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MASTER

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DISCLAIMER

SUMMARY OF THE RESEARCH REPORT

The original objectives of this research program were: to interface d.c. plasma atomic emission spectrometer with an ion chromatograph; to characterize and optimize the combined systems for application in the speciation of metals in aqueous solutions; to use this system in the study of the solution chemistry of various metals; and to find ways in which the measurement sensitivity of the method can be enhanced, thereby allowing the detection of metal species at low ppb concentration levels.

This approach has been used to study the chemistry of and speciate several elements in solution including: arsenic, chromium, iron, manganese, nickel phosphorus, platinum, selenium, and vanadium. Most of these elements can exist in more than one form in solution. By using appropriate chromatographic columns, all of them have been speciated and quantitated using the d.c. plasma as an element selective detector for the ion chromatograph.

Since many of the elements or some species of certain of the elements can exist in a sample in very small concentrations, detection capability for low ppb concentrations is required. In this research, several approaches have been employed to improve measurement sensitivity. They include: the use of large sample loops which ensure the injection of a large sample size on the column; modifications of the d.c. plasma sample introduction mechanisms; and sample preconcentration, both on column and off-column.

During the course of this research, we have found that the solution chemistry of the elements studied and the speciation data obtained can vary considerably depending on the solution , and the chromatographic conditions employed. The speciation of chromium, iron, and vanadium was found to be highly influenced by the acidity of the sample. The element selective nature of the d.c. plasma detector allows these changes to be monitored, thereby providing quantitative information on the new moieties formed.

New approaches are being developed including the use of chelating ligands as preconcentration agents for purposes of reducing further the detection limits of the elements of interest and to improve the overall element speciation scheme. New thrusts are being directed towards the employment of post-column derivatization method coupled with colorimetric measurements to detect and quantify metal species eluting from the

chromatographic column. The influence of sample acidity on these investigations will be carefully evaluated. These new thrusts are described in the accompanying Project Renewal Proposal.

I. INTRODUCTION

This Annual Performance Report is submitted to accompany the Project Renewal Application which is attached to this report. The report discusses the accomplishments of the research program from its inception in 1986 to the present time. It also sets a stage for new thrusts which have been determined to be the "next step" in the pursuit of the original objectives of the research program.

II. PURPOSE OF THE RESEARCH

The fundamental objective of the research was to combine the proven capabilities of d.c. plasma atomic emission spectrometry (DCPAES) with those of ion chromatography (IC), a relatively new analytical technique, producing an analytical system with capabilities for element speciation at the low ppb concentration range. The choice of DCPAES was based on its suitable features for this kind of analysis, including: high excitation energy; freedom from matrix effects; simplicity; and most important, its ability to excite different species of a given element with equal efficiency. On the other hand, IC was chosen owing to the generally simple chromatography obtainable with it; the fact that the required mobile phase systems are aqueous buffers or other inorganic solutions readily available in the laboratory; and that the mobile phase flow requirements fall within the range required for sample uptake rate for the DCPAES.

The instrumentation employed in this research to date includes: an ion chromatograph, Dionex Corporation Model 2010i equipped with a Conductivity detector; a d.c. plasma spectrometer equipped with a high resolution echelle grating, Model Spectraspan IV, Fisions Corporation. The DCPAES and the IC were interfaced by inserting the outlet tubing of the chromatographic column into the sample inlet tubing of the d.c. plasma. When desired, the DCPAES can be used in tandem with the conductivity detector, which comes with the IC system, otherwise the interface bypasses the conductivity detection system. Recently, a UV-Vis detection system was installed on the ion chromatograph, allowing the detection of the chromatographic effluents by spectrophotometric measurements. This unit, which can also be used in tandem with the d.c. plasma, is intended for multielement detection via post-column derivatization as described below and in the attached Renewal Application.

Data acquisition and handling was data with an Apple IIe earlier in the project. However, more sophisticated chromatographic software utilizing an IBM Model PS 60 is now being used. Interface between the chromatographic detector and the IBM computer is achieved with an interface unit obtained from Dionex Corporation.

A variety of chromatographic columns have been used, including cationic, anionic, low capacity, high capacity, and mixed bed. Speciation studies, and characterization of the solution chemistry of several elements were done with synthetic solutions prepared from high purity reagent grade chemicals. Applications to real samples was done on natural water, wastewater, sediments, soils, and industrial process stream samples.

III. ACCOMPLISHMENTS

A. CHARACTERIZATION OF THE COUPLED IC-DCPAES SYSTEM

The IC-DCPAES system was characterized with respect to the following parameters:

1. Mobile Phase Flow Rate Effects

One important parameter to consider in coupling IC with DCPAES is mobile phase flow characteristics. Increase in mobile phase flow rate results in a dilution effect such that the analytical signal obtained from a sample introduced into the d.c. plasma via the IC column is considerbly smaller than that obtained when the sample is directly aspirated. Thus, at a mobile phase flow rate of 1.5-2.0 mL/min, which is the range suitable for sample uptake rate for a typical cross-flow nebulizer, the signal is 2-4 times smaller than that obtained by aspirating the sample directly.

For an IC-DCPAES system, decreased measurement sensitivity can alsobe attributed to chromatographic processes (peak broadening, dilution of the analyte in the mobile phase, and incomplete recovery of the injected analyte), and also to the interface mechanism employed (low nebulizer efficiency, loss of analyte in the aerosol chamber, dilution of the analyte by the plasma and carrier gases, and inefficient introduction of the aerosol into the excitation zone).

Low measurement sensitivity can be imporved by using low mobile phase flow rates, using large sample introduction loops, or by preconcentrating the analyte prior to its introduction onto the analytical column. These will be discussed below.

2. Effects on Chromatographic Peaks

The chromatographic peaks obtained with the DCPAES detector have slightly longer retention times and wider peak widths than those obtained with the conductivity detector (Figure 1). This is attributed to the longer distance the effluent travels before reaching the excitation zone and the dispersion occuring in the spray chamber of the d.c. plasma system. With this detector, the shortest measurable retention time for an unretained species is approximately one minute. This retention time determines the shortest tubing that can be used for interfacing the chromatographic column witth the d.c. plasma, sample tube.

3. Plasma Stability Effects

Typically, detector capability is evaluated on the basis of its measurement sensitivity and selectivity, baseline reproducibility, and noise level. While measurement sensitivity obtained by using DCPAES can be quite high for many elements, baseline drift and noise level can be somewhat troublesome depending on the experimental. However, if the plasma is properly optimized and a suitable spectral line for the element of interest is chosen, these limitations can be kept to a minimum. Figure 2 shows the chromatograms obtained over a period of one hour at ten-minute intervals without readjusting the plasma. It is evident that if the plasma is properly optimized, the chromatography can be quite reproducible.

B. SPECIATION AND SOLUTION CHEMISTRY OF SELECTEDELEMENTS

1. Methods Development

Table I gives a summary of the elements studied, the species separated, and the chromatographic conditions employed.

The element selectivity of the DCPAES detection method is demonstrated in Figure 3. As shown in Figure 3(b), the chromatographic peaks obtained for As(III)/As(V) in the presence of other common ions were poorly resolved when the conductivity detector was employed. (Conducitivity detectors are universal detectors). On the other hand, when DCPAES was employed with arsenic atomic emission line selected, only AS(III) and As(V) were detected. Well resolved peaks were obtained and quantitation of these peaks was highly simplified. These results were published in 1987 (I.T. Urasa, et al. Anal Chem., 59, 1987, 1563-1568).

Because DCPAES can measure different species of a given element with equal efficiency,only one analytical curve is required for all the moieties of that element which may be in the sample. This is demonstrated in Figure 1 in which shows the chromatographic peaks obtained for equal amounts of Se(IV) and Se(VI), on the one hand using conductivity detector, (Figure 1(a)), and on the other hand using DCPAES (Figure 1(b)). With the latter detector system, the peak areas are identical. With the former, the peak area of the Se(IV) is only about 60% of the Se(VI) peak area. Se(IV) is derived from selenious acid which does not dissociate to the same degree as selenic acid (Se(VI)). Thus, the analytical signals obtained with the conductivity detector for both species differ. Such is not the case when DCPAES is used because the degree of dissociation of a compound containing a targeted element is inconsequential to the detection of the element with DCPAES. The results have been reported in: Urasa, et al, Anal. Chem, 59, 1987, 1563-1568.

The equal measurement efficiency achieved with DCPAES is further depicted in Figure 4. Here, a correlation was drawn between the peak areas obtained for varying concentrations of Cr(III) with similar concentrations of Cr(VI).

2. Chemical Transformations

The characteristics of elements, especially transition metals can vary considerably as solution conditions change. Changes in solution conditions can lead to element transformation. Such transformations can be monitored by employing the IC-DCPAES method. For example, the speciation of vanadium was found to be highly influenced by solution acidity. When a solution of $VOSO_4$ was placed in increasing concentrations of HCl, different moieties with different chromatographic

properties were formed. These moieties were separated and measured using the IC-DCPAES locked on an emission wavelength of vanadium at 437.9 nm. These results were reported in 1989 : (Urasa et al, J. Chromatogr. Sc., 1989, 27, 468-473). Also see Figure 5.

The DCPAES was used to monitor and study similar transformations for several other metals including the following: the degradation of hydrogen hexachloroplatinate(IV), a platinum containing compound which when placed in solution breaks down into several platinum containing fractions; (2) oxidation reduction reaction of Mn(VII)/ Mn(II); (3) oxidation of Fe(II) to Fe(III) in acid medium, and (4) the hydrolysis of Fe(II) and Fe(III) in aqueous solutions. These data have been published in: Jr. Chromatogr. 1991, 547, 211-223. The work on the hydrolysis of Fe(II) and Fe(III) has been submitted to: Int. J. Environ. Anal. Chem. (1991). These studies are summarized in Figures 6-9.

3. Element Fractionation Study

The DCPAES method has the capability for not only measuring species in solutions but also particulate forms of an element. This was demonstrated by our work with industrial process stream samples for which the analysis for chromium was done in three modes. In the first mode, the unfiltered sample was aspirated directly into the dc plasma system. The chromium concentration obtained in this way was for total chromium present, including ionic, particulate, and other unfilterable forms. In the second mode, the sample was first filtered with a 0.2-μm membrane filter before aspiration int the dc plasma system. This provided information on the unfilterable fraction of the total chromium present. In the third mode, the sample was filtered and then injected on the cation separator column. This provided information on the Cr(III) and Cr(VI) species present. The results are summarized in Table II. The power of the IC-DCPAES system to speciate chromium is well depicted in these data. These data were published in J. Chromatogr Sci. 1989, 27, 30-37.

Similarly, the IC-DCPAES method was applied in the study of the solution chemistry of several phosphorus compounds including orthophosphate, pyrophosphate, AMP, ADP and ATP. Figure 10 shows the chromatography obtained for a mixture of orthophosphate, pyrophosphate, and ATP. The chromatography was

for a mixture of orthophosphate, pyrophosphate, and ATP. The chromatography was monitored by measurements of the atomic emission line of phosphorus at 213.6 nm.

4. Improvement of Measurement Sensitivity

Considering that some of the species of the elements of interest can exist in very small concentration in a sample, it is imperative that the analytical method used has the sensitivity necessary to detect such species. Often, their concentration range is in the low ppm to ppb levels. The following attempts have been made to improve measurement sensitivity:

(a) The use of large sample loops This approach ensures that a large amount of the analyte is injected into the analytical column. Significant improvement was obsered when 1.0 mL loop was used compared to 100 μL loop. As shown in Figure 11, a linear relationship was observed between analytical signal and the loop size employed. This suggests that with loops as large as 1.0 mL, peak broadening and/or column overloading do not occur to any significant degree. Recovery studies indicated that virtually all the analyte injected with the 1.0 mL loop was eluted.

(b) Sample Peconcentration Sample preconcentration can be done on-column or off-column. We have employed both approaches. On-column preconcentration was done using chromium as the analyte. This was based on the principle that strong retention of the analyte in the column coupled with rapid regeneration of the column can serve as a simple and effective means of preconcentrating the analyte. By making multiple injections of the dilute sample, the highly retained analyte essentially builds up on the column. If this is then followed by the injection of a relatively high concentration of an appropriate eluting ion as discussed above, the built-up analyte will elute as a sharp peak whose concentration is now higher than in the original sample. In this way, detection capability can be imporved considerably, allowing the determination of ultratrace analyte concentrations.

This approach was applied to a solution consisting of 0.1 ppm each of Cr(III) and Cr(VI) in deionized water. A 1-mL aliquot of solution was injected onto the cation separator column using water as mobile phase. Following the elution of Cr(VI), which eluted as an unretained peak, 1.0 M HCl aliquot was injected to elute

injecting the acid, but in each case, the Cr(VI) was allowed to elute first before a subsequent injection. Not only did the analytical signals obtained for Cr(III) increase with the number of sample injections made, but his increase was linear with the injection steps. In order to verify that the number of injection steps correlated with solutions containing equivalent chromium concentration, a solution of 0.1 ppm Cr(III) was used for 1, 2, 5, and 10 injection steps as described above. The peak areas obtained were compared with those obtained with solutions of 0.1, 0.2, 0.5, and 1.0 ppm, respectively. As shown in the data in Table III, the correlation was almost a perfect 1 to 1. The same thing was found to be true for Cr(VI). Thus, this method of sample preconcentration is indeed a viable one and should be suitable for trace determination of chromium species, as will be shown below. The detectable concentration measured in this way was below 10 ppb for both Cr(III) and Cr(VI). These data were published in J. Chromatogr. Sci., 1989, 27, 30-37.

Off-column preconcentration was done by using a special preconcentration column, arsenic (V) serving as the analyte. The data obtained are shown in Figure 12.

(c) Improvement of Sample Introduction into the d.c. Plasma

The inability to introduce the sample into the excitation zone of the d.c. plasma with high efficiency has been one major drawback of the DCPAES approach. Two attempts have been made to correct this weakness.

Improvement of Nebulization Efficiency

The introduction of samples into the excitation zone of the d.c. plasma is done by conversion of the solution into fine aerosol using a nebulizer. Pneumatic nebulizers with which the d.c. plasma is traditionally equipped is a very low efficiency device.

We constructed a different type of nebulizer using glass frit, hoping that this would solve the problem. Two types of glass frit nebulizer were constructed. Type I consisted of a 5-cm diameter glass frit cemented between two glass

chambers. Two such units, one equipped with "medium" and the other with "fine" frit were constructed. Type II consisted of an 8 mm diameter rod-type glass frit attached to the end of a glass tubing; see Figure 13. The assembly in this case constituted a double aerosol chamber nebulizer system, the frit itself being demountable. In this way, frits of different pore sizes can easily be interchanged. Both "fine" and "very fine" frits were constructed for the study. Also, the type II nebulizer system can be used with the desolvation system depicted in Figure 13.

Evaluation of nebulizer performance was done putting into consideration the d.c. plasma characteristics. Typically, the nebulizer gas used also serves as a carrier of the analyte into the excitation zone. Thus, the flow velocity must be sufficient for the penetration of the aerodynamic barrrier attendant in the plasma region and at the same time be suitable for the maintenance of a stable plasma. Neither of the large diameter frit nebulizers could fulfil these requirements.

However, the reduction of the frit diameter to 8 mm produced remarkable improvements. Using the fine frit, a stable plasma could be maintained at 12.5 psi, allowing the device to be evaluated with respect to solution flow rate, sample acidity, linearity of the analytical data, and the integrity of the chromatographic peaks produced.

Even though the aerosol chamber employed is relatively large, chromatographic peak-tailing was not much worse than when a cross-flow nebulizer was used. The chromtographic data for the separation of Fe(II) and Fe(III) are shown in Table 4

Because of the much lower operating pressure employed with the frit nubelizer, the analytical curve data obtained correspondingly worse as indicated below:

The low operating pressure of the frit nebulizer did not provide the required velocity to push the analyte into the excitation zone of the plasma. This did not imporve even after employing "very fine" frit coupled with a desolvation chamber.

Modification of Plasma Geometry

Another attempt made to improve the efficiency of sample introduction into the excitation zone of the plasma involved modification of the plasma angle. Normally, the plasma angle, i.e., the angle between the two plasma arcs is approximately 70^{o}. The aerodynamic barrier created as a result of the plasma gas streams contributes to the reduced amount of sample aerosol reaching the excitation zone. Theoretically, this barrier can be minimized by reducing the plasma angle, thereby making the two arcs more collinear.

The reduction of the plasma angle resulted in very unstable plasma. The plasma plume became diffuse, making it impossible to locate the optimum excitation zone. No improvements were observed.

From the results obtained with the glass frit nebulizers discussed above and the plasma geometry modifications employed, we concluded that: (1) as long as pneumatic nebulizers are used, only minimal improvements will be made in increasing the amount of sample aerosol reaching the excitation zone; and (2) the plasma geometry of the d.c. plasma is best the way it is in the commercial system. Thus, not much can be gained by trying to change the design.

(d) The Use of Naturally Occurring Chelating Ligands to Preconcentrate Metal Ions

Work reported in the literature indicates that a number of synthetic organic complexing ligands are available for use in the preconcentration of metal ions in solution. In a few cases, naturally occurring ligands have been employed.

We have performed some preliminary studies involving the evaluation of chitin and chitosan as possible materials for preconcentrating metal ions in solution. Chitin is a polymeric material found in crab shells, insects, shrimp, and other crustacea. Chitosan is a derivative of chitin in which the acetyl groups found on the polysaccharide polymer have been converted into simple amino groups, thereby making them strong binding sites for metal ions.

Chitosan can selectively bind with metals such as Fe, Ag, Cd, Pb, Ni, Cu, Cr, and Mn. Our preliminary work has been centered around developing and characterizing

these materials for use in preconcentraing metal ions in dilute solutions, thereby serving as another way for improving measurement sensitivity in our metal speciation work.

A second area of application of our chitin/chitosan study is in the immobilization of toxic metals in environmental systems. Two features make this kind of application attractive: (1) the high abundance of these materials; and (2) they have no known toxicity.

Although we have started isolating chitin/chitosan from locally obtained raw materials (crab shells), most of the preliminary work has utilized commercially obtained supplies.

We have complexed iron, lead, and copper with chitosan by using both static mode (chitosan packed in a column) and dynamic mode (chitosan dispersed in a mixture with the metal ion solution). The data obtained for Pb are shown in Table 5, which indicates that at low solution concentrations, over 90% of Pb can be removed from solution when incorporated with chitosan. Similar results were obtained for Cu and Fe.

The metal-chitosan complex is formed on the solid polymeric backbone. Thus, if the objective is to use the material for preconcentration purposes, a suitable solvent must be used to strip off the metal ions from the polymer or dissolve the polymer altogether after the preconcentration process. If, on the other hand, the objective is to use the material to remove metal ions from solution (immobilization of metal ions), then it will be necessary that the complex formed is not only stable but insoluble.

In the case of Pb-Chitosan, solubility in water is insignificant. However, as solution acidity increases, dissolution increases as shown in the solubility curve in Figure 14. Increase in solubility was also accompanied by increase in the viscosity of the solution.

During the next Project Period, complex formation with chitosan will be continued focusing on: the binding characteristics of different trace heavy metals with chitosan; an evaluation of the stability constant of each metal-chitosan complex; solubility characteristics; complex formation kinetics; and inter element interference effects. Complex formation with chitosan will also be developed and characterized for

application as a metal ion preconcentration procedure, and as a means of immobilizing metal ions from environmental systems, such as natural waters and wastewaters.

Further discussion on future work with chitosan as a complexing ligand for metal ions is presented in the accompanying Renewal Application.

(e) Metal Speciation via Post Column Derivatization

In post column derivatization, the chemical species separated on the chromatographic column are derivatized down stream forming a new moiety that is more amenable to detection by some physical-chemical measurement technique. Where metal ions are involved, post column derivatization has generally resulted in the formation of metallochromic species, usually complexes, that can be monitored colorimetrically. There are two advantages to this approach: (1) several metals can be determined with one sample injection, providing multi-element detection capability; and (2) generally, the complexes formed have very high extinction coefficients, which is necessary for high measurement sensitivity.

Post column derivatization agents must meet several criteria, including: high extinction coefficient; soluble in water; should form stable complexes with the metals of interest; should have some selectivity for desired metal ions; and the reaction should be fast. We have done some preliminary work with post column derivatization using 4-(2-pyridylazo) or resoncinol (PAR) as the complexing agent.

We have characterized PAR with respect to its UV-Vis absorption as a free ligand and in complex with metal, using iron as an example; its molar extinction coefficient as a free lignad and in Fe-complex form; and the effect of ligand concentration on the metal complex formed.

Figure 15 shows a typical chromatogram obtained for Cu, Pb, Cd, and Co. We have observed that: (1) when sample size is increased, not only does peak size increase but also retention times change considerably, generally increasing; (2) the chromatography obtained in acid solution, especially when HCl is used becomes rather complex, producing sparious peaks.

The use of post column detection has a clear advantage in that several elements can be speciated simultaneously. However, even though work with PAR has been reported in the literature by others, the behaviour and usefulness of this ligand in metal speciation work still requires a thorough investigation. Sample conditions is one parameter that can significantly influence metal speciation. For example, many metals form chlorocomplexes with HCl. Yet where environmental samples are involved, acidification with HCl is a standard procedure. How does this affect the metal species present and is the ability of the PAR to form stable complexes affected? How about measurement selectivity - do Fe(II) and Fe(III), for example, form similar complexes with PAR such that one calibration curve could be used for both, as is the case when DCPAES is used? Are there other ligands which may be better than PAR for trace metal speciation?

These are among the questions that this research will attempt to find answers for during the next project period as described in the Renewal Application.

IV. OTHER ACCOMPLISHMENTS

A. PUBLICATIONS AND OTHER SCHOLARLY OUTCOMES

Publications: The following is a listing of publications which have resulted from this research.

1. Isai T. Urasa, Ward J. Mavura, Valerie D. Lewis, and Sang Ho Nam, "The Speciation of Iron, Manganese, Phosphorus, and Platinum in Aqueous Solutions by using Ion Chromatography Coupled with an element Selective Detector", J. Chromatogr., 1991, 542, 211-223.

2. I.T. Urasa and W.J. Mavura, "The Influence of Sample Acidification on the Speciation of Iron (II) and Iron (III)", Int. J. Environ. Anal. Chem., submitted, June 1991.

3. I.T. Urasa, S.H. Nam, and V.D. Lewis, "Element Selective Detectors for Ion Chromatographic Separations", In: Advances In Ion Chromatography, Petr Jandik and Richard M. Cassidy, Eds. Vol. 2 Century International, Medfield, MA, 1990.

4. I.T. Urasa, V.D. Lewis, and S.H. Nam, "Sepeciation of Trace Metals by Ion Chromatography with Element Selective Detectors", J. Chromatogr. Sci. 1989, 27, 468-473.

5. I.T. Urasa and S.H. Nam, "Direct Determination of Chromium (III) and Chromium (VI) with Ion Chromatography Using Direct Current Plasma Emission as Element-Selective Detector", J. Chromatogr. Sci., 1989, 27, 30-37.

6. I.T. Urasa, V.D. Lewis, J. DeZwaan, and S.E. Northcott, "Chracterization and Purity Determination of trans (±) 1,2-diamin cyclohexane platinum (IV) tetrachloride using Ligand Chromatography with a platinum selective detector", Analytical Letters, 1989, 22(3), 597-619.

7. I.T. Urasa and Fernus Ferede, "Use of Direct Current Plasma as an Element Selective Detector for Simultaneous Ion Chromatographic Determination of Arsenic (III) and Arsenic (V) in the Presence of other Common Anions", Anal. Chem, 1987, 59, 1563-1568.

8. I.T. Urasa and A.M. O'Reilly, "The Application of Direct Current Plasma Spectrometry to the Study of the Fractionation of Iron and Phosphorus in Surface Waters", Talanta, 1986, 33, 593-599.

9. I.T. Urasa and Fernus Ferede, "The Determination of Phosphates Using Ion Chromatography: An Evaluation of Influential Factors" Int. J. Environ. Anal. Chem. 1986, 23, 189-206.

10. I.T. Urasa, "Determination of Arsenic Boron, Carbon, Phosphorus, Selemiun, and Silicon in Natural Waters by Direct Current Plasma Atomic Emission Spectrometry", Anal. Chem. 1984, 56, 904-908.

B. SELECTED PRESENTATIONS

1. "Element Speciation by Using Ion Chromatography Coupled with Element Selective detector", 21st International Symposium on Environmental Analytical Chemistry, Jekyll Island, GA., May 20-22, 1991.

2. "Analytical Applications of Chitin/Chitosan", Virginia Academy of Sciences Meeting, Blacksburgh, VA., May 23-25, 1991.

3. "Application of Chitosan in Environmental Problems", Southeast Regional Meeting American Chemical Society, Richmond, VA., November 12-15, 1991.

4. "Element Speciation by Using Chromatographic Techniques Coupled with Element Selective Detectors", 18th Annual National Conference of the National Organization of Black Chemists and Chemical Engineers, Washington, D.C., Aptil 1-5, 1991.

C. M.S. THESES

Below is a listing of M.S. Theses (in Chemistry) prepared by graduate students who were involved in this research.

1. "Evaluation of Chitin/Chitosan as a Complexing Ligand for Metals: Application in Trace Metal Speciation"
   M.S. Thesis: Completion date - expected December 1991
   Candidate: Julio C . Arce, Advisor: I.T. Urasa

2. "The Influence of Acidification on the Speciation of Iron"
   M.S. Thesis: Completion date: December, 1990
   Candidate: Ward J. Mavura, Advisor: I.T. Urasa

3. "Chromatographic and Spectroscopic Characterization of Isofenphos"
   M.S. Thesis: Completion date: August, 1990
   Candidate: Stephanie Braye-Peebles, Advisor: I.T. Urasa

4. "A Study of the Solution Chemistry of Selected Platinum Compounds"
   M.S. Thesis: Completion date: April 1989
   Candidate: Valerie D. Lewis, Advisor: I.T. Urasa

5. "Speciation of Trace Metals by Using Ion Chromatography with Direct Current Plasma Detection"
   M.S. Thesis: Completion date: December 1988
   Candidate: Sang Ho Nam, Advisor: I.T. Urasa

6. "An Evaluation of the Factors that Influence Ion Chromatographic Determination of Arsenic, Phosphorus, and Selemin Species"
   M.S. Thesis: Completion date: April 1986
   Candidate: Fernus Ferede, Advisor: I.T. Urasa

V. PLANS FOR THE NEXT PROJECT PERIOD

We have demonstrated in this research that when d.c. plasma atomic emission spectromety is used in combination with ion chromatography to do element speciation measurments, three advantages are gained. First, the element species separated on the chromatographic column are measured with equal efficiency, requiring only one calibration curve for a given element. Second, changes that may occur to the analyte during sample processing or storage can be monitored; thus, the appearance or disappearance of a certain form of the element can always be determined. Third, the appearance of spurious peaks, as may be encountered when universal detectors are used, is eliminated. Therefore, even though the detection limits obtained with the d.c. plasma detector may not be in the low ppb concentration range, which might be required for some analyses, it will continue to be an important tool in any metal speciation work.

During the next project period we plan to achieve the following objectives:

I. Evaluation of Syntethic and Naturally occuring Chelating Ligands as Preconcentration Agents for Trace Metal Speciation

As discussed in the report, chitin/chitosan appears to have suitable properties for its use as a chelating agent for trace metals. Preliminary studies have shown that Pb, Fe, and Cu form strong complexes and that over 90% can be removed from solution. Further studies on this material will focus on: (1) the isolation and characterization of this polymer from locally obtained crab shells; (2) characterization of complexes formed between this polymer and selected metals including measurment of stability constants, solubility, and metal recovery studies; (3) evaluation of sample matrix effects; (4) reaction kinetics; and (5) its possible use for the immobilization of metals from solution (this would be of particular significance in remediation operations).

Also to be evaluated as an agent for trace metal preconcentration is a synthetic chelating ligand which is commercially available as Metpac CC-1 chelating resin consisting of weak acid (COOH) and weak base (NH) functional groups. This resin has a complexing selectivity for transition metals and lanthanide metals in the pH range of 5-6. However, here too, the effect of sample acidity will critically be evaluated.

II. Post Column Derivatization in Combination with Element Selective Detector for Metal Speciation

The use of post column derivatization in metal determination has two advantages. First, generally the ligands used form coloured complexes with more than one metal; thus, the method is a simultaneous multielement one. Second, in some cases, extermely high measurement sensitivities can be obtained. However, information is needed on how the reactivity of the ligands used is affected by sample conditions. For example, what is the effect of sample acidification? Transition metals and the lanthanides form stable chlorocomplexes. These may rob the sample solution of the free metal ions that would be needed to form the metallochromic complex.

We will use the DCPAES in combination with postcolumn derivatization system to study the interaction of several metals with PAR, evaluating such parameters as completeness of reaction; reaction products; etc.

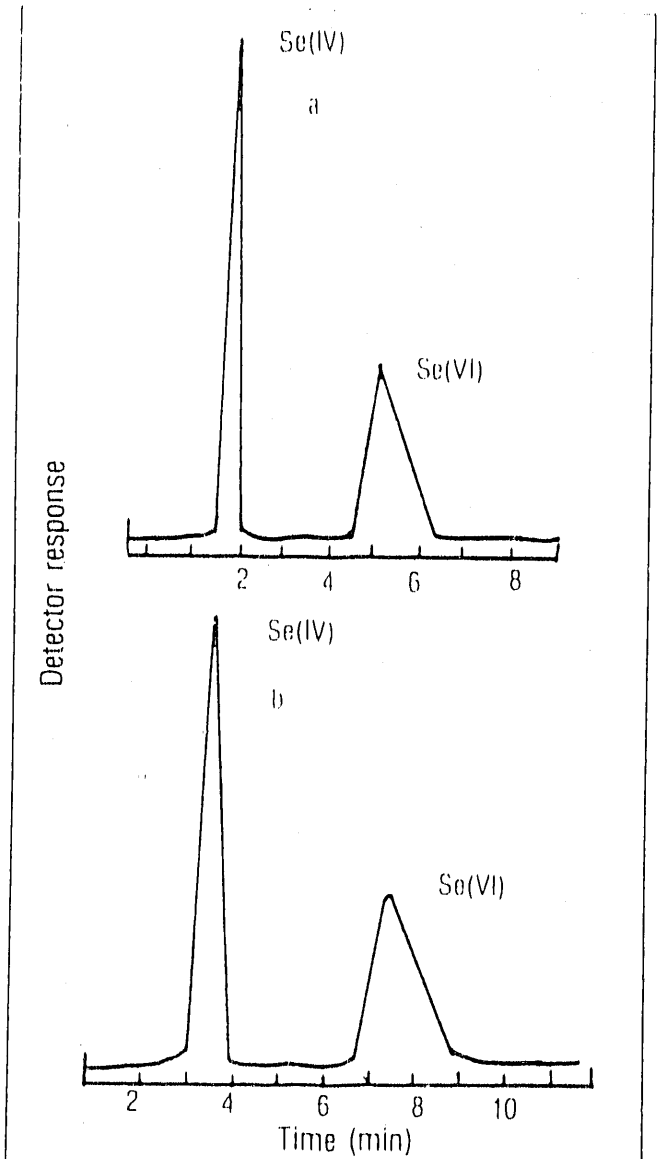
III. The Influence of Sample Conditions on Metal Speciation

One fundamental requirement of speciation is that the analyte is not influenced by sample processing procedures. However, where environmental samples are involved, acidification is often required.

We will evaluate the effect of sample acidification in three ways: (1) the transformation that it may cause on the analyte; (2) the possible changes that it may induce on the PAR ligand hence affecting the stability of the metal complex formed; and (3) its effect on the effectiveness of chitosan as a preconcentration agent.

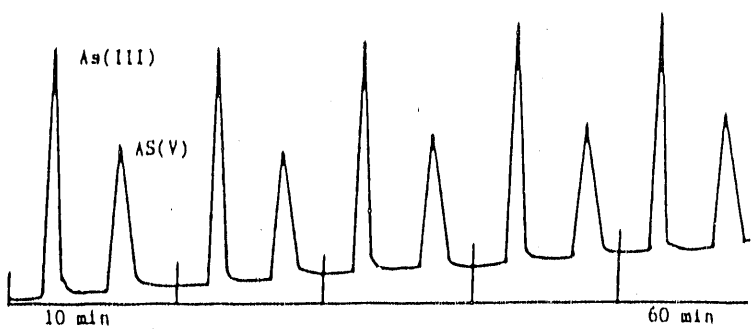
The three new thrusts outlined above are discussed in detail in the accompanying Project Renewal Application.

Figure 1. Comparison of IC peaks obtained using Conductivity Detector with those obtained usingD.C. Plasma Atomic Emission Detector.



Ion chromatographic peaks of Se(IV) and Se(VI) obtained with (a) conductivity detection and (b) dc plasma atomic emission detection Column HPIC As4 eluent 3 0 mM $NaHCO_3$-2 4 mM Na_2CO_3

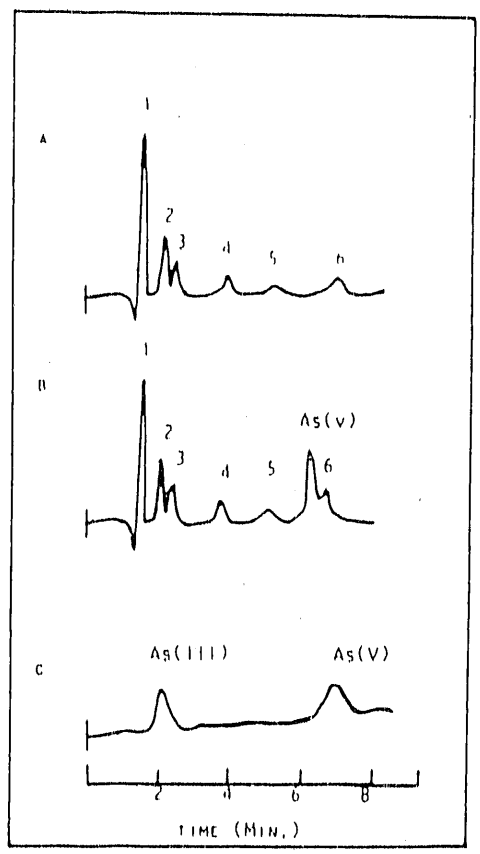
Figure 2. Influence of analysis time on Plasma stability and peak quality.



Column: HPIC-AS4
Eluent: 3 mM $NaHCO_3$ /2.4 mM Na_2CO_3

.. Ion chromatographic peaks of As(III) and As(V) obtained at ten-minute intervals with d.c plasma atomic emission detection.

Figure 3. Speciation of As(III) and As(V) in the presence of other ions.



Ion chromatographic separation of As(III) and As(V) in the presence of other anions: (A) 1.0 ppm each of F^- (1), Cl^- (2), NO_2^- (3), PO_4^{3-} (4), NO_3^- (5), and SO_4^{2-} (6), with conductivity detection; (B) same as (A) plus 10 ppm each of As(III) and As(V) with conductivity detection; (C) same as (B) with dc plasma detection. Eluent: 3.0 mM $NaHCO_3$/2.4 mM Na_2CO_3.

Figure 4. Comparison between chromatographic peak areas of Cr(III) and Cr(VI) obtained with IC-DCPAES

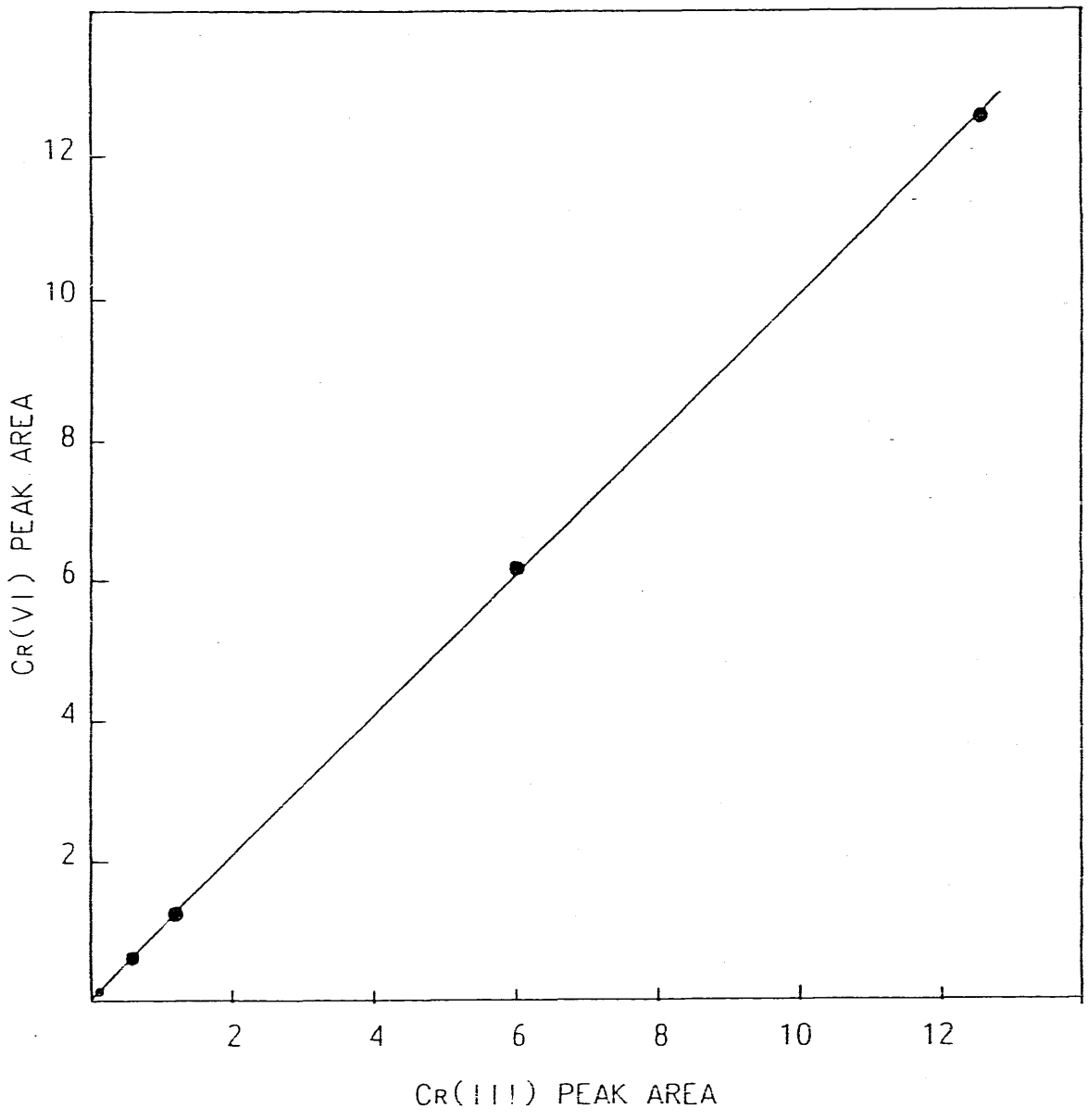
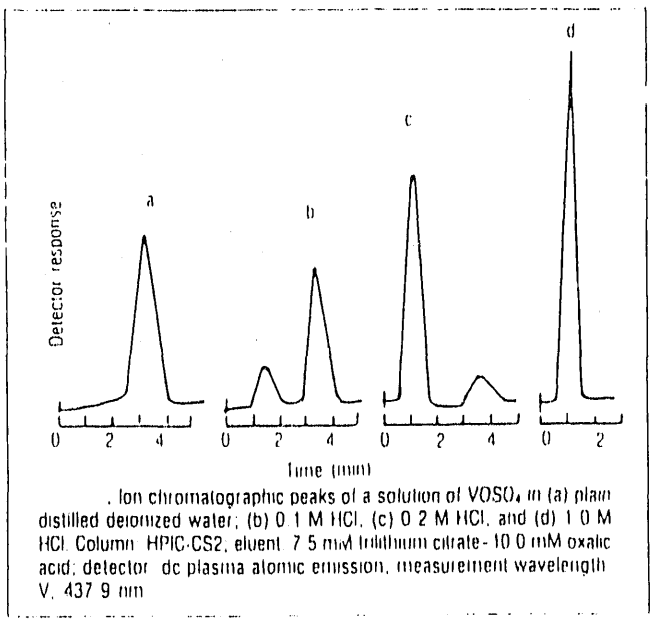
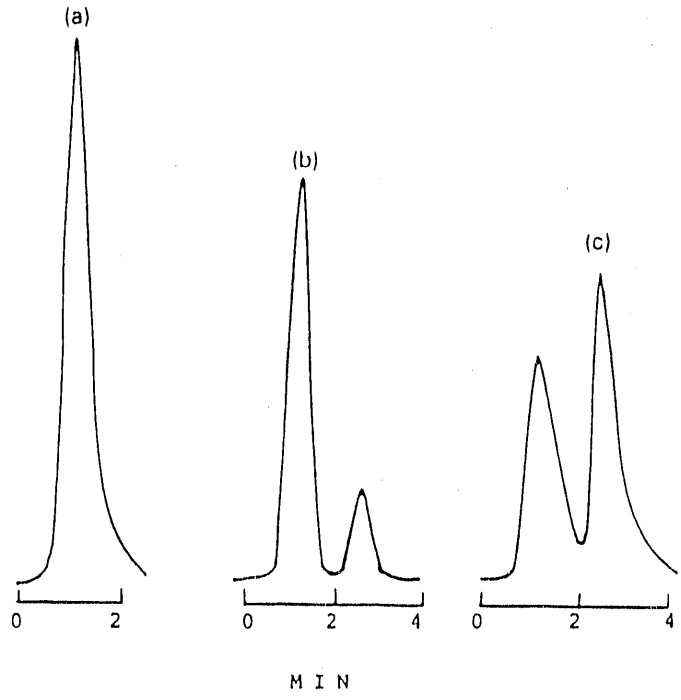


Figure 5. Effect of sample Acidification on the Speciation of Vanadium.



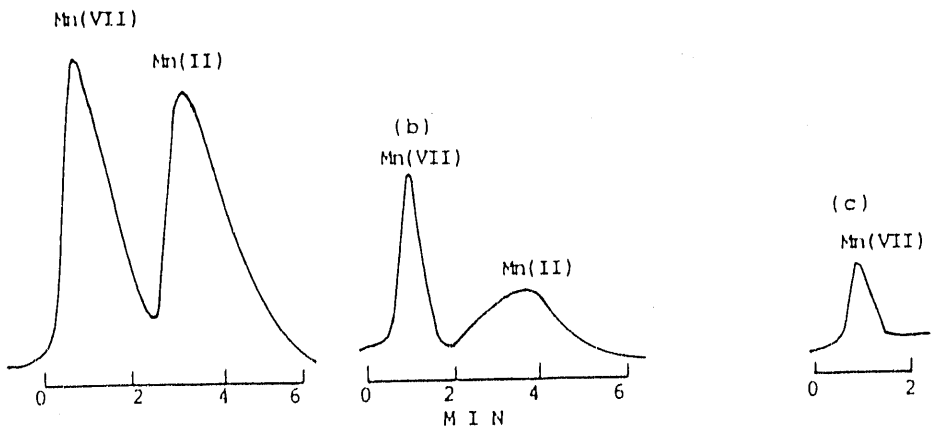
. Ion chromatographic peaks of a solution of $VOSO_4$ in (a) plain distilled deionized water; (b) 0.1 M HCl, (c) 0.2 M HCl, and (d) 1.0 M HCl. Column: HPIC-CS2, eluent: 7.5 mM trilithium citrate - 10.0 mM oxalic acid; detector: dc plasma atomic emission, measurement wavelength: V, 437.9 nm

Figure 6. Degradation of hexachloroplatinate (IV) monitored by IC-DCPAES.



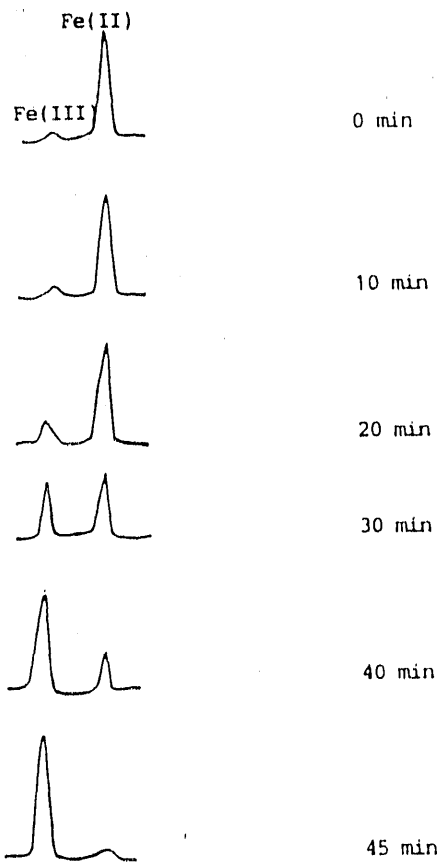
Ion chromatograms of hydrogen hexachloroplatinate(IV) obtained with d c plasma atomic emission spectroscopy detection of platinum; eluent = 10 m*M* oxalic acid-7.5 m*M* trilithium citrate (a) Fresh solution; (b) 14 day-old solution and (c) 28 day-old solution.

Figure 7. Oxidation of Mu(II) by Mn(VII) monitored by IC-DCPAES.



Ion chromatographic separation of a mixture of manganese(II) and manganese(VII) obtained with d.c. plasma atomic emission spectroscopy detection; sample = 1.0 ppm Mn(II) 1.0 ppm Mn(VII); eluent = 20 m*M* oxalic acid 15 m*M* trilithium citrate (a) 1 Min, (b) 5 min and (c) 10 min after mixing

Figure 8. Oxidation of Fe(II) to Fe(III) by dilute HNO_3 monitored by IC-DCPAES.



Oxidation of Fe(II) in 0.5 *M* nitric acid monitored with ion chromatography and plasma atomic emission spectroscopy; sample = 1.0 ppm Fe(II), eluent = 10 m*M* oxalic acid-7.5 m*M* trilithium citrate.

Figure 9. Hydrolysis of Fe(II) and Fe(III) in aqueous solution monitored by IC-DCPAES.

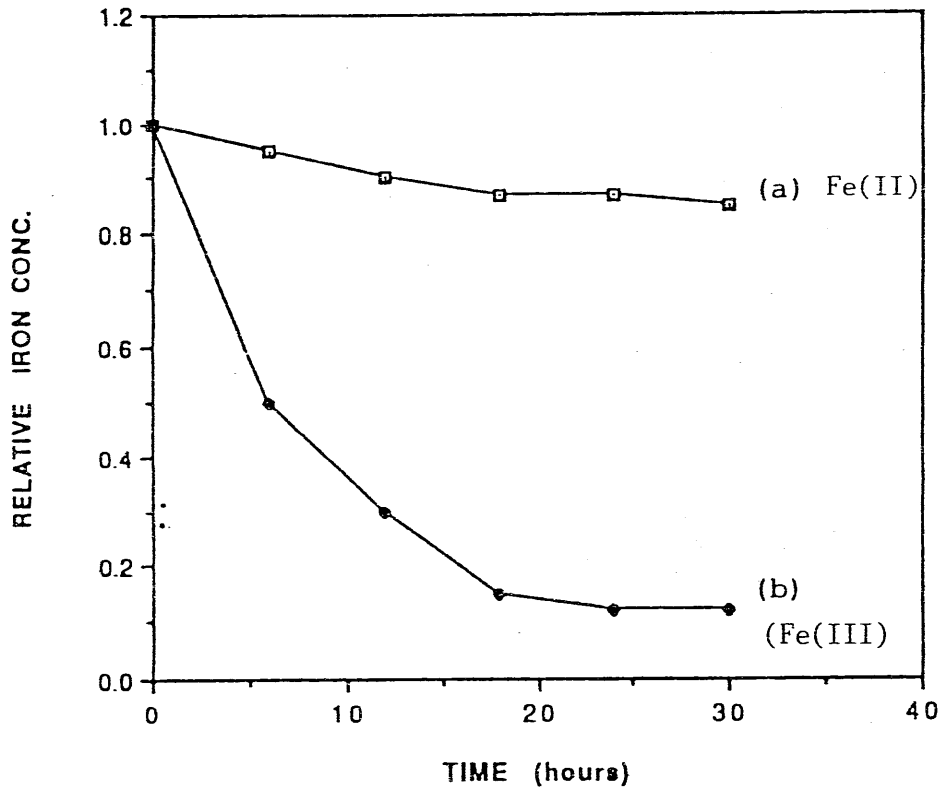
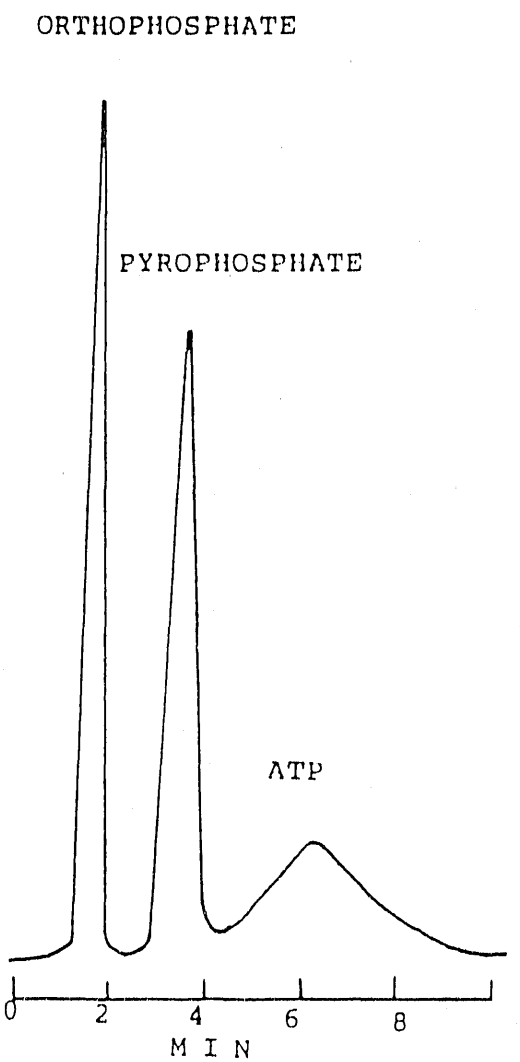
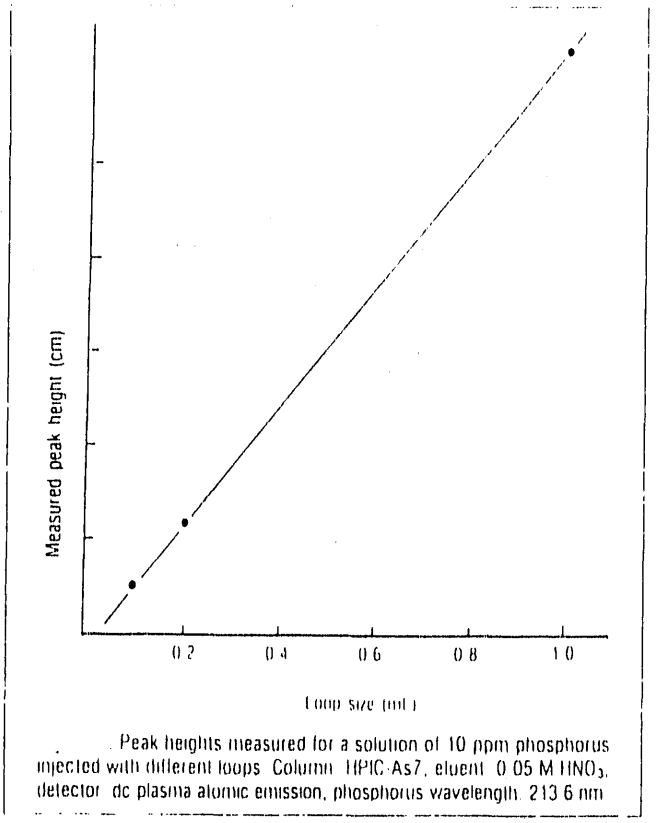


Figure 10. Separation of orthophosphate, pyrophosphate, and ATP using IC-DCPAES.



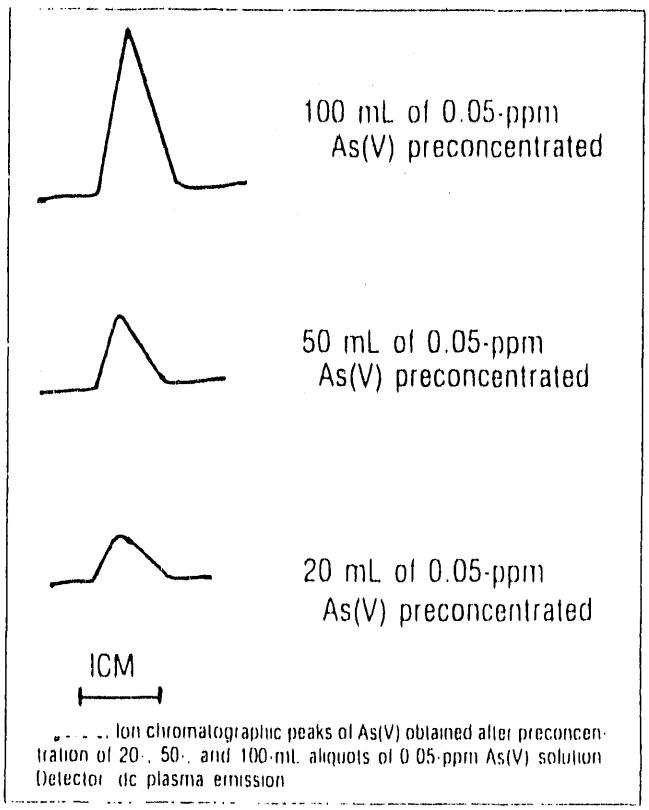
Ion chromatographic separation of orthophosphate, pyrophosphate, and ATP obtained with d.c. plasma atomic emission spectroscopy detection of phosphorus; column = HPIC-AS-7; eluent = 0.5 *M* nitric acid.

Figure 11. Relationship between sample loop size and chromatographic peak size.



Peak heights measured for a solution of 10 ppm phosphorus injected with different loops. Column: HPIC-As7, eluent: 0.05 M HNO_3, detector: dc plasma atomic emission, phosphorus wavelength: 213.6 nm

Figure 12. Preconcentration of As(V); monitored with IC-DCPAES.



...ion chromatographic peaks of As(V) obtained after preconcentration of 20-, 50-, and 100-mL aliquots of 0.05-ppm As(V) solution. Detector: dc plasma emission

Figure 13. Glas Frit Nebulizer used in combination with Desolvation System.

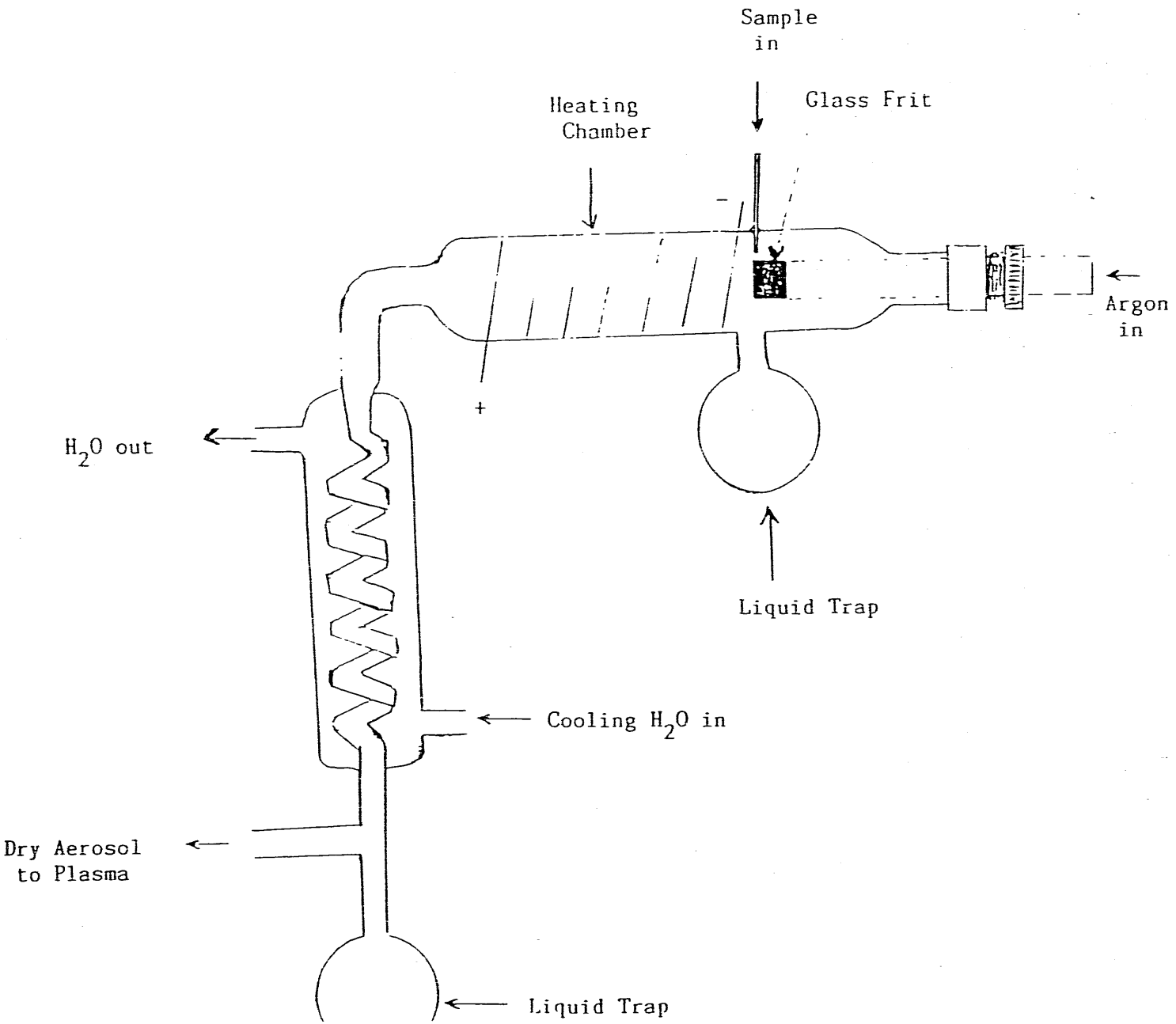


Figure 14. Effect of solution pH on the Complexation of Pb by Chitosan.

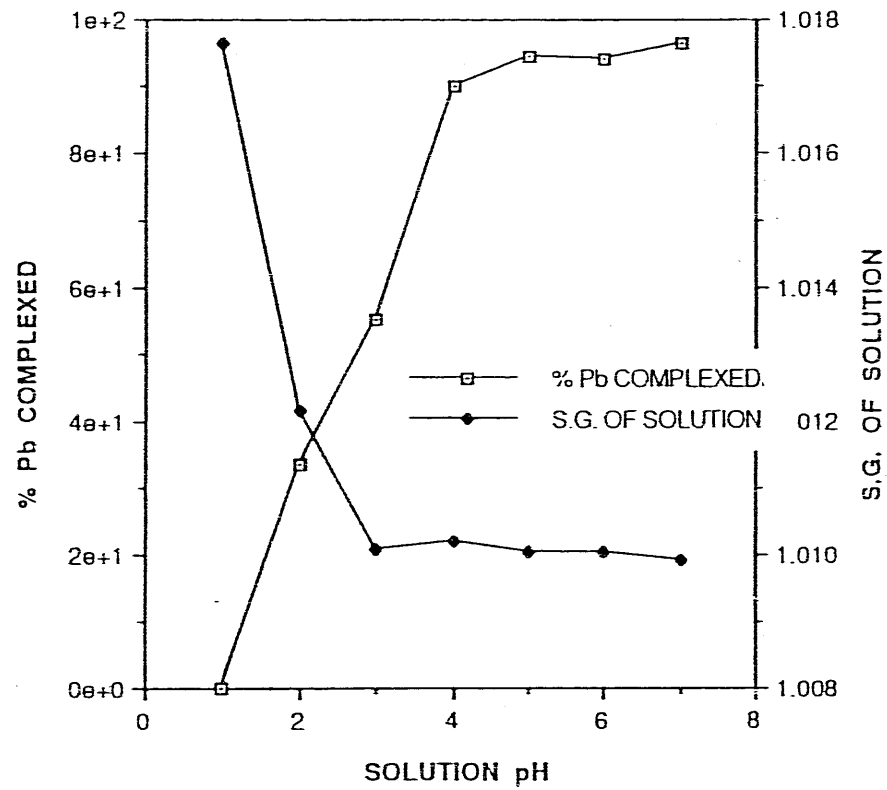


Figure 15. Chromatogram of Pb, Cu, Cd and Co obtained via Post column Derivatization detection.

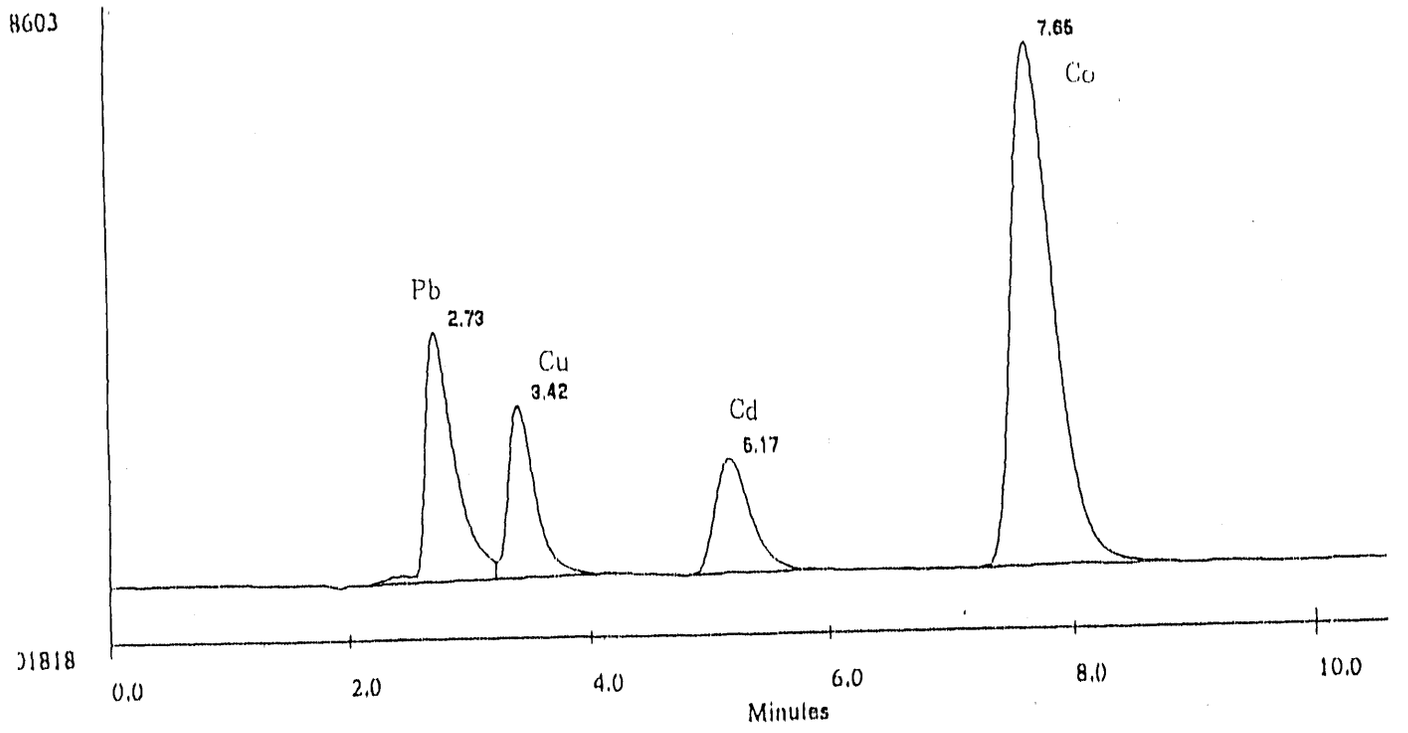


Table 1. The Speciation of Selected Elements Using IC-DCPAES*

Element	(nm)	Measurable Concentrations (ppm)+	
		Without preconcentration	With preconcentration
As(III), As(V)	197.2	1.0	0.5
Cr(III), Cr(VI)	425.4	0.1	0.01
Fe(II), Fe(III)	373.4	0.1	0.005
Mn(II), Mn(VII)	403.0	0.05	0.005
P	213.6	0.2	0.1
Pt(IV)	204.9	10.0	1.0
V(IV), V(V)	437.9	0.1	0.05

*In all cases, a 1.0 mL loop was used for sample injections.
+Measurements were done at optimum chromatographic and spectroscopic conditions.

Table 2. Analysis Results of the Determination of Chromium Species in Industrial Prosess Stream Samples

Analysis Mode Cr Con. (ppm) Sample	[1]D.C. Plasma; Direct Injection, Unfiltered	[2]D.C. Plasma; Direct Injection, Filtered	[3]IC-DCP; Column Injection Filtered
I	111.6±7.0	107.7±4.3	Cr(VI)=99.4±5.0 Cr(III=2.6±0.1
II	450.0±9.0	404.5±8.0	Cr(VI)=367.8±11.0 Cr(III=38.7±2.0
III	115.5±3.0	103.2±3.0	Cr(VI)=93.6±5.0 Cr(III=2.6±0.1

1. Sample was aspirated directly into the d.c. plasma
2. Sample was aspirated into the d.c. plasma after filtration with 0.μm.
3. Filtered sample was injected onto cation column, the effluent was aspirated directly into the d.c. plasma

± Values are standard deviations of the mean of three replicate measurements.

Table 3. A Correlation between Peak Areas Obtained with Sample Preconcentration and those Obtained with different Standard Solutions (1.0 mL loop used)

	By Preconcentration of 0.1 ppm (Cr(III)		By Using Different Solutions		
Number of	Corresponding Mass (μg)	Peak Area (V. Min.)	Sample Conc. (ppm)	Mass (μg)	Peak Area (V. Min)
1	0.10	0.5±0.04	0.10	0.10	0.48±0.03
2	0.20	0.95±0.05	0.20	0.20	1.02±0.05
5	0.50	2.50±0.1	0.50	0.50	2.50±0.1
10	1.00	5.00±0.2	1.00	1.00	4.80±0.1

± Values are standard deviations of three relicate measurements.

Table 4(a). Chromatographic Data Obtained with Two Types of Neublizers

Fe Species	Retention Time, Min.	
	Cross-Flow Neb.	Glass Frit Neb. (Fine pore)
Fe(III)	1.60	1.75
Fe(II)	2.60	2.70

Table 4(b). Analytical Parameters for Two Nebulizers

Nebulizer	Operating Pressure	Background	Slope of Anl. Curve
Glass Frit (fine pore)	12.5 psi	500 nA	0.40
Cross Flow Nebulizer	20.0	150 nA	0.88

Table 5. Complex Formation between Pb andChitosan

Moles PB Incorporated	Moles PB Recovered	% Complexed
0.482	0.026	94.700
1.446	0.032	97.800
2.413	0.057	97.600
4.826	0.157	96.700
7.239	0.665	90.800
9.651	1.222	87.300

END

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