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The speciation of iron, manganese, phosphorus and platinum in aqueous solutions by using ion chromatography coupled with an element selective detector

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ABSTRACT

A method is described that employs ion chromatography in combination with d.c. plasma atomic emission spectroscopy to speciate iron, manganese, phosphorus and platinum in aqueous solutions. The element selective nature of the d.c. plasma allows its use as a chromatographic detector for all species of a targeted element eluting from a chromatographic column. This procedure is not only insensitive to matrix effects but is also suitable for monitoring element transformation that can occur as a result of biological or chemical changes.

INTRODUCTION

The fundamental objective in element speciation is to identify and quantify the various forms of a targeted element in a sample. The analytical data obtained in this kind of procedure is important in the evaluation of the impact of the element on biological and environmental systems.

The existence of an element in more than one form may be due to the chemistry of that element (many transition metals can exist in nature in two or more oxidation states, manifesting quite different chemical properties); biological and/or chemical activities which may cause the element to be transformed into a different form; or man-made sources, such as industrial discharges, which may introduce into the environment a form of the element which may not have been there originally. Generally, the concentration of these species is very small so that they can only be detected by analytical techniques and methodologies having detection capabilities for low ppb concentration ranges or less.

The employment of metal species in clinical and pharmaceutical processes has considerably accelerated the development of methods which are suitable for analytical measurements in complex matrices. Every aspect of analytical chemistry has been explored in the search for efficient speciation procedures, including electrochemical [1–9], spectroscopic [10–14], chromatographic [13–17], and a combination of these techniques [18–27]. While some of these techniques have been proved to have suitable features for speciation work, an ideal speciation method is defined as one which can provide the desired information without altering the original sample in any way. While, in principle, techniques such as element selective electrodes have this property, they are limited by their inability to respond to all the species that might be present with good measurement sensitivity.

In the absence of such a method, the approach which appears to be most suitable for preserving analyte integrity is the one which can physically separate the species which are present and then quantify them independently. Such an approach has been employed in several laboratories, whereby chromatographic systems have been interfaced with a detector that only responds to the species of a targeted element in the sample [28–41]. In this way, all the chemical entities containing the element of interest are measured with equal efficiency. In our approach, d.c. plasma atomic emission is used as an element selective method for the detection of ion chromatographic effluents [37–41].

The use of d.c. plasma atomic emission as an element selective method of detection was first reported by Uden *et al.* who employed it in the detection of transition metal complexes separated with high-performance liquid chromatography [28]. Direct current plasma atomic emission spectroscopy has an inherent advantage in that all forms of a given element are equally excited when introduced into the excitation zone of the plasma; and that the analytical signal obtained is only based on the atoms of the targeted element. Furthermore, even when different mobile phase systems are used, representing a different sample matrix, the effect on the signals obtained are negligible. Thus, whether the element species is anionic, cationic, or neutral, the signal obtained is based only on the atomic concentration of the element.

The work presented in this paper was based on employing this approach to study the behavior of iron, manganese, platinum, and phosphorus and to evaluate the factors that influence their speciation in aqueous solutions. These elements were chosen because of their importance in biological and environmental processes. As with many other elements which can exist in more than one form, their chemical activities and their impact on biological systems are highly influenced by the form in which they exist. The data presented here can serve as a model for developing analytical measurement protocols for speciating similar elements, in particular heavy metals.

EXPERIMENTAL

Our objective was to develop speciation procedures for iron, manganese, platinum and phosphorus by using ion chromatography in combination with a d.c. plasma atomic emission spectrometer. The ion chromatograph was used to separate species of these elements in solution, while the d.c. plasma was used as an element selective detector for the ion chromatograph. The chromatographic effluents were monitored by measuring the atomic emission of each element at a selected wavelength. In this way, all the chromatographic effluents containing that element were detected with equal efficiency.

Equipment

The chromatographic system used consisted of an ion chromatograph, Dionex Model 2010i (Dionex, Sunnyvale, CA, USA) equipped with a conductivity detector

Model CDM-1, and the following separator columns: cation separator column, Model HPIC-CS2, and HPIC-CS5; and an anion separator column, Model HPIC-AS5. All separator columns were used with corresponding guard columns.

The detector consisted of a three electrode d.c. plasma atomic emission spectrometer, Model Spectraspan IV (Applied Research Instruments). Interfacing of the chromatograph and the d.c. plasma system has been described elsewhere [38].

Reagents and chemicals

Chemicals and other materials used included ACS certified ferrous ammonium sulfate, ferric nitrate, manganous chloride, potassium permanganate, sodium bicarbonate, oxalic acid, all from Fisher Scientific (Fairlawn, NJ, USA). Hydrogen hexachloroplatinate(IV) hydrate, and trilithium citrate were obtained from Aldrich Chemicals (Milwaukee, WI, USA). Redistilled hydrochloric acid and double-distilled nitric acid were obtained from GSF Chemicals (Columbus, OH, USA). A Nanopure II water purification system from Sybron (Boston MA, USA), was used in the preparation of deionized (18-MΩ) water. Sodium phosphate was obtained from Mallinckrodt (Paris, KY, USA) and adenosine triphosphate, adenosine diphosphate and adenosine monophosphate were obtained from Sigma Chemicals (St. Louis, MO, USA).

General procedure

Characterization of the solution chemistry of the elements studied in this work relied on the use of standard solutions. Analytical solutions were prepared by the dilution of appropriate volumes of 1000 ppm of Fe(II) (ferrous ammonium sulfate; Fe(III) (ferric nitrate); Mn(II) (manganous chloride); Mn(VII) (potassium permanganate); and Pt (IV) (hydrogen hexachloroplatinate(IV) hydrate. In each case, solutions were prepared in 0.1 *M* hydrochloric acid.

Samples were injected onto the chromatographic column with a 1.0-ml injection loop. The mobile phase flow-rate was kept constant at 2.0 ml per min.

Chromatographic effluents were detected by measuring the atomic emission signal of the element of interest at the respective wavelengths shown in Table I.

The chromatography was monitored using commercially obtained chromatographic software which gave data on peak areas, peak height, retention time, and the fraction of the species present. In the case of iron, the data obtained with the element selective detector approach was compared with that obtained with the classical 1,10-phenanthroline method. Measurements involving phosphorus were carried out using both the d.c. plasma approach and a conductivity detector.

TABLE I

ELEMENTS AND WAVELENGTHS USED

Element	Wavelength (nm)
Iron	373.4
Manganese	403.0
Phosphorus	213.6
Platinum	204.9

RESULTS AND DISCUSSION

Speciation of iron

In aqueous solutions, iron can exist as hexaaquairon(II) ($Fe(H_2O)^{2+}{}_6$), or hexaaqua iron(III) ($Fe(H_2O)^{3+}{}_6$), depending on the prevailing solution conditions. Since Fe(II) is the form that is more readily available to biological functions, it is important to not only know the actual concentrations of this species present in a sample, but also to be able to monitor the transformation that it may undergo. The ability to separate and quantify the iron species in which we are interested by using a detector sensitive only to iron avoids errors associated with methods that rely on the conversion of one form into the other before quantitation, such as the 1,10-phenanthroline method.

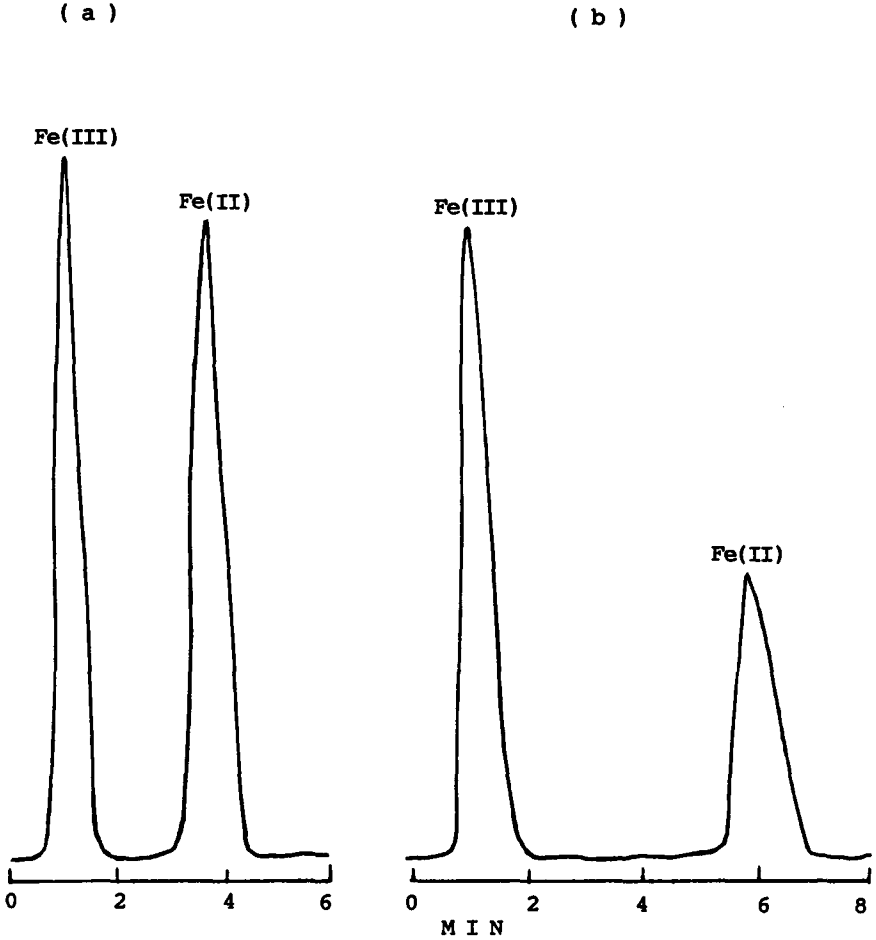

Fig. 1. Ion chromatographic separation of Fe(II)–Fe(III) obtained with d.c. plasma atomic emission spectroscopy detection; sample = 5 ppm Fe(II)–5 ppm Fe(III). (a) Eluent = 10 m*M* oxalic acid–7.5 m*M* trilithium citrate; and (b) eluent = 5.0 m*M* oxalic acid–3.75 m*M* trilithium citrate.

The chromatograms shown in Fig. 1 were obtained by injecting equal concentrations of iron(II) and iron(III) and monitoring the effluent by measuring the atomic emission of iron at 373.4 nm. The resolution between the two peaks is dependent on the concentration of the mobile phase.

This factor can be manipulated to shorten the analysis time, as required without compromising the quality of the analytical signal obtained, as can be seen in Fig. 1b. The analytical signal obtained is based on the atom population of the central metal; in this case, iron. In this way, only one analytical curve is required in the determination of both iron(II) and iron(III) species present in the sample. The analytical curves obtained for the two iron species have practically identical slopes with correlation coefficients greater than 0.9999.

Because an element selective detector responds only to the targeted element in the chromatographic effluent, it is useful in monitoring *in situ* chemical and biological changes that a sample or component of a sample may undergo. This is demonstrated in Fig. 2 which represents the oxidation of Fe(II) in dilute nitric acid. The oxidation process was monitored by injecting a small sample of the solution mixture onto a

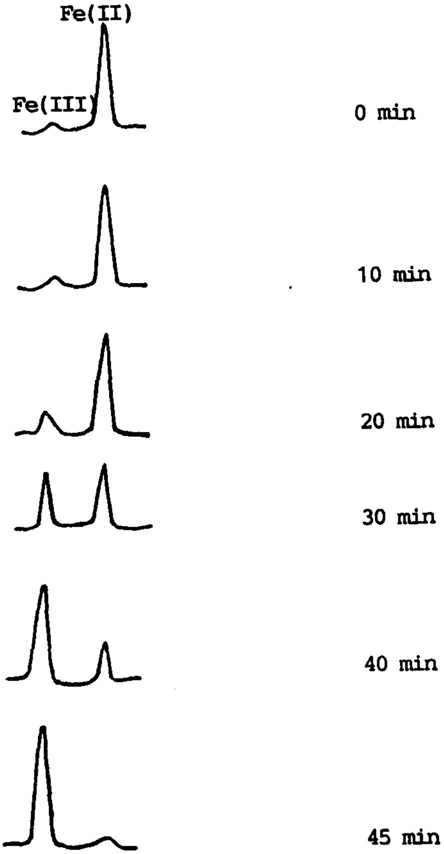

Fig. 2. Oxidation of Fe(II) in 0.5 M nitric acid monitored with ion chromatography–d.c. plasma atomic emission spectroscopy; sample = 1.0 ppm Fe(II); eluent = 10 mM oxalic acid–7.5 mM trilithium citrate.

cation chromatographic column and measuring the atomic emission signal obtained every several minutes. Such measurements are made possible by two features of the element selective detector approach: (1) the ability to measure species of the same element with equal efficiency; and (2) the ability to monitor these species independently without having to convert one into the other. This method is suitable for monitoring biological activity in which metal ions are involved.

The element selective detector approach for the determination of iron species was compared with the classical 1,10-phenanthroline method for the determination of iron. In this method, iron(III) is first converted into iron (II), which is then complexed with the 1,10-phenanthroline ligand, forming a colored complex. When comparing these two methods, not only is the 1,10-phenanthroline method less sensitive as is shown in Table II, but the necessity to first reduce iron(III) into iron(II) makes the method tedious, and more susceptible to errors.

Solution chemistry of manganese

Manganese has three stable oxidation states, Mn(II), Mn(IV), and Mn(VII). Manganese(IV) is insoluble in aqueous solutions; therefore the studies on manganese speciation were limited to the Mn(II) and Mn(VII) species. Manganese(VII) is a powerful oxidizing agent which, when mixed with manganese(II), will quickly oxidize the latter to the insoluble manganese(IV) species. Therefore, initial studies of the two manganese species were carried out separately in water to determine their chromatographic properties.

Manganese(II) and manganese(VII) cannot be studied together in a mixture because the former is oxidized to manganese(IV) which is insoluble, and, concurrently manganese(VII) is reduced to manganese(IV). The oxidation–reduction process was monitored by injecting a mixture of Mn(II) and Mn(VII) on the chromatographic column immediately after mixing them. This was repeated every five minutes and the ensuing chromatographic data are shown in Fig. 3. Initially, the two peaks obtained, Fig. 3a, for equal concentrations of Mn(II) and Mn(VII) were almost identical

TABLE II

SENSITIVITY COMPARISON BETWEEN ION CHROMATOGRAPHY–d.c. PLASMA ATOMIC EMISSION SPECTROSCOPY (IC–DCPAES) AND 1,10-PHENANTHROLINE METHODS FOR THE DETERMINATION OF IRON SPECIES IN ESTUARY AND RIVER SEDIMENTS

Slopes of the analytical curves for iron species Fe(II) and Fe(III) using the IC–DCPAES method are 1.21 and 1.19, respectively. Slopes of the analytical curves for iron species Fe(II) and Fe(III) using the 1,10-phenanthroline method are 0.22 and nil, respectively.

Sample	Method		
	IC–DCPAES		1,10-phenanthroline
	Fe(III)[a]	Fe(II)[a]	Fe(II)[a]
Estuary sediment	5.21 ± 0.03	9.55 ± 0.2	15.33 ± 0.43
River sediment	14.24 ± 0.84	31.12 ± 0.95	47.11 ± 1.05

[a] ppm.

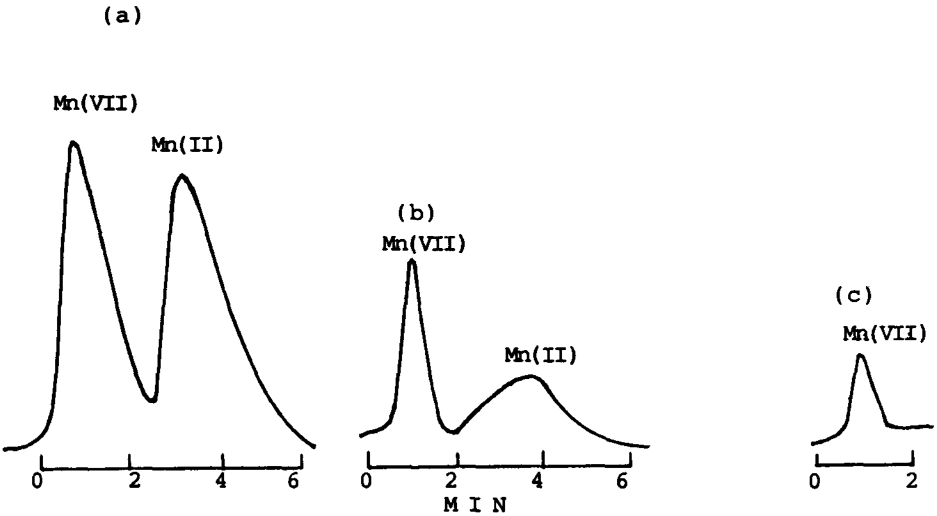

Fig. 3. Ion chromatographic separation of a mixture of manganese(II) and manganese(VII) obtained with d.c. plasma atomic emission spectroscopy detection; sample = 1.0 ppm Mn(II)–1.0 ppm Mn(VII); eluent = 20 m*M* oxalic acid–15 m*M* trilithium citrate. (a) 1 Min; (b) 5 min and (c) 10 min after mixing.

in peak area. However, as time elapsed, the oxidation of Mn(II) and the reduction of Mn(VII) continued until the stoichiometric amount of Mn(II) was used up, leaving an excess of Mn(VII), which remained unreduced, as shown by the residual peak in Fig. 3c. These data are consistent with the redox equation

$$2MnO^-_4 + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+, \qquad E = 0.46\ V$$

in which all the Mn(II) initially present has been converted into Mn(IV) leaving the excess Mn(VII) in the mixture. This is an example of an application of the chromatographic method coupled with a spectroscopic method to study oxidation–reduction reactions. These results also point to the difficulty of studying the two manganese species together. In such cases, only total manganese can be determined by digesting the Mn(IV) with hydrochloric acid according to the equation

$$MnO_2 + 4HCl \rightleftharpoons MnCl_2 + Cl_2(g) + 2H_2O$$

Platinum

In recent years, much interest has been directed towards the application of the unique chemical activity of certain heavy metals in the treatment of ailments such arthritis, skin diseases, and, cancer [42–46]. A number of platinum compounds have been studied and tried as cancer treatment agents. Among these are the commonly known short form names such as cisplatin, carboplatin, iproplatin, and tetraplatin. The successful use of these materials has been hampered by not only chemical side effects but also by poorly understood solution chemistry. Some of them, *e.g.*, cisplatin, are known to have very poor solubility in aqueous systems. Others, such as tetraplatin, have been found to undergo rapid degradation when placed in solution.

A commercial compound having chemical similarities with some of these materials was chosen as a model for studying the behavior of these platinum containing compounds. The compound chosen, hydrogen hexachloroplatinate(IV) (HCP), is readily soluble in water. However, when an aliquot of its solution was separated on a chromatographic column, it was observed that more than one species were present, as indicated in Fig. 4. The apparent degradation of HCP was accompanied by the dissociation of the chloride ions which, as shown in Fig. 5, appeared to reach a steady state.

The data presented above point to the utility of the d.c. plasma detector to monitor transformations that chemical species can undergo in solution. Here, the degradation of HCP, which is accompanied by a loss of chloride ions, results in at least two platinum-containing moieties, both of which can be monitored by atomic emission measurements monitored at the platinum excitation wavelength of 204.9 nm. The information obtained here is significant in that it can be used as a model for studying platinum containing compounds whose pharmaceutical and clinical use has grown steadily in recent years. Similar studies have been conducted for tetraplatin, a compound which has been shown to have potential as an anti-tumour agent [43].

Of interest is how this method can be applied in studying the interaction of these materials with biological molecules. Fig. 6 shows the chromatograms obtained

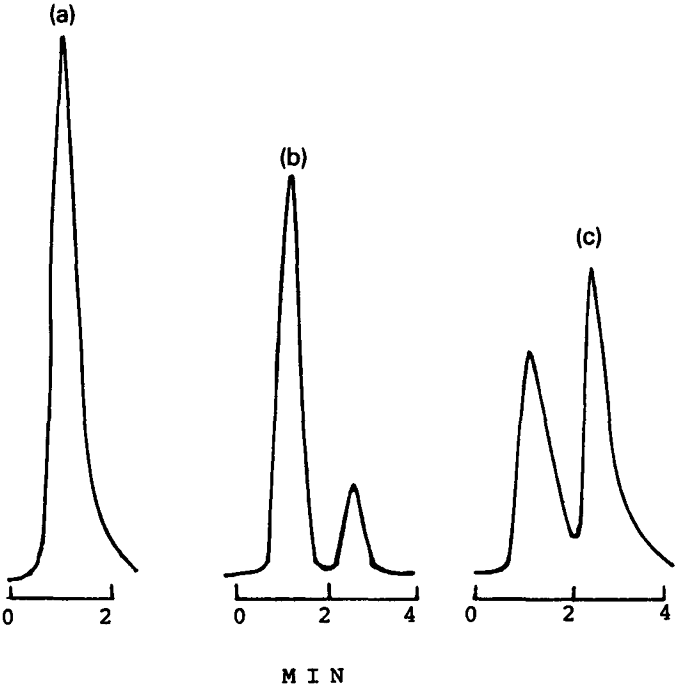

Fig. 4. Ion chromatograms of hydrogen hexachloroplatinate(IV) obtained with d.c. plasma atomic emission spectroscopy detection of platinum; eluent = 10 m*M* oxalic acid–7.5 m*M* trilithium citrate. (a) Fresh solution; (b) 14 day-old solution and (c) 28 day-old solution.

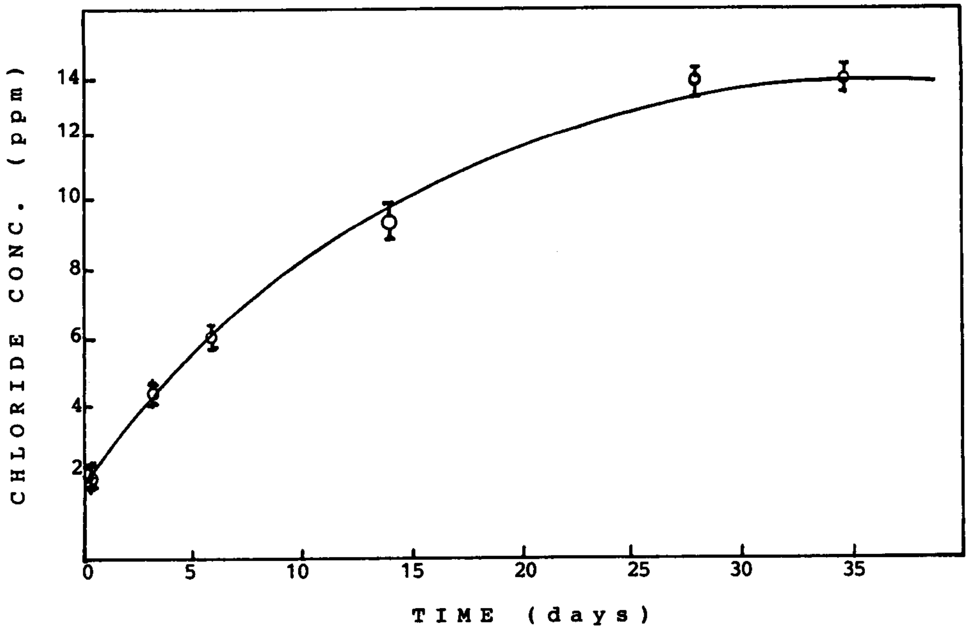

Fig. 5. Chloride content of the solution used in Fig. 4 monitored with an ion chromatograph equipped with a conductivity detector; eluent = 28 mM sodium bicarbonate–23 mM sodium carbonate.

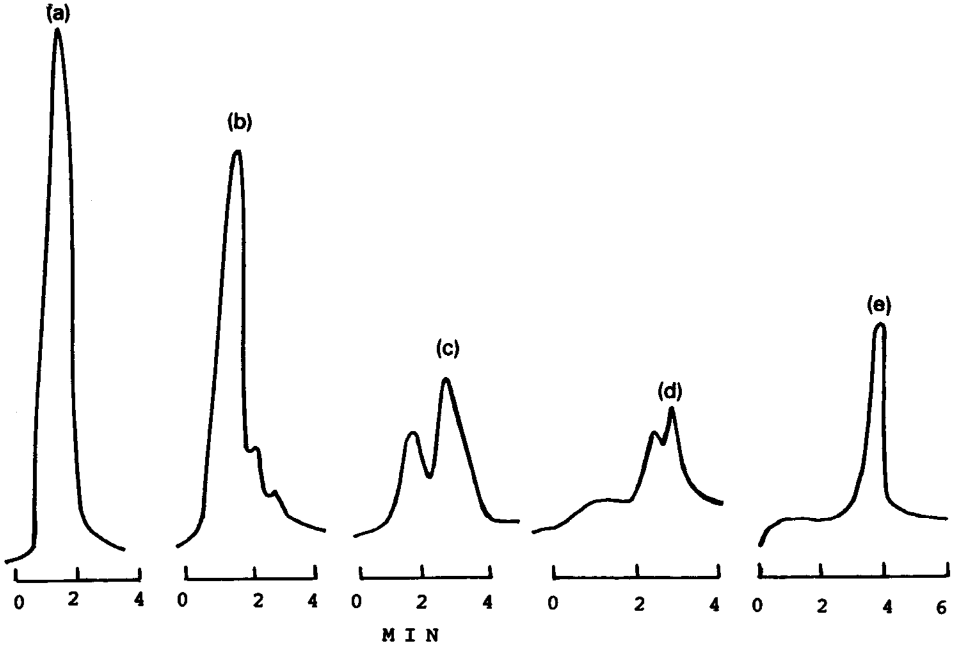

Fig. 6. Ion chromatograms of hydrogen hexachloroplatinate(IV) spiked with cysteine and monitored with d.c. plasma atomic emission spectroscopy detection of platinum. (a) Fresh unspiked solution; (b) cysteine mol ratio = 0.5; (c) cysteine mol ratio = 1.0; (d) cysteine mol ratio = 2.0; and (e) cysteine mol ratio = 10.0.

when a solution of HCP was spiked with incremental amounts of cysteine. Aliquots of the spiked solutions were injected on the cation column and the effluents were monitored by the atomic emission of platinum as was carried out earlier. The chromatograms appear to indicate that at certain concentrations of the ligand cysteine, at least three platinum-containing moieties were formed, but then this was also accompanied by a decrease in the peak size. The appearance of a third peak may correspond to the interaction of cysteine with one of the hydrated platinum species resulting from the degradation of HCP. It appears that the presence of cysteine leads to a diminishing of the platinum peaks. This is probably due to the possible complexation or precipitation of platinum via bond formation with the sulfur side of the ligand. A study of the interaction of such materials with biomolecules is essential as these materials are becoming more and more useful in clinical areas.

Solution chemistry of phosphorus

Phosphorus was included in this study to represent non-metallic elements whose chemical activities can have significant consequences on both biological and environmental systems.

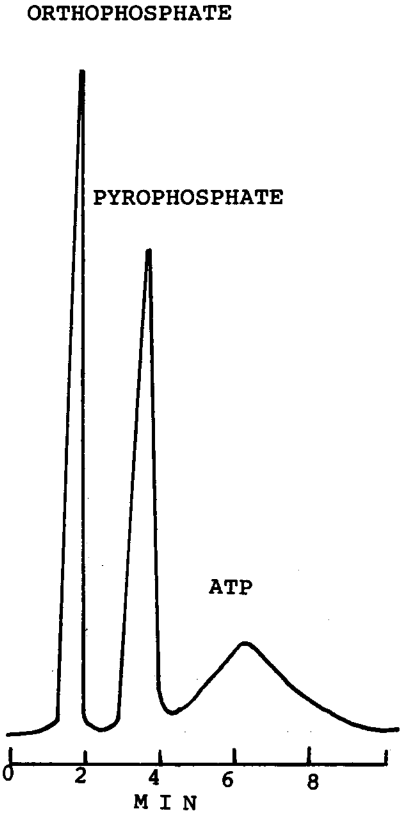

Fig. 7. Ion chromatographic separation of orthophosphate, pyrophosphate, and ATP obtained with d.c. plasma atomic emission spectroscopy detection of phosphorus; column = HPIC-AS-7; eluent = 0.5 *M* nitric acid.

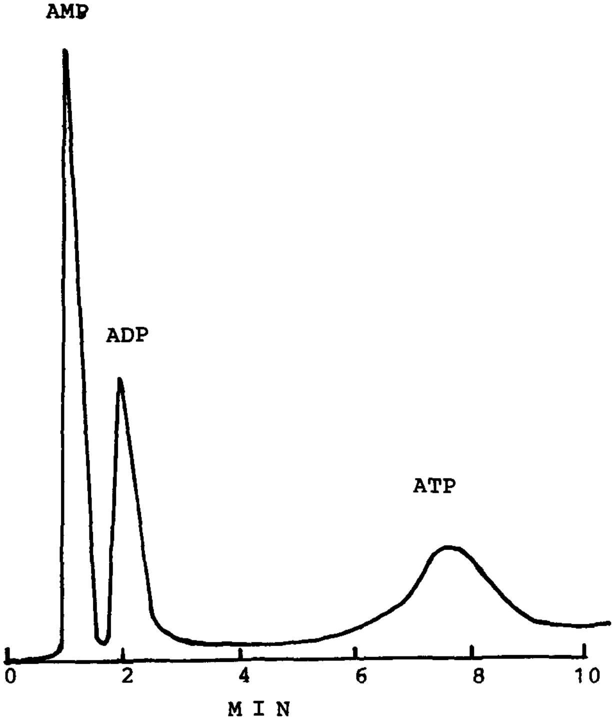

Fig. 8. Ion chromatographic separation of AMP, ADP and ATP obtained with d.c. plasma atomic emission spectroscopy detection of phosphorus; column = HPIC-AS-7; eluent = 0.5 *M* nitric acid.

The ion chromatography–d.c. plasma (IC–DCP) method was applied in the characterization of the solution chemistry of orthophosphate, pyrophosphate, AMP, ADP and ATP. Figs. 7 and 8 show the chromatograms obtained when mixtures of three of these compounds with equal phosphorus content were separated using an anion separator column. The chromatographic effluent was monitored by measuring the atomic emission of phosphorus at 213.6 nm. As with the metallic elements discussed earlier, all the phosphorus species were measured with equal efficiency. Identical linear regression lines, with a regression coefficient of 0.9999, were obtained when analytical curves for phosphorus as orthophosphate and ATP were plotted. This, as with the other elements, permits the determination of the various phosphorus species in a sample using a single analytical curve.

Fig. 9 is a chromatogram obtained when a sample of a detergent solution was injected on the column. The peak at 1.5 min corresponds to orthophosphate, followed by pyrophosphate, and the rest of the rather poorly defined peak was attributed to polyphosphates which, with time, degrade to the simplest inorganic orthophosphate form.

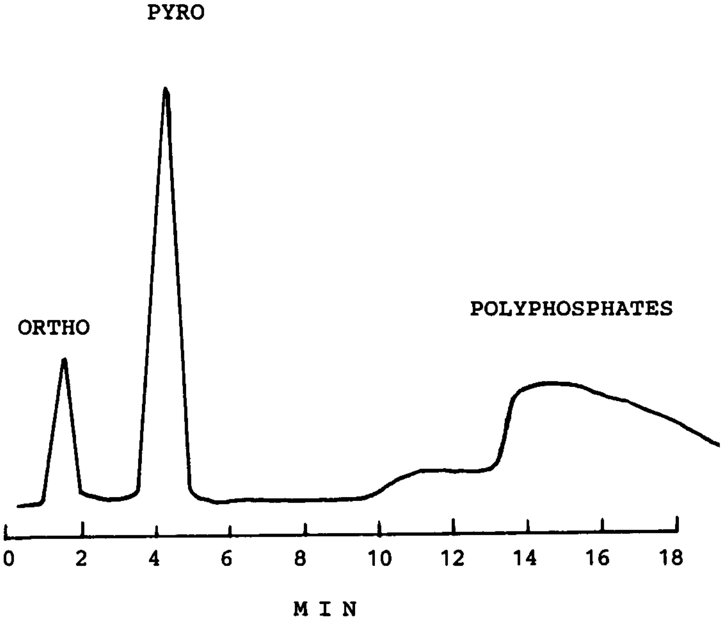

Fig. 9. Ion chromatogram of a solution of Tide detergent obtained with d.c. plasma atomic emission spectroscopy detection of phosphorus; column = HPIC-AS-7; eluent = 0.5 *M* nitric acid.

CONCLUSIONS

The work presented in this paper points to the utility of ion chromatography as a tool for studying the solution chemistry of trace elements and the speciation of these elements in aqueous samples. This capability is enhanced considerably if the chromatographic system is coupled with an element selective detector which responds only to a targeted element in the sample. The use of a d.c. plasma detector enables us to make analytical measurements on samples of varying matrix, and to monitor the element transformations that may occur in solution.

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