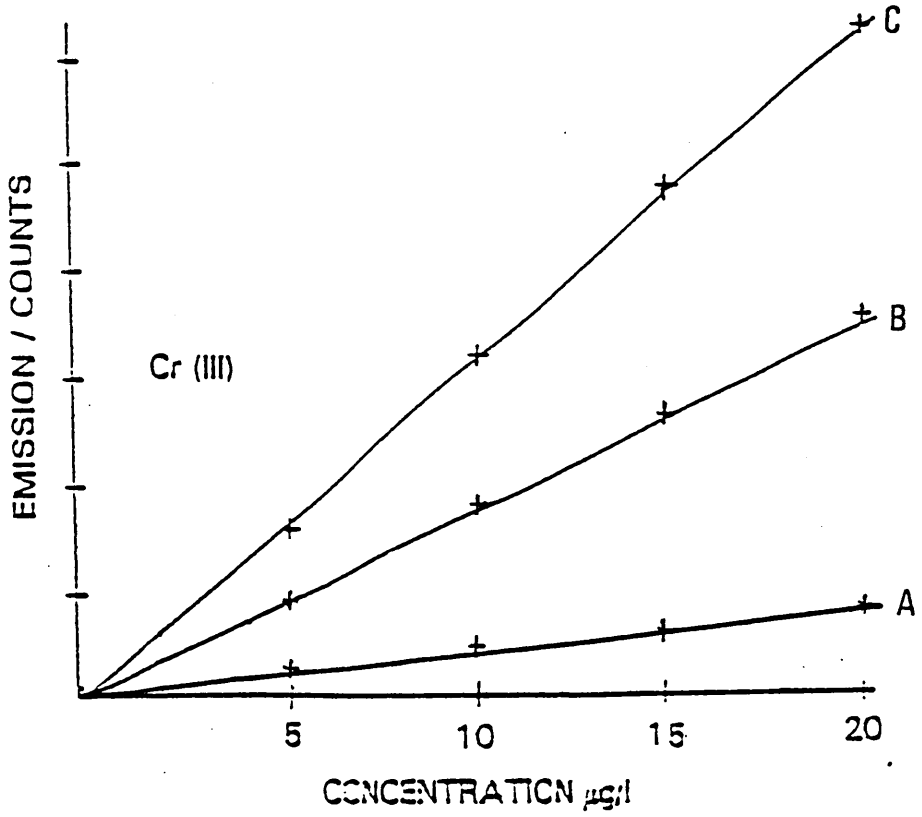

Figure 4.7 Calibration graphs for various injection volumes of Cr (III) solution: A, 2.0 ml; B, 4.0 ml; C, 8.0 ml.

4.4 Determination of chromium (III) in reference waters.

The FI - ICP - ES system was applied to the determination of chromium (III) in National Research Council Canada reference water SLRS - 1, this is a very low level reference water with a certified total chromium value of 0.36 ± 0.04 μg/l. This low value means that a high level of preconcentration will be needed if analytical data is to be obtained.

Freshly prepared chromium (III) standard solutions (5.0, 2.0, 1.0, 0.5 and 0.2 μg/l) were used to obtain a calibration graph based on a sampling volume of 8 ml. The SLRS - 1 reference water was then injected (8.0 ml), and the results obtained from the calibration graph are shown in Table 4.6.

Sample Injection Volume (ml)	Concentration / μg/l	
	SLRS - 1	
	Cr (III)	Cr (VI)
8.0	0.33 ± 0.02	N.D.

Note: Number of Injections for each measurement, 7

Uncertainty Limits, ± 2σ

N.D. Not Detected

Table 4.6 Determination of Cr (III) and Cr (VI) in Reference Water SLRS - 1

The data shows that the only chromium species present was the chromium (III) and the results are consistent with the certified value.

4.5 Conclusion

A technique for the rapid sequential determination of chromium (III) and chromium (VI) using a micro column of activated alumina (basic form) in a FI - ICP - ES system has been developed. Key operating parameters, as discussed previously for Cr (VI), were investigated and optimised. The preconcentration capability for chromium (III) and the successful long term reliability of the basic alumina micro column were shown. The limit of detection for chromium (III) was 0.063 µg/l with a sample volume of 8 ml. Analytical performance and the application of the technique to the determination of chromium (III) in reference waters were successfully demonstrated.

The rapid measurement time (approximately 14 samples per hour) and the detection limit achieved are a significant advance over procedures presently available.

This work formed the basis of a publication (59).

CHAPTER FIVE

IN SITU MICRO COLUMN FIELD SAMPLING FOR CHROMIUM SPECIATION IN RIVERS

5.1 Introduction

It was Paulsen (39) that first recognised the problems in trace metal analysis centred on the problems of obtaining a representative sample. He proposed that in situ sampling should be used to render the sample both chemically and physically inert at the time of sampling. Subsequently a number of workers have used packed columns to preserve one or other of the chromium species, but no one packing material has displayed the ability to speciate and preserve both the chromium (III) and (VI) species. The two previous chapters have shown that an activated alumina micro column in the acidic form will separate and retain chromium (VI), and in the basic form will separate and retain chromium (III).

It is proposed to apply the in situ concept to activated alumina micro columns (in the acidic and basic forms) and, coupled with the flow injection manifold, obtain new speciation data for chromium for selected rivers.

5.2 Design criteria for in situ sampling

As well as introducing the concept of in situ sampling Paulsen (39) also proposed certain design criteria that would have to be part of the in situ system. These are :

1) The "system" must be sampled in a manner so that it is rendered physically and chemically inert.

2) The sample must be in a form to be directly analysed - preferably one step and involve no chemical preparative steps.

3) The in situ "instrumentation" must be rugged, inexpensive and durable.

4) The analytical method must provide high quality resolution for simultaneous identification of several elements.

5) The analytical method must also be quantitative with respect to initial concentrations of each element in the original environment.

6) Samples must occupy a small space for convenient storage.

The following point should also be added:

7) The in situ "instrumentation" must be simple to use in the field.

The two previous chapters have shown that activated alumina micro columns, incorporated within a flow injection manifold (FI), provide a means of separation and preconcentration of chromium (III) and (VI) prior to determination by inductively coupled plasma - emission spectrometry (ICP - ES). The FI - ICP - ES system meets criteria 4 and

5, and the activated alumina micro columns meet criteria 3 and 6. What needs to be shown is whether the system can meet the remaining criteria 1, 2 and 7. The key parameters to be examined are :

1) **Column to column variability**

   The signal response, due to the chromium species, for a given sample must be independent of the column used.

2) **Sample pH**

   The pH of river waters generally is in the range 5 - 9. It is desirable that the alumina micro column retains both chromium species within this range without alteration of the sample pH.

3) **Preconcentration capability**

   The activated alumina micro column must be able to concentrate the desired chromium species (at the time of sampling) and so extend the ICP -ES detection capability.

4) **Species stability**

   Once the desired chromium species has been collected on the activated alumina micro column there should be no loss of the retained species from the column over a period of time prior to analysis.

These four factors were evaluated, first in the laboratory on synthetic samples and then at two field sites / the River Rother and the River Don.

5.3 Laboratory studies

The results in this section are based on freshly prepared aqueous chromium (III) and (VI) solutions which contain no matrix ions, suspended solids or organic matter. A pH of 7.5 and concentrations of 25 μg/l were chosen.

5.3.1 Column to column variability

The acidic FI manifold was set up and a chromium (VI) solution (100 μg/l, 250 μl) injected onto the column. The chromium (VI) was then eluted from the column, with ammonia solution (2.0 M, 250 μl), into the ICP - ES and the measurement obtained. The data collected for ten replicates is given in Table 5.1. Ten separate alumina micro columns were inserted, one at a time, into the FI manifold (this was achieved without stopping the carrier flow or turning off the plasma), 2 minutes were allowed for micro column conditioning before the chromium (VI) (100 μg/l, 250 μl) was deposited and eluted as before. The data are given in Table 5.2.

To simulate field sampling ten micro columns were conditioned and sampled off line. The micro columns were conditioned by passing nitric acid solution (0.02 M, 2.0 ml) through each of them using a calibrated (2.0 ml) disposable polyethylene syringe. The acid was pushed through each column at a steady flow rate, this took approximately 1 minute for each volume of 2.0 ml. Chromium (VI) solution (100 μg/l, 250 μl) was

then drawn through each micro column in turn using a disposable polyethylene calibrated (1.0 ml) syringe. The sample was then passed back through the micro column to waste. This process took approximately 1 minute to complete. The micro columns were then separately inserted into the FI manifold and the retained chromium (VI) eluted as before. The intensity data are given in Table 5.3.

The complete experiment was then repeated using the basic FI manifold. The results are presented in Tables 5.4, 5.5, and 5.6.

Replicate Number	Signal Intensity Cr (VI)
1	382
2	378
3	384
4	376
5	370
6	373
7	375
8	379
9	375
10	370
Mean	**376**
SD	**4.70**
RSD	**1.24**

Table 5.1 Cr (VI) Signal intensity data for a single column with on-line loading of Cr (VI) solution (0.1 mg/l, 250 µl). Elution, 250 µl of 2.0 M ammonium hydroxide

Column Number	Signal Intensity Cr (VI)
1	380
2	375
3	368
4	364
5	368
6	374
7	374
8	368
9	364
10	370
Mean	**371**
SD	**5.15**
RSD	**1.40**

Table 5.2 Cr (VI) Signal intensity data for ten columns with on-line loading of Cr (VI) solution (0.1 mg/l, 250 µl). Elution, 250 µl of 2.0 M ammonium hydroxide

Column Number	Signal Intensity Cr (VI)
1	382
2	370
3	374
4	365
5	364
6	376
7	370
8	380
9	378
10	384
Mean	**374**
SD	**6.80**
RSD	**1.81**

Table 5.3 Cr (VI) Signal intensity data for ten columns with off-line loading of Cr (VI) solution (0.1 mg/l, 250 µl). Elution, 250 µl of 2.0 M ammonium hydroxide

Replicate Number	Signal Intensity Cr (III)
1	368
2	358
3	365
4	356
5	367
6	370
7	372
8	365
9	360
10	366
Mean	**365**
SD	**5.18**
RSD	**1.42**

Table 5.4 Cr (III) Signal intensity data for a single column with on-line loading of Cr (III) solution (0.1 mg/l, 250 ul). Elution. 250 µl of 2.0 M nitric acid

Column Number	Signal Intensity Cr (III)
1	365
2	368
3	355
4	358
5	369
6	360
7	354
8	370
9	362
10	356
Mean	**362**
SD	**6.02**
RSD	**1.67**

Table 5.5 Cr (III) Signal intensity data for ten columns with on-line loading of Cr (III) solution (0.1 mg/l, 250 ul). Elution, 250 µl of 2.0 M nitric acid

Column Number	Signal Intensity Cr (III)
1	360
2	355
3	380
4	375
5	370
6	365
7	368
8	374
9	358
10	374
Mean	**368**
SD	**8.24**
RSD	**2.24**

Table 5.6 Cr (III) Signal intensity data for ten columns with off-line loading of Cr (III) solution (0.1 mg/l, 250 ul). Elution, 250 µl of nitric acid

The results shown in Tables 5.1- 5.6. testify to the good precision obtained whether using single or multiple micro columns.
The off line results (Table 5.3 and 5.6) show that the chosen method of preparing the micro columns, using a small discrete volume of acid or base to condition them was effective; the eluted chromium signals being the same as the results obtained in the other experiments for each chromium species. If the columns had not been properly conditioned the results would have been lower in both cases, indicating that analyte breakthrough had occurred.

The fact that the elution results were generally the same in both cases (Table 5.3, Cr (VI) = 374 and Table 5.6, Cr (III) = 368), shows that

the sampling procedure, drawing sample through the micro column then pushing out to waste, was reliable for achieving retention of chromium (III) and chromium (VI).

What is apparent and satisfying from Tables 5.1 - 6 is that the alumina micro columns display fairly uniform deposition and elution characteristics and that the column to column variability is low (for all sets of data the %RSD is less than 3%). This means that it is possible to retain the chromium species on different columns and obtain reproducible results from the separately eluted chromium signals. This study has shown that the activated alumina micro column (linked with the versatility of the FI manifold) meets the first criterion needed for in - situ sampling and analysis.

5.3.2 The effect of sample pH

As the river water samples will typically be in the pH range 5 -9, and low concentrations of chromium (particularly the chromium (VI) species) are expected (typical range 1 - 14 μg/l total chromium), there may be a need to process relatively large sample volumes in order to achieve the necessary sensitivity required for measurements to be made.

The passage of large sample volumes through the micro column could alter the acidity / basicity of the alumina and mean that the required chromium species is not quantitatively retained i.e. breakthrough may result. In order to study the effect of sample volume against signal

breakthrough, separate single solutions of chromium (III) and (VI) (25 µg/l) were prepared at pH 7.5 and the results are presented in Figure 5.1.

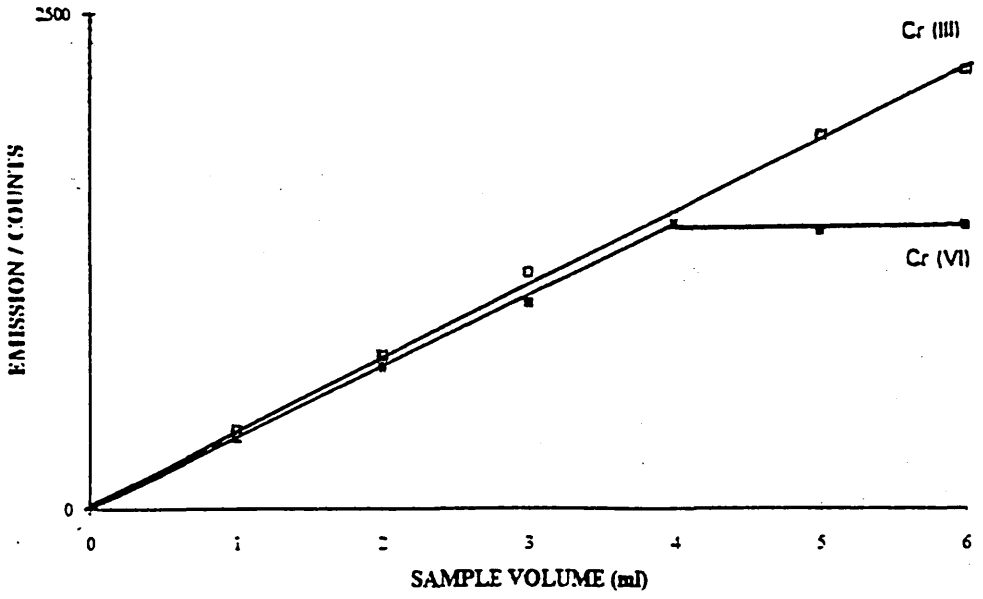

Figure 5.1 Effect of sample volume upon Cr (III) - Cr (VI) deposition (25 µg/l). Elution, 250 µl of nitric acid and ammonium hydroxide respectively

The results show that chromium (VI) was not quantitatively retained for sample volumes greater than 4 ml. This lack of retention is attributable to a gradual change in the properties of the alumina as a result of the passage of the sample at pH 7.5. It is possible that with the passage of large volumes of sample the acidic alumina will gradually lose the active

exchange sites for the anionic chromium (VI) species and so breakthrough of chromium is observed. Chromium (III) was quantitatively retained and shows a linear response for sample volumes up to 8 ml.

5.3.3 Stability of immobilised species

As already pointed out if the proposed in situ process is to be valid, the chromium species in the sampled waters need to be immobilised on the alumina micro column and rendered stable. This enables storage of samples prior to analysis with minimal degradation. Five acidic alumina micro columns were separately loaded (on line) with a chromium (VI) solution (100 μg/l, 2.0 ml) and then eluted using the FI manifold. These same micro columns were then loaded (on - line) with the same chromium (VI) solution (100 μg/l, 2.0 ml), taken out of the FI system and stored in polyethylene sample tubes for 12 hr. After this time the micro columns were inserted into the FI system, one at a time, for elution. This procedure was repeated but with five micro columns stored for 24 hr before elution. The data are presented in Table 5.7. The complete process was repeated for basic alumina micro columns using a chromium (III) solution (100 μg/l, 2.0 ml) and the data are presented in Table 5.8.

Time on Column	(hr)	Signal Intensity Cr (VI) 0	12	24
Column Number	1	2586	2538	2520
	2	2550	2580	2508
	3	2634	2610	2550
	4	2604	2568	2562
	5	2568	2634	2556
mean		2588	2586	2539
SD		32.50	37.23	23.77
RSD		1.25	1.44	0.94

Table 5.7 Stability study of Cr (VI) solution (100µg/l, 2.0 ml) retained on alumina micro columns. Elution 250 µl of 2.0 M ammonium hydroxide

Time on Column	(hr)	Signal Intensity Cr (VI) 0	12	24
Column Number	1	2640	2694	2580
	2	2676	2628	2592
	3	2628	2676	2628
	4	2658	2652	2610
	5	2610	2646	2598
mean		2642	2659	2601
SD		25.67	25.94	18.29
RSD		0.97	0.97	0.73

Table 5.8 Stability study of Cr (III) solution (100 µg/l, 2.0 ml)retained on alumina micro columns. Elution, 250 µl of 2.0 M nitric acid

For chromium (VI) the results again show very good between - column reproducibility with relative standard deviations of 1.25, 1.27 and 1.4 % for the on line, 12 hr (off - line) and 24 hr (off - line) results respectively. There is no signal loss for the samples stored on the alumina micro columns for 12 hr and 24 hr compared with the on line signals. The chromium (III) results give between - column reproducibility of 1% for the on - line, 12 hr (off - line) and 24 hr (off - line) results. Again there is no significant signal loss between the on line and the samples stored for 12 hr and 24 hr.

Both systems show that once the chromium species have been effectively immobilised on the alumina micro column they are held stable for at least 24 hr, resulting in reliable and meaningful speciation data for chromium (III) and (VI). This means that another criterion for the proposed in - situ method has been met, on condition that the analysis is carried out within 24 hr of the chromium sample being taken. Further work needs to carried out to evaluate the effectiveness of immobilisation and hence stability over longer periods.

5.3.4 Analytical performance

On - line calibration for chromium (III) and chromium (VI) was carried out at pH 7.5. Standard chromium (III) and (VI) solutions (10, 20, 50, 100 μg/l) were separately injected onto the basic and acidic FI manifolds respectively in triplicate. Two sample volumes were chosen 250 μl and 2.0 ml. The graphs for chromium (III) (Figure 5.3) and chromium (VI) (Figure 5.4) both give good linearity with correlation coefficients of 0.9994 (250 μl), 0.9993 (2.0 ml), 0.9992 (250 μl) and 0.9996 (2.0 ml), respectively. Limits of detection calculated as twice the standard deviation of the background noise signal, based on the 2.0 ml sample volume, were 0.2 μg/l for both chromium (III) and (VI). Off - line calibration for chromium (III) and chromium (VI) was again carried at pH 7.5, with the alumina micro columns conditioned and standards loaded off - line. Standard chromium (III) and (VI) solutions (10, 20, 50, 100 μg/l) were loaded onto the basic and acidic alumina micro columns respectively, prior to being inserted into the appropriate FI manifold for elution of the chromium signal. The same two sample volumes were used (250 μl and 2.0 ml) and the procedure repeated three times to give results in triplicate. The graphs for chromium (III) and chromium (VI) again give good linearity with correlation coefficients 0.9994 (250 μl), 0.9997 (2.0 ml), 0.9993 (250 μl) and 0.9998 (2.0 ml), respectively. Limits of detection calculated as twice the standard deviation of the background noise signal, based on the 2.0 ml sample volume, were 0.2 μg/l for both chromium (III) and chromium (VI).

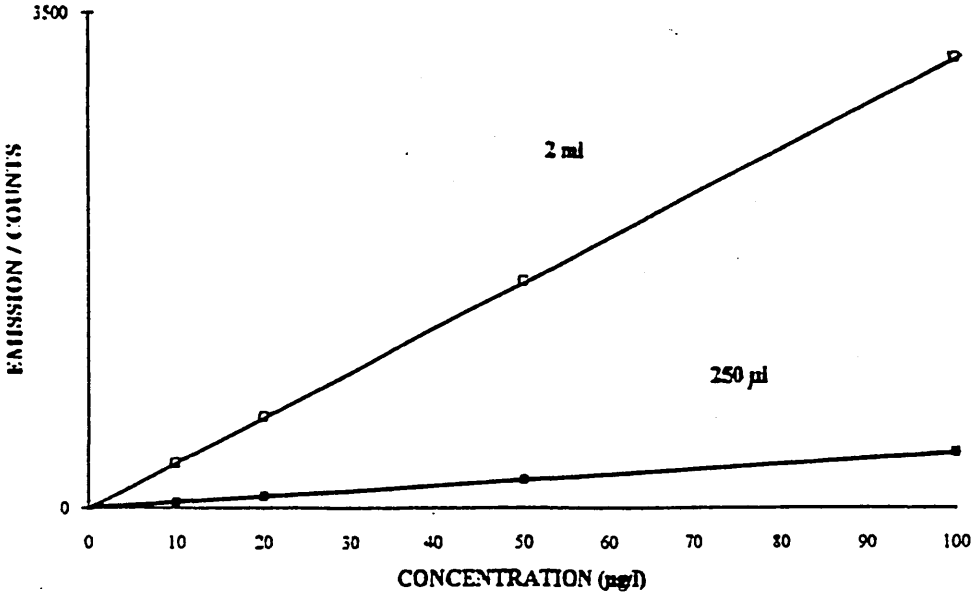

Figure 5.2 On - line calibration graph for Cr (III) solutions. Elution, 250 µl of 2.0 M nitric acid

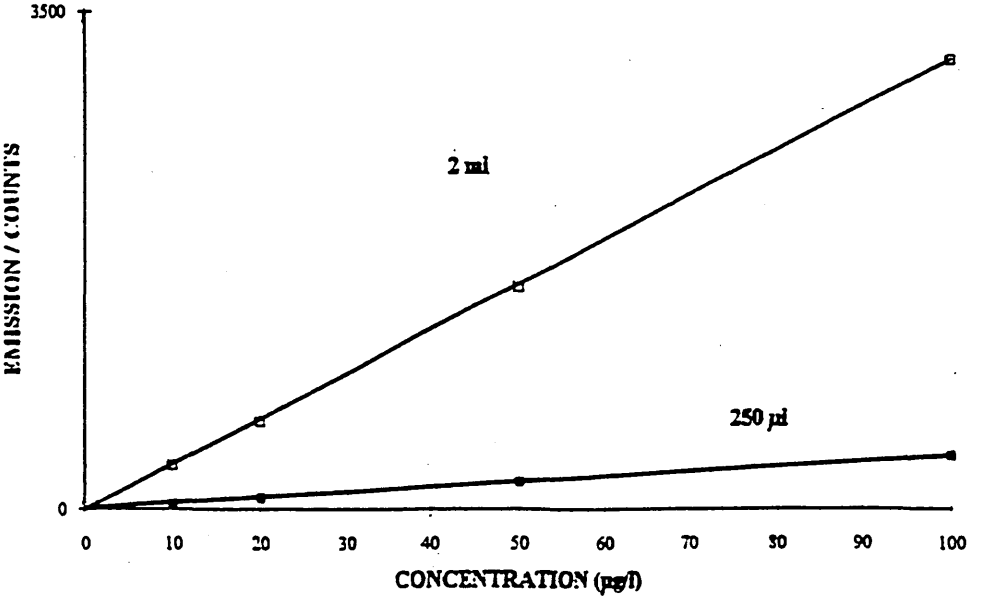

Figure 5.3 On - line calibration graph for Cr (VI) solutions. Elution 250 µl of 2.0 M ammonium hydroxide

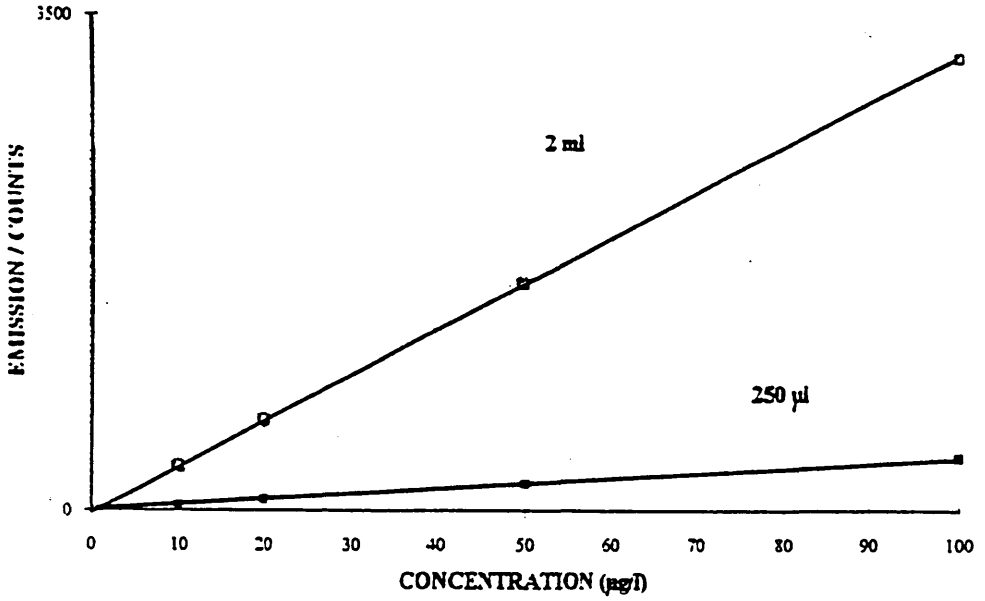

Figure 5.4 Off - line calibration graph for Cr (III) solutions. Elution, 250 µl of 2.0 M nitric acid.

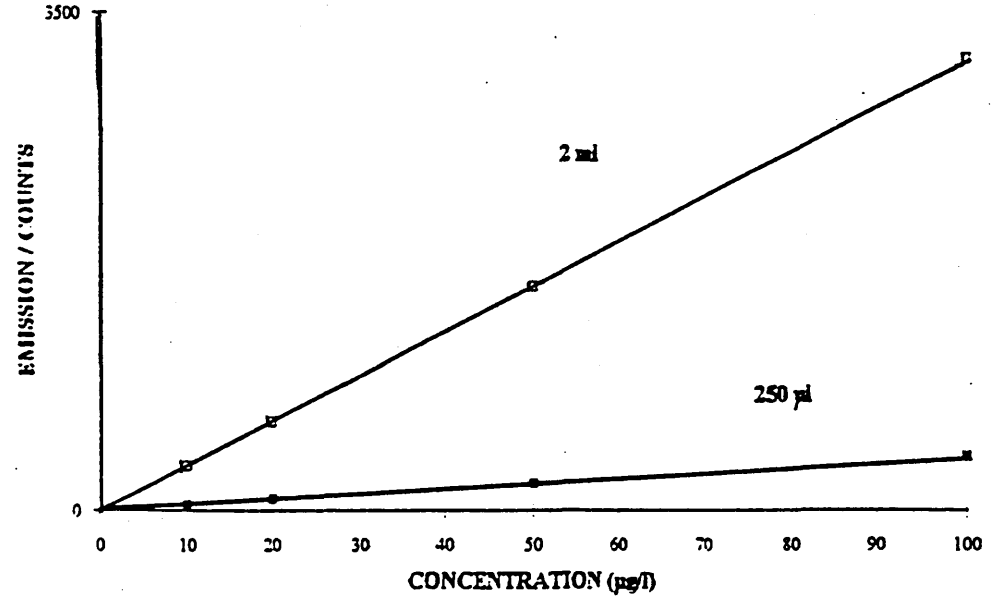

Figure 5.5 Off - line calibration graph for Cr (VI) solutions. Elution, 250 µl of 2.0 M ammonium hydroxide

The calibration graphs obtained for both methods of sampling (on - line and off - line) display remarkably similar results, showing that the performance of the alumina micro column is not affected by off line conditioning and sampling.

The ability of the alumina to preconcentrate the chromium species from the sample and effectively extend the ICP - ES detection capability is shown in the limit of detection (0.2 μg/l) achieved from using the 2.0 ml sample volume. This means that although the acidic alumina micro column is affected by large sample volumes (greater than 4 ml at pH 7.5), the preconcentration achieved using 2.0 ml sample volume gives a limit of quantitative determination for chromium (defined as five times the detection limit) of 1 μg/l. It remains to be seen if this level of determination is low enough to obtain meaningful chromium speciation data in river water samples, and especially for chromium (VI) data).

5.4 Laboratory studies - concluding remarks

The aim of these laboratory studies was to provide data to show whether alumina micro columns had the capability for use in an in situ method before taking samples from the field. The laboratory studies have demonstrated that key parameters needed for the in - situ method have in large part yielded acceptable results. Alumina micro columns could be easily handled off - line, conditioned and sampled to retain the appropriate chromium species and then be inserted into the FI - ICP - ES system for elution and quantification. What remains to be seen is what effect the pH and matrix of the river water has on the alumina micro column.

5.5 Field studies

As already pointed out no compensation was made for the fact that all the laboratory work was carried out using synthetic chromium solutions despite river water samples being relatively complex. The river matrix will contain other cations (e.g. calcium and magnesium) and anions (e.g. phosphate and sulphate) which may compete with chromium (III) and chromium (VI) for the active sites on the respective basic and acidic alumina. Chromium could also be present in the particulate, colloidal, complexed and non ionic forms as well as ionic.

To study the effect this matrix may have on the alumina micro column and its ability to speciate and retain chromium, three parameters were investigated using river waters. These were : The effect of sample volume, the acid / base column conditioning concentrations and the column to column variability. Field sampling was performed on two rivers in the South Yorkshire area, the River Don and the River Rother. Both chosen sites are official sampling stations of the National Rivers Authority (NRA), the River Don site at map reference SK 423 861 and the River Rother at map reference SK 435 897. Both rivers pass through heavy industrial areas and are classified as grade 4 according to the Water Quality Directives of the European Community . The rivers are known to contain elevated chromium levels (survey data for total chromium, 1 - 14 μg/l) and are monitored on a regular basis by the NRA.

5.5.1. The effect of sample volume

The aim of this study was to investigate what effect, if any, the river matrix and pH would have on the alumina micro column and its ability to retain the desired chromium species using large sample volumes. Samples from both rivers were taken (as described in Chapter two) and the pH measured (River Rother 7.20, River Don 7.52). It should be noted (section 5.3.2) that laboratory studies at pH 7.5 have shown that the chromium (VI) species was not quantitatively retained on the acidic alumina micro column above sample volumes of 4 ml.

A water sample was taken at the River Don site and four alumina micro columns were conditioned by passing nitric acid solution (0.02 M, 2 ml) through. The acidic alumina micro columns then had different, individual, sample volumes drawn through (1, 2, 4 and 8 ml) then pushed out to waste. This was then repeated for four further alumina micro columns using ammonium hydroxide solution (0.02 M, 2 ml) for conditioning. These basic alumina micro columns having 1, 2, 4 and 8 ml sample volumes drawn through then pushed out to waste. The charged micro columns were then returned to the laboratory inserted into the appropriate FI manifold for elution and quantification of the chromium species, (Figure 5.6). This process was repeated using 0.2 M nitric acid (2 ml) and 0.2 M ammonium hydroxide solution (2 ml) to condition the alumina micro columns (Figure 5.7) and 0.5 M nitric acid (2 ml) and 0.5 M ammonium hydroxide solution (2 ml) to condition the alumina micro columns (Figure 5.8) the whole study being carried

out on the same river sample.

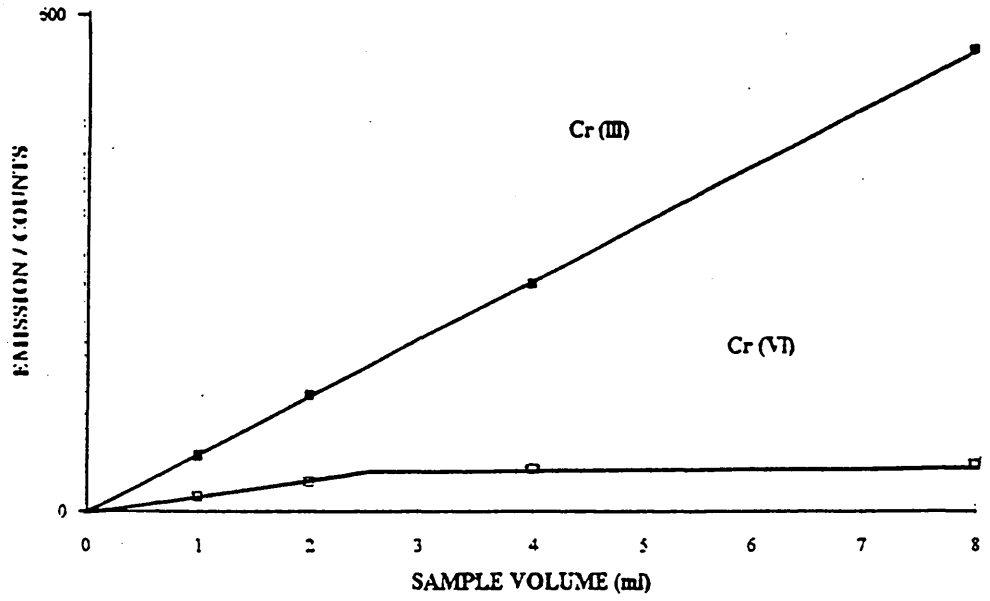

Figure 5.6 Effect of river sample volume on retention capability of alumina micro column with(0.02 M) NH_4OH / HNO_3 conditioning

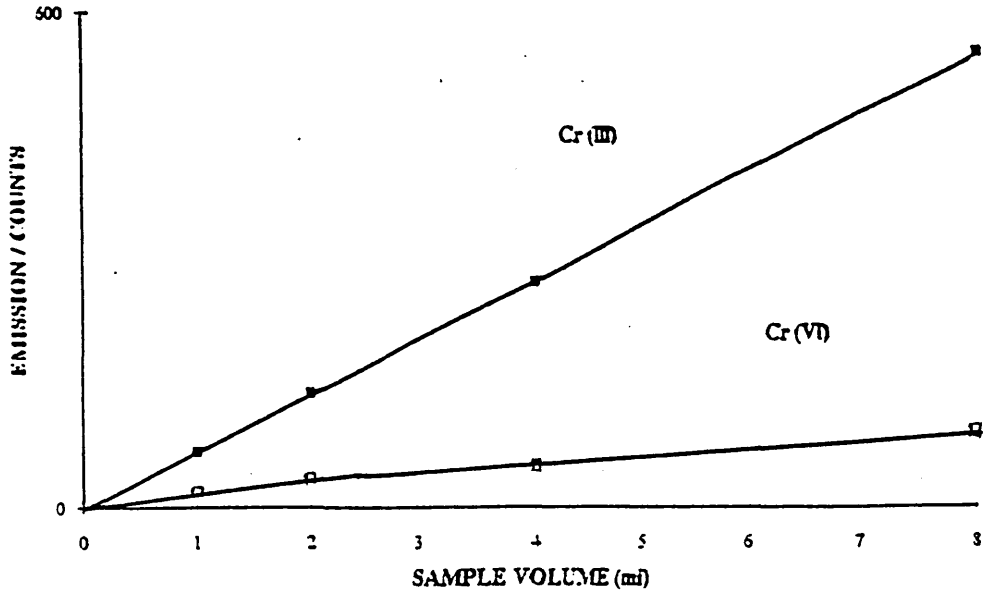

Figure 5.7 Effect of sample volume on retention capability of alumina micro column with (0.2 M) NH_4OH / HNO_3 conditioning

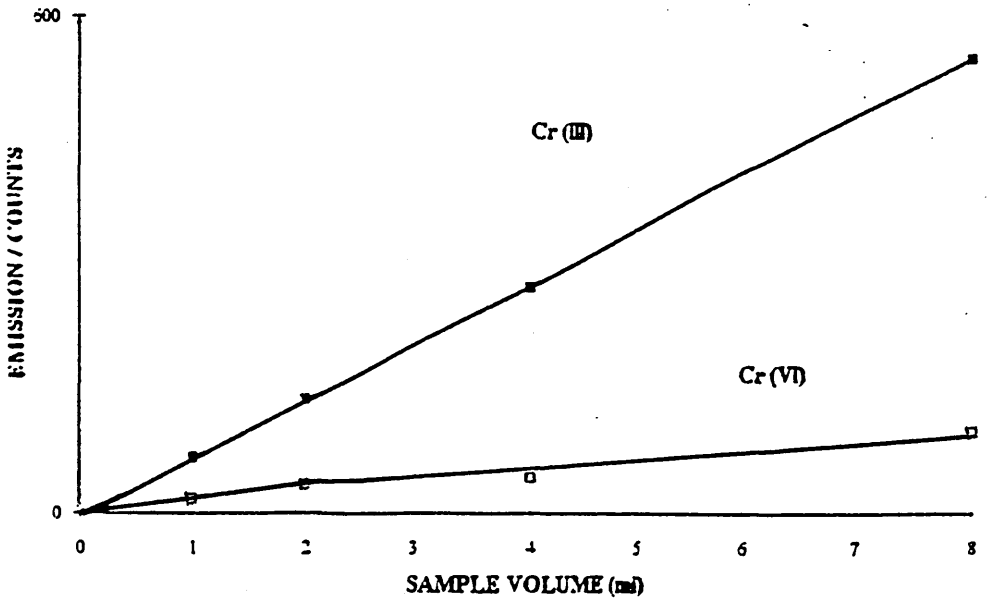

Figure 5.8 Effect of sample volume on retention capability of alumina micro column with (0.5 M) NH_4OH / HNO_3 conditioning

The graph for chromium (VI) (Figure 5.6), if compared with that obtained in the laboratory study (Figure 5.2), shows that chromium (VI) breakthrough occurred at a lower sample volume (i.e. greater than 2 ml against greater than 4 ml). This means that chromium (VI) was not quantitatively retained on the alumina micro column for sample volumes greater than 2 ml.

In an attempt to understand this effect the alumina micro columns were conditioned with 0.2 M (Figure 5.7) and 0.5 M (Figure 5.8) nitric acid and ammonium hydroxide solutions (2 ml). Breakthrough of the chromium (VI) occurred at the same volume for all three acid concentrations.

This loss of anion exchange sites means that the alumina micro column capacity is reduced and apparent breakthrough of chromium (VI) occurs. The difference in the sample volume at which this chromium (VI) breakthrough occurs, greater than 2 ml as against greater than 4 ml found in the laboratory studies, is possibly due to competition for the available anion exchange sites, with other anions in the river water. Therefore there is again a reduction in the number of available exchange sites for chromium (VI) and breakthrough will occur sooner than in the laboratory study which used only pure synthetic chromium solutions. These findings mean that although the enrichment capability of the acidic alumina micro column has been reduced it is still possible to preconcentrate chromium (VI) with 2 ml of sample, this will give a limit

of quantitative determination of 1 µg/l for chromium (VI). Conditioning the alumina micro column with 0.2 and 0.5 M nitric acid solution gives no improvement in chromium (VI) retention and so the use of 0.02 M nitric (2 ml) to condition prior to sampling was adopted.

The graphs for chromium (III) (Figure 5.6, 5.7, 5.8) show the same linearity and ability to preconcentrate chromium (III) on the basic alumina column even with 8 ml of sample (pH 7.52). This mirrors the results found in the laboratory study (Figure 5.2) and shows that the cation exchange sites (- NH_3^+) are not affected by the passage of sample and remain available for exchange with the chromium (III) cation. Although there will be competition for the exchange sites with other cations, unlike the acidic alumina, there is no loss of the available sites due to pH changes and so no loss of the alumina micro column capacity. There will almost certainly be cation selectivity and a cation retention order dependent upon the pH of the sample (49). From the results the chromium (III) cation appears to have a high retention order with no breakthrough occurring.

Increasing the concentration of the ammonium hydroxide solution to condition the alumina micro column shows no improvement in performance, therefore 0.02 M ammonium hydroxide solution was used in all further work.

5.5.2 Column to column variability.

A water sample was taken (as described in chapter two) at the River Rother sampling site.

Ten alumina micro columns were conditioned using nitric acid solution (0.02 M, 2 ml). Each acidic alumina micro column was then dipped in turn into the sample and using a polyethylene syringe 2.0 ml of water drawn through the column and passed out to waste.

Ten further alumina microcolumns were then conditioned using ammonium hydroxide solution (0.02 M, 2 ml) and the sampling procedure repeated. Both sets of alumina micro columns were returned to the laboratory inserted one at a time into the appropriate FI manifold for elution, and chromium species data obtained (Table 5.9). It is apparent from this data that column to column variability is low for both chromium (III) and (VI), 2.1 and 3.8 % relative standard deviation, respectively. The results also show that chromium (III) and chromium (VI) can be separately retained on conditioned alumina micro columns at the field sampling site, returned to the laboratory coupled to the appropriate FI manifold and yield acceptable data.

Basic Column Number	Signal Intensity Cr (III)	Acidic Column Number	Signal Intensity Cr (VI)
1	205	1	46
2	208	2	47
3	204	3	48
4	212	4	50
5	200	5	50
6	207	6	48
7	212	7	48
8	200	8	52
9	206	9	50
10	209	10	47
Mean	206	Mean	48.6
SD	4.24	SD	1.84
RSD	2.10	RSD	3.80

Table 5.9 Signal intensity data for Cr (III) and Cr (VI) for ten separate alumina micro columns with in situ loading of river water sample (2.0 ml)

5.5.3 Survey analysis

Having completed the studies into the parameters highlighted at the beginning of this section (5.5) and with the condition that sample volumes were limited to 2 ml, in situ field sampling was performed over a one month period at the River Don and River Rother sites. Sampling (in triplicate) followed the adopted procedure, with 2 ml of sample being processed using both the acidic and basic alumina micro columns. For each water sample, measurement of total chromium was also performed by conventional ICP - ES analysis. On return to the laboratory separate calibration graphs for chromium (III) and chromium (VI) were established on - line, using 2.0 ml sample volumes in each case and the results are presented in Table 5.10 and 5.11. A separate study was undertaken at the River Don site over a three day period using a simplified method to condition the alumina micro column. In this the alumina micro columns were stored in solutions of nitric acid (0.02 M) and ammonium hydroxide (0.02 M) in an attempt to condition them prior to sampling.

At the River Don site the alumina micro columns were removed from the conditioning solution one at a time and 2 ml sample volumes were immediately drawn through as before. These sets of columns were then left for 24 hr prior to analysis. The analysis of the sample for total chromium by ICP - ES was still carried out on return to the laboratory and the results are shown in Table 5.12.

Date of Analysis	Concentration µg/l		
	Cr (III)	Cr (VI)	Total Cr
27-10-90	19.4	3.2	22.0
1-11-90	12.8	3.3	16.8
3-11-90	13.2	3.2	16.3
8-11-90	8.5	4.5	13.4
10-11-90	10.2	3.1	13.4

Note: Data is the mean of 3 replicates

Sample volume 2.0 ml. Elution volume 250 µl (NH_4OH / HNO_3)

Table 5.10 Speciation data for chromium in the River Don

Date of Analysis	Concentration µg/l		
	Cr (III)	Cr (VI)	Total Cr
17-10-90	12.5	3.1	15.5
23-10-90	8.6	1.7	10.0
27-10-90	16.2	2.7	19.2
3-11-90	16.1	2.8	18.4
10-11-90	19.5	3.0	22.5

Note : Data is the mean of 3 replicates

Sample volume 2.0 ml. Elution volume 250 µl (NH_4OH / HNO_3)

Table 5.11 Speciation data for chromium in the River Rother

Date of Analysis	Concentration µg/l		
	Cr (III)	Cr (VI)	Total Cr
18-6-91			8.4
19-6-91	6.2	2.7	
19-6-91			14.7
20-6-91	10.4	4.2	
20-6-91			15.8
21-6-91	12.2	3.3	

Note: Data is the mean of 3 replicates

Sample volume 2.0 ml. Elution volume 250 µl (NH_4OH / HNO_3)

Table 5.12 Speciation data for chromium in the River Don after storage for 24 hr

The results confirm that the two rivers contain appreciable amounts of chromium, and that a significant fraction is the chromium (VI) species. The simplified method used to condition the columns also proved successful and reduces on site column manipulation.

A remarkable finding is that for all the data sets, including the sampled alumina micro columns stored for 24 hr prior to analysis, there is near perfect agreement between the total chromium values and the summations of the chromium (III) and chromium (VI) data.

This was not expected as the total chromium figure is based on an

unfiltered water sample and could contain colloidal, particulate and complexed chromium and which, if present, would be measured by the ICP - ES. The sample for total chromium was not filtered because it can cause changes in the concentration of trace metals by either adsorption or contamination. Furthermore this will reduce requirements on sample manipulation and thereby reduce the complexity of the overall analytical procedure.

The NRA provided total chromium data for the two sites, covering an eighteen month period, which showed a chromium range for the sites of between 1 - 14 μg/l. The results obtained by ICP - ES for this short study are shown to be of the same order. The sampling method used, where the water sample is drawn through the alumina micro column before being passed out to waste, could mean that the column acts as a filter for particulate chromium. Then once inserted into the FI manifold particulate chromium is eluted along with the retained ionic chromium species. Colloidal chromium because of the sampling method and the pore size of commercial alumina (13 nm) should not be retained. Chromium also exists in natural waters in the non ionic form (14), this would not be retained on either acidic or basic alumina and again will pass out to waste.

5.7 Conclusions

The use of alumina micro columns for field sampling of chromium (III) and chromium (VI) has been highly successful. For the first time samples from rivers have been taken and transferred to the laboratory without any significant change in speciation. This was achieved by passing river water samples through two separate activated alumina micro columns. One column, in the acidic form, retains only the chromium (VI) species (CrO_4^{2-}, $HCRO_4^-$), and the other in the basic form retains only the chromium (III) species ($Cr(OH)_2^+$, $Cr(OH)^+$).

The pH of the river water limits the sample volume for the acidic alumina micro column to 2 ml, because at typical pH values of 7 to 8 the nature of the alumina changes, particularly when large sample volumes are passed through the micro columns, and breakthrough of the chromium (VI) species occurs..

The preconcentration of chromium is limited to a factor of about 8, because 2 ml of river water is sampled and 250 µl of eluant is used to elute the retained chromium species from the micro column. Limits of detection (twice the standard deviation of the background signal) of 0.2 µg/l for Cr (VI) and 0.3 µg/l for Cr (III) were obtained for sample volumes of 2 ml.

The stability of the chromium on the columns is excellent over a 24 hr period, with no detectable change observed for River Don samples containing 2.7 μg/l Cr (VI) and 6.2 μg/l Cr (III).

Extension of the work described in this thesis is possible in a number of ways. The applications have been limited to two rivers in the South Yorkshire area. Other waters, particularly trade effluents, are likely to introduce new problems when high concentrations of ionic species other than chromium compete for the exchange sites.

Particulate, colloidal and non ionic chromium in waters is expected to affect the accuracy of analysis, and an investigation into this is required. Surprisingly, our results show that the sum of the speciated chromium concentrations was equal to that for total chromium.

Further investigation of the stability of retained chromium species is needed beyond the 24 hr evaluation reported here, since in different circumstances the time between sampling and laboratory measurement could be considerably longer.

It is likely that some natural waters contain chromium levels below the limit of detection so far achieved, the application of inductively coupled plasma - mass spectrometry (ICP - MS) instead of ICP - ES is likely to enable significantly lower concentrations to be monitored.

The field sampling work formed the basis of a publication (60).

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STUDY PROGRAMME

As part of the research programme the author has :

Attended selected lecture courses and departmental research meetings .

Presented work at departmental research meetings.

Presented work at :

i) The Second Biennial National Atomic Absorption Spectroscopy Meeting held in Leeds, July, 1984.

ii) The Third Biennial National Atomic Absorption Spectroscopy Meeting held in York, June, 1986.

iii) The Flow Analysis (III) Meeting held in Birmingham, May, 1985.

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