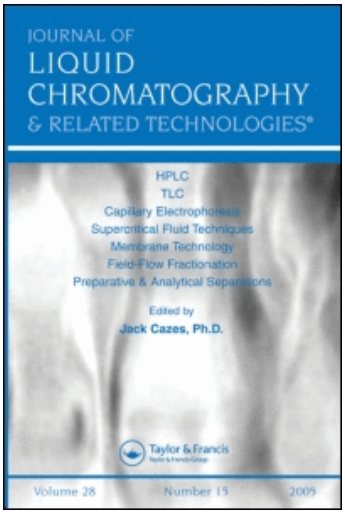

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Metal Cation/Anion Speciation via Paired-Ion, Reversed Phase HPLC with Refractive Index and/or Inductively Coupled Plasma Emission Spectroscopic Detection Methods

D. Bushee[a]; I. S. Krull[b]; R. N. Savage[a]; S. B. Smith Jr.[a]
[a] Institute of Chemical Analysis Northeastern University, Boston, Massachusetts, USA [b] Analytical Instrument Division Instrumentation Laboratory, Wilmington, Massachusetts, USA

To cite this Article Bushee, D. , Krull, I. S. , Savage, R. N. and Smith Jr., S. B.(1982) 'Metal Cation/Anion Speciation via Paired-Ion, Reversed Phase HPLC with Refractive Index and/or Inductively Coupled Plasma Emission Spectroscopic Detection Methods', Journal of Liquid Chromatography & Related Technologies, 5: 3, 463 — 478
To link to this Article: DOI: 10.1080/01483918208066908
URL: http://dx.doi.org/10.1080/01483918208066908

JOURNAL OF LIQUID CHROMATOGRAPHY, 5(3), 463-478 (1982)

METAL CATION/ANION SPECIATION VIA PAIRED-ION, REVERSED PHASE HPLC WITH REFRACTIVE INDEX AND/OR INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPIC DETECTION METHODS

D. Bushee and I.S. Krull*
Institute of Chemical Analysis
Northeastern University
360 Huntington Avenue
Boston, Massachusetts 02115 USA

and

R.N. Savage and S.B. Smith, Jr.
Analytical Instrument Division
Instrumentation Laboratory, Inc.
Jonspin Road
Wilmington, Massachusetts 01887 USA

ABSTRACT

Conventional high performance liquid chromatography instrumentation and packing materials can be inexpensively and rapidly utilized for the qualitative and quantitative analysis of various metal cations or anions. The final approaches utilize reversed phase HPLC in the form of paired-ion separations. The detection of individually eluted, fully resolved metal cations or anions is possible via conventional refractive index or inductively coupled plasma emission spectroscopic detection. In many cases, unresolved mixtures of metal cations, eluted as a single peak on HPLC, can be resolved and identified via the use of ICP detection. Both metal cations and anions can be easily resolved, according to oxidation states, using paired-ion techniques, in combination with ICP detection. Final data representation can be in the form of conventional, continuous RI and/or ICP chromatograms, via pulsed data ICP presentations, and/or via tabular ICP data presentation.

INTRODUCTION (1)

Inorganic metal toxicity has long been an area of intense biological, toxicological, and medical interest. The apparent toxic properties of most,

* Author to whom correspondence and reprint requests should be addressed.

if not all, metals (free metals, cationic/anionic valences, chelates, and/or organometals) have been elucidated and extensively described for several decades (2-6). Unfortunately, the vast majority of published metal toxicity studies have never involved appropriate analytical methodology. Wherein analytical methods have been used as part of the biological studies, these provided total metal concentrations or levels, rather than the more desirable specific metal speciation profiles for the particular biological, toxicological, or medical samples of interest (7-17). Some of the more commonly employed instrumental methods of analysis for total metal determinations have been: direct flame/flameless atomic absorption spectroscopy (FAA, GFAA), direct current (DCP) or inductively coupled plasma (ICP) emission spectroscopy, flame emission spectroscopy, atomic fluorescence spectroscopy, anodic stripping voltammetry, pulse polarography, spark source mass spectrometry, X-ray fluorescence, and others (18, 19).

Within recent years it has become apparent to most scientists and some decision makers that partial or complete metal speciation of environmental, biological, toxicological, and/or medical type samples must be undertaken on a regular basis. That is, only when all or most metal species present in any sample are accurately known, can we then appropriately describe and ascribe biological, medical, or toxicological properties to that particular mixture of metals and/or metallic compounds/ions. Many metals exist as the free metal, various cationic and/or anionic oxidation states, organically bound chelates/complexes, and/or organometals. Obviously, the final speciation of metals in a complex sample matrix, often in the presence of other metals and their species, must involve some sort of an initial separation process. Considerable attention has been devoted in recent years towards the HPLC separation and detection of various metal species, usually employing UV, AA, ICP, or electrochemical detection (8-17, 20-31). Initially, HPLC was applied to the separation and identification of mainly organometals and/or metal chelates/complexes. Within the past few years, a tremendous interest has emerged towards inorganic metal cation/anion analyses, especially in the use of ion chromatography (IC) and/or high performance ion-exchange type chromatography, together with conductivity and/or electrochemical detection (15, 20-22, 32-39). It has become obvious that IC, especially via the use of commercially available instrumentation, has become quite popular, very useful, and can be readily utilized with pre-concentration methods for trace environmental and/or toxicological studies. Unfortunately, such chemical instrumentation has become quite expensive ($15,000-$25,000/unit), and must be dedicated to the performance of inorganic/organic cation or anion type analyses. IC does not lend itself to the performance of conventional HPLC separations via

liquid-solid, liquid-liquid, bonded phase, reversed phase, paired-ion, or gel permeation techniques and approaches.

Unfortunately, relatively little non-IC or non-ion-exchange type work has been reported in recent years, especially with regard to utilizing any commercial type HPLC instrumentation for performing inorganic metal cation/anion type analyses. Quite obviously, this situation should be remedied, and the work described here, in part, has been designed with this goal in mind. All of this work has utilized conventional reversed phase type packing materials, C_{18}, with paired-ion modified mobile phases. In the recent past, others have briefly reported on the use of such approaches for the separation of various cations and anions, but such work was most often not interfaced with the latest advances in ICP detection. That work which has used ion-exchange HPLC and/or chelation chromatography has generally used conductivity detection, atomic absorption spectroscopy, and/or electrochemical detection (8-16, 20-39). Very little work has been described with regard to metal cation or anion separations via conventional reversed phase HPLC interfaced with ICP detection. The work of Gast et al. is a notable exception to this last statement (30). Valenty and Behnken have described the use of C_{18} type columns together with paired-ion reagents for the complete separation of certain positively charged ruthenium complexes, followed by UV detection (40). Some inorganic anions have recently been analyzed using paired-ion reversed phase HPLC approaches, using UV, RI, and/or graphite furnace AA detection (11, 12, 26, 41-45). Perhaps Molnar et al. have reported the most extensively on the possible applications of paired-ion RP-HPLC for the separation of inorganic cations and anions, but this particular work involved conductivity detection (45). The overall detection limits in this study were quite impressive (ppb).

We describe here results utilizing paired-ion RP-HPLC techniques for metal cation and anion separations, wherein this is interfaced with RI and/or ICP detection methods. Paired-ion RP-HPLC allows for the separation of each group of cations combined with speciation within a cation group via ICP detection. This same approach also allows for the separation and ICP speciation of various arsenic containing oxyanions, as in the original work of Gast et al. (30). Thus, by applying these different separation methods together with RI and/or ICP detection, it is now possible to quickly and easily separate and speciate for a large number of metal cations and anions.

EXPERIMENTAL

Reagents

Inorganic salts, reagent grade, were obtained from the following sources: Baker analyzed reagents from VWR Scientific, Inc. (Boston, Mass.); Fisher

ACS certified grade from Fisher Scientific, Inc. (Medford, Mass.); Pfaltz & Bauer, Inc., grade unspecified (Stamford, Conn.); and Alfa/Ventron Inorganics, Inc., grade unspecified (Danvers, Mass.). The ion-pairing reagents, PIC A or PIC B, were obtained from Waters Associates, Inc. (Milford, Mass.), and the mobile phase water was purchased from the J.T. Baker Chemical Co. (Phillipsburg, N.J.), or used directly from a Corning Mega-Pure still (Corning Corp., Corning, N.Y.).

Apparatus

We have utilized a number of HPLC instrumental arrangements for the present work, and all have proven satisfactory. A typical HPLC arrangement consisted of a Laboratory Data Control (LDC) (Riviera Beach, Fla.) Model 711 solvent delivery system, modified with a special pulse dampener (Analabs, Inc., North Haven, Conn.), or a newer LDC Constametric III pump, a Rheodyne Model 7125 syringe injection valve (Rheodyne Corp., Cotati, Calif.), an Altex/Beckman variable wavelength UV-VIS detector (Altex/Beckman Corp., Irving, Calif.), a Waters Model 401 RI detector (Waters Assocs.), or a Micromeritics Model 771 RI detector (Micromeritics Corp., Norcross, Ga.), a modified Instrumentation Laboratory Model Plasma-100 inductively coupled plasma emission spectrometer (Instrumentation Laboratory, Inc., Wilmington, Mass.), and a Linear Corp. (Irvine, Calif.) or Honeywell Corp. (Minn., Minn.) dual pen recorder. The RI/ICP data were obtained *via* a dual pen recorder, and/or a separate ICP print-out from the Plasma-100 system. Often, both the recorder ICP chromatogram and the tabular data format from the ICP were obtained at the same time. At other times, the tabular data presentation could be manually used to reconstruct a pulsed type or continuous type HPLC-ICP chromatogram. This was done knowing the timed integration sequence of the tabular data presentation. In later runs, the Plasma-100 system was operated to present both pulsed type chromatograms, as below, and simultaneous tabular data presentations. This provided additional confirmation of the ICP results for the final metal speciation.

In the work described, the HPLC columns were all of the C_{18} type, and were usually obtained commercially, as follows: 1) Hibar II RP-18 pre-packed column (4.6mm x 25cm)(MCB Chemicals, Inc., Cinc., Ohio); 2) Alltech C-18 (4.6mm x 25cm)(Alltech Assocs., Inc., Deerfield, Ill.); 3) Altex/Beckman Ultrasphere ODS (4.6mm x 15cm)(Altex/Beckman Corp.); or 4) slurry packed in-house columns using Lichrosorb RP-18 (4.6mm x 25cm)(MCB Chemicals, Inc.).

Methods

In all studies involving paired-ion RP-HPLC, using the PIC B-5 or PIC B-8 counter-ions, the mobile phase consisted of the PIC reagent (0.005M)

prepared exactly according to the manufacturer's directions, at a final pH= 2.9-3.0. It would appear that a low pH is necessary for successful metal cation separations by a paired-ion RP-HPLC approach. Use of the PIC A reagent (0.005M) for arsenic oxyanion separations involved its preparation also according to the manufacturer's directions, with a final pH = 7.15. Specific flow rates, effluent split ratios, and more specific HPLC-detector operating conditions are presented below. An approximately 50:50 effluent split ratio was used in almost all of the dual detector studies, making use of a fixed ratio "T" type splitter (Alltech Assocs., Inc.).

In all of the paired-ion work, a mobile phase saturation, silica gel pre-column was used, on-line and just before the injection valve, in order to extend column lifetimes. The recommendation of Waters Assocs. was followed with regard to washing the C_{18} columns at the end of each day with 50:50 MeOH:HOH. Columns protected in these ways have lasted for at least six months, with no apparent change in overall column efficiencies or retention times. The analytical column was always thermostated in a constant temperature water bath at or about 25°C, in order to improve retention time reproducibility and decrease ambient temperature effects on capacity factors.

Detection limits by RI were determined directly from the resulting chromatograms, using minimum settings possible on the detector together with a signal:noise ratio of at least 3:1 in each case. Detection limits by ICP were determined using a 2:1 signal:noise ratio from the tabular data format, wherever this was feasible and practical.

RESULTS AND DISCUSSION

The use of an organic counter ion in the mobile phase to perform paired-ion reversed phase (RP) -HPLC has been described for many years, but almost exclusively with regard to organic ion separations (46-48). This method has proven to be an extremely useful alternative to traditional ion-exchange type HPLC for organic compounds that are able to form ion-pairs in aqueous solutions. Its use for inorganic cation/anion HPLC separations has been described much less, and the recent work of Molnar *et al*. just indicates some of the potentials which this approach holds (45). Wherein this approach has been described for inorganic ions, it has mostly been applied to the separation of anions, with much less work having been reported for metal cations (41-45).

We have been quite interested in demonstrating the possible uses of ion-pairing for metal cation and anion separations, and with the eventual interfacing of such approaches to ICP detection (49). All of the work that

we describe here has used a commercially available C_{18} type reversed phase column, of various dimensions, with mobile phases consisting of either PIC-B or PIC A type ion-pairing reagents at a single concentration. Quite obviously, other combinations of column packings, column dimensions, mobile phases, mobile phase concentrations, and final flow rates could be used in the future to improve or modify the final separations. Table I summarizes some of the results obtained using both the PIC B-8 and PIC B-5 type reagents, both for univalent and divalent metal cations. These RI results have been confirmed in almost all instances via ICP detection under similar HPLC conditions. In the case of the PIC B-8 reagent, it was not possible to get the divalent metal species to elute within a reasonable amount of time after observation of the univalent species. We therefore investigated the use of the analogous PIC B-5 reagent, Table I, wherein the univalent cations elute just after the solvent front, as a group, and the divalent species now elute at about 8.0 mins (t_r), again as a single peak on the RI. It is to be emphasized that in all of this metal cation ion-pairing work, we have not yet attempted to resolve either the +1 or +2 species from one another, but rather we have emphasized the overall group separations of +1 from +2.

TABLE I

Paired-Ion Reversed Phase HPLC of Metal Cations With RI Detection

Mobile Phase	Metal Cation	t_r (mins)	k' (cap. factor)
PIC B-8[a]	Na^+	8.25	6.2
	K^+	8.6	6.5
	Li^+	8.15	6.1
	Cu^+	8.2	6.1
PIC B-5[b]	K^+	2.85	0.36
	Cu^+	2.85	0.36
	Cu^{+2}	7.8	2.7
	Zn^{+2}	7.9	2.8
	Cd^{+2}	8.0	2.8
	Fe^{+2}	8.1	2.9
	Pb^{+2}	7.6	2.6

a. HPLC-RI conditions: Alltech RP-18 column (4.6mm x 25cm) with a mobile phase of 0.005M octane sulfonic acid (Waters PIC B-8), pH = 2.9, flow rate of 3.0ml/min.

b. HPLC-RI conditions: Alltech RP-18 column (4.6mm x 25cm) with a mobile phase of 0.005M octane sulfonic acid (PIC B-5), pH=2.85, flow rate 2.0 ml/min, Waters Assocs. Model 440 RI detector at 4X.

Thus, as in Table I, we have not attempted to resolve Cu^{+2} from Zn^{+2} or Cd^{+2}, but instead have tried to obtain useful group separations of all the +1 cations from the +2 cation group. Molnar et al. in their earlier work, described the successful resolution of Na^{+1}, K^{+1}, and NH_4^{+1} from each other, using similar paired-ion techniques, but these workers had to use three C_{18} type columns placed in series to achieve this resolution (45). Their use of a non-selective conductivity detector necessitated the initial chromatographic resolution of each +1 species, in order to qualitatively and quantitatively identify each species present. Our desire to interface this HPLC method with ICP detection does not demand complete HPLC resolution of either the +1 or +2 species, as demonstrated below.

Fig. 1 illustrates a typical paired-ion RP-HPLC-RI separation of Cu^{+1} and Cu^{+2}, injected initially as 26.8ug Cu^{+1} in the form of CuCl (cuprous chloride). This was an old sample of CuCl from the Chemistry stockroom at the University, prepared in the mobile phase, which apparently existed more as Cu^{+2} than the expected Cu^{+1}. Clearly, the reading of bottle labels does not guarantee the contents of a bottle are as represented at the time of sale. A recently purchased sample of CuCl showed via this method almost no Cu^{+2} ion present. When a new sample of cupric acetate ($Cu(OAc)_2$) was prepared and analyzed, this sample existed almost entirely as Cu^{+2}, with only a very small contribution from the peak at t_r = 2.85 mins, which is that of Cu^{+1}. Also, when solutions of Cu^{+1}, prepared from old CuCl were analyzed by paired-ion RP-HPLC-RI-ICP techniques, the ICP clearly showed the presence of two distinct forms of copper, as expected from the above.

We have observed that under certain sample preparation conditions, depending on which acid may be used to dissolve the initial copper salts, it is possible to bbserve three distinct copper containing ionic species via paired-ion RP-HPLC-ICP conditions. In order to dissolve certain copper salts, we have used, in some instances, hydrochloric or sulfuric acids (dilute concentrations), and these final solutions were then used for the paired-ion analyses. In certain instances, we have clearly observed via both RI and ICP detection, three distinct copper containing species. Two of these are as already indicated, Figure 1, and a third copper containing species has a retention time in between those for the Cu^{+1} and Cu^{+2} species. It is possible that this third species is a mixed ligand, Cu^{+2}, tripartite ion species, perhaps containing only one counter-ion derived from the PIC B-5 reagent and the remaining ion Cl^{-1}.

It has, of course, now been possible to interface a large number of paired-ion RP-HPLC separations of metal cations, such as those in Table I, directly to the ICP. In this manner, element specific ICP chromatograms can

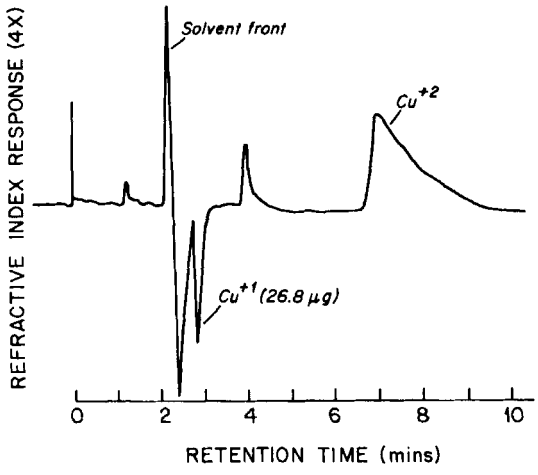

FIGURE 1

be readily obtained, either in continuous print-out or tabular formats. These tabular formats are then readily converted into either a pulsed or continuous type chromatogram, and this can be done manually or instrumentally. The true analytical capabilities for metal cations or anions resides, in part, in the multi-element capabilities of the ICP detector. That is, in order to determine how much of each possible valence state a metal may exist as in any given sample, it is really only necessary for the analyst to physically separate all of the +1 species from the +2s, or the +2s from the +3s, and so forth. Once the different valence states are all resolved from each other, chromatographically or otherwise, then the ICP can resolve each individual metal species present within a mixture of +1s, +2s, +3s, etc. Indeed, using this approach, but purely as an illustration of the possible capabilities and potentials of HPLC-ICP analyses for metal ions, Figure 2 indicates a synthetic mixture of three separate divalent metal cations. These are Fe^{+2}, Cd^{+2}, and Zn^{+2}, injected as a mixture of all three, at the levels indicated, Figure 2, using a split of the column eluent to both RI and ICP detectors. Naturally, the RI detector shows only a single peak for all three divalent species, since these are not chromatographically distinguishable from each other on the non-selective RI. Indeed, if one only used the non-selective RI detector, then it would be impossible to know that more than one species was present under the single chromatographic peak. However, the ICP is able to monitor a number of emission wavelengths, in rapid sequence, and to measure each light intensity at these various wavelengths as a function of

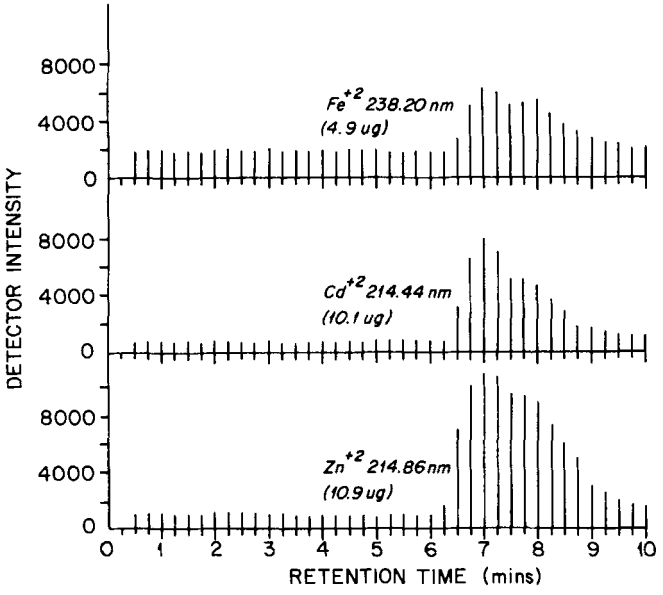

FIGURE 2

time. It is then able to store this information, as pre-determined by the particular program that operates the ICP, and to integrate each light emission at the appropriate wavelengths every one, two, five, or x seconds during the entire HPLC process. One therefore obtains an ICP print-out, Figure 2, here re-constructed manually from the tabular format, for each metal species wavelength of emission. The wavelengths used here are indicated, wherein we have previously determined no spectral interferences for any of the three metal wavelengths involved. In essence, one has three distinct HPLC-ICP chromatograms for all of the metal cations present in the initial sample. We have performed analogous, illustratuve studies, using other +1 and +2 species, wherein all of the +1s are separated from the +2s, and where the ICP is then able to determine how much of each +1 and +2 species were present in the original, simulated mixture of metal ionic species. This is therefore true metal speciation, wherein the analyst now has the ability to determine a very large number of metallic cations present in the same sample matrix, all with a bare minimum of sample work-up, handling, and preparation prior to the HPLC-ICP. This method avoids any form of sample derivatization before injection onto the HPLC-ICP system.

We, as well as others, have investigated the capabilities of paired-ion RP-HPLC-ICP for performing metal anion analyses, with the initial emphasis here on the speciation of various arsenic containing oxyanions. We have also applied these same techniques for the speciation of chromium ions, *viz.*, chromate and chromic ions, but this work will be presented elsewhere (50). The analysis-speciation of arsenic containing compounds is of intense current interest, as evidenced by the number of literature references within recent years (11-14, 25, 26, 30, 51). Most of the reported work with arsenic oxyanions has involved the use of ion-exchange packings in conventional HPLC, but some work has been done using paired-ion RP-HPLC in combination with graphite furnace AA (11) or ICP (30, 51). We have investigated the paired-ion RP-HPLC resolution of three distinct arsenic species, *viz.*, sodium arsenite ($NaAsO_2$), sodium dimethyl arsenate (sodium cacodylate, $Na(CH_3)_2AsO_2.3HOH$), and sodium arsenate ($Na_2HAsO_4.7HOH$). Using the PIC A type reagent, it has been possible to satisfactorily resolve all three arsenic oxyanions within about 10 mins. HPLC-RI, Figure 3, indicates the presence of at least three compounds, but there are a number of additional RI peaks present in the synthetic mixture of standards. Using RI alone, it would not be possible to assign individual peaks to any of the arsenic oxyanion materials. However, once the paired-ion RP-HPLC separation is interfaced with ICP detection, it becomes apparent precisely which chromatographic peaks are indeed the correct arsenic containing species. Figure 3 is a typical, manually re-constructed HPLC-ICP chromatogram of the three arsenic species involved, all clearly baseline resolved within about 10 mins. The arsenic emission was monitored here at a wavelength of 228.83nm, in combination with an integration time of about 1 sec. Each intensity reading at these 1 sec intervals was then used, after background subtraction, to produce the final ICP chromatogram.

We have intentionally omitted any discussion here of minimum detection limits *via* HPLC-ICP or HPLC-RI. However, from the data presented thus far, it should be apparent that our detection limits in either detection mode do not fall below the ppm levels for any of the metals studied here. In other work, we have made direct comparisons of direct-ICP and HPLC-ICP detection limits, especially for cadmium and chromium (50). Because of the band broadening present within all HPLC-detector interfacing, due to the nature of the HPLC process and the interfacing hardware dead volume, there *must* always be a worsening of the detection limits in the interfaced mode. One would automatically expect that this difference should be about 15-25 fold worse for the HPLC-ICP case, but we and others have seemingly found this difference to be somewhat more than this estimated value. In some instances, the overall difference between direct-ICP and HPLC-ICP can be as much as 2-3 orders of

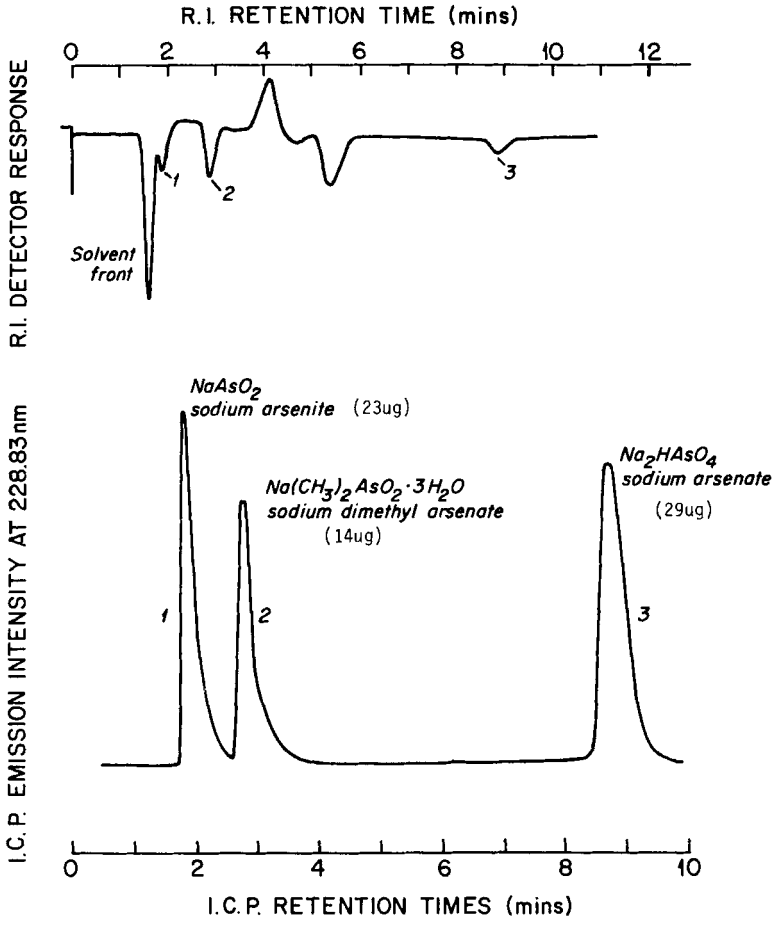

FIGURE 3

magnitude, and we are currently trying to understand the specific reasons for this effect. Obviously, for any HPLC-ICP method to have value in real world applications, there must be detection limits which rival or equal those already possible via direct-ICP. At the same time, we are somewhat surprised and truly impressed by those reports in the literature which report HPLC-ICP detection limits which are equal to or, in some cases, better than those possible/ reported for direct-ICP. What is called for in these studies is a direct comparison of direct-ICP vs. HPLC-ICP for the same analytes and absolute amounts, but such studies are somewhat lacking in the existing literature (30, 51).

CONCLUSION

We have attempted to develop and perfect a variety of HPLC approaches for the successful and efficient resolution of a wide variety of inorganic, metallic cations and anions. We have especially wanted to use the tremendous amount of information and expertise that has evolved over the past few years with regard to paired-ion RP-HPLC methods/applications. There is every reason to believe that alternative methods of performing inorganic ionic separations will provide just as much useful, overall results as those described here. However, in the case of low pressure ion chromatography, the question remains of the general applicability of this approach for performing inorganic, metal ion analyses in combination with ICP, wherein this would mean the virtual exclusion of all other forms of HPLC separations. On the other hand, the reversed phase columns that we have utilized for RP-HPLC-RI-ICP are still readily available for performing other types of organic HPLC analyses, using the exact same type of HPLC instrumentation and hardware. This would appear to be a very significant advantage in using reversed phase HPLC approaches for inorganic, ionic or organometallic type separations.

The combination of ionic chromatography and element specific ICP detection is quite obviously an extremely powerful method for inorganic type analyses. ICP apparently has fewer matrix interference and salt interference problems as compared with either flame AA or graphite furnace AA methods of today. Most importantly, ICP has true multi-element capabilities, something which conventional AA and/or GFAA do not really possess. ICP can also be quite compatible with high salt concentrations in the HPLC mobile phase (49, 50), without producing spectral or sample matrix interferences for the metal of interest. This may not be the case with FAA and/or GFAA approaches. Also, ICP would appear to be somewhat more compatible with gradient elution HPLC methods, especially with those which would involve the use of methanol, ethanol, or isopropanol. We and others have noted this potential for using mixed aqueous:organic type solvents in ICP operations, at times with increased signal responses for particular analytes. A number of other organic HPLC solvents may also prove compatible with routine ICP operation, and considerable more work remains to be undertaken in this area (16, 30, 52). Obviously, it would be extremely advantageous to undertake gradient elution RP-HPLC separations in combination with ICP detection, for this approach would then allow for a complete metal speciation profile determination for a very large number of metal elements/species. Quite clearly, our work here is but one step in that direction.

We have only briefly discussed detection limits in the HPLC-ICP mode, but the literature does already contain a certain amount of information in

this regard. It is our belief that, in general, an insufficient amount of work has been devoted to maximizing HPLC-ICP sensitivity and minimizing its detection limits. These must be brought more in line with the corresponding HPLC-GFAA or direct GFAA limits/sensitivities. Thus far, most reports of HPLC-GFAA detection limits indicate a significant advantage over the analogous HPLC-ICP detection limits for the same samples and HPLC conditions. Unfortunately, there are very few meaningful direct comparisons of HPLC-GFAA and HPLC-ICP for the same HPLC conditions and analytes of interest. It is our hope, as well as that of others, that the future will bring forth greatly improved limits of detection for HPLC-ICP methods, and that this approach will take its rightful place as a highly versatile and quite useful method of trace element analysis and speciation.

ACKNOWLEDGEMENTS

The authors wish to thank B.L. Karger and B. Bidlingmeyer for their interest and encouragement in the HPLC areas, as well as G. Davies for his assistance in the inorganic chemistry areas. We also thank R.N. Reeve and G. Chiu for providing us with certain unpublished work and results. We appreciate the assistance of T. Gilbert in reading the final manuscript, and in making appropriate suggestions for its final improvement.

This work was supported, in part, by a research and development contract from the Analytical Instrument Division of Instrumentation Laboratory, Inc. Additional funding was provided by a grant from the NIH Biomedical Research Support Grant to Northeastern University, no. RR07143. We wish to indicate here our sincere appreciation for these sources of financial assistance.

This is contribution number 97 from the Institute of Chemical Analysis, Applications, and Forensic Science at Northeastern University.

REFERENCES

1. Abbreviations used: HPLC = high performance liquid chromatography; ICP = inductively coupled plasma emission spectroscopy; RI = refractive index detection; RP = reversed phase; PIC B = alkyl sulfonate counter-ion; PIC A = tetrabutylammonium counter-ion; UV = ultraviolet detection; FAA = flame atomic absorption spectroscopy; GFAA = graphite furnace atomic absorption spectroscopy; DCP = direct current plasma emission spectroscopy; IC = ion chromatography; MeOH = methanol; t_r = retention time; k' = capacity factor; ppb = parts-per-billion.

2. Berman, E., Toxic Metals and Their Analysis, Heyden & Son, Ltd., London, 1980.

3. Hammond, B.P. and Beliles, R.P., in Toxicology - The Basic Science of Poisons, Second Edition, Doull, J., Klaasen, C.D., and Amdur, M.O., eds., MacMillan Publishing Co., Inc., New York, 1980, p. 468.

4. Sigel, H., ed., Metal Ions in Biological Systems. Carcinogenicity and Metal Ions, Vol. 10, Marcel Dekker, New York, 1980.

5. Some Metals and Metallic Compounds. IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Volume 23. International Agency for Research on Cancer, Lyon, 1980.

6. Harrison, R.M. and Laxen, D.P.H., Chemistry in Britain, 316 (June, 1980).

7. Scheutzle, D., ed., Monitoring Toxic Substances, ACS Symposium Series No. 94, American Chemical Society, Washington, D.C., 1979.

8. Van Loon, J.C., Anal. Chem., 51, 1139A (1979).

9. Van Loon, J.C., American Laboratory, 47 (May, 1981).

10. Parks, E.J., Brinckman, F.E., and Blair, W.R., J. Chrom., 185, 563 (1979).

11. Brinckman, F.E., Jewett, K.L., Iverson, W.P., Irgolic, K.J., Ehrhardt, K. C., and Stockton, R.A., J. Chrom., 191, 31 (1980).

12. Jewett, K.L. and Brinckman, F.E., J. Chrom. Sci., in press (1981).

13. Anonymous, Chem. & Eng. News, 29 (Feb. 16, 1981).

14. Ricci, G.R., Shepard, L.S., Colovos, G., and Hester, N.E., Anal. Chem., 53, 610 (1981).

15. MacCrehan, W.A., Anal. Chem., 53, 74 (1981).

16. Krull, I.S. and Jordan, S., American Laboratory, 21 (October, 1980).

17. Miyazaki, A. and Barnes, R.M., Anal. Chem., 53, 364 (1981).

18. Pinta, M., Modern Methods for Trace Element Analysis, Ann Arbor Science Publishers, Inc., Ann Arbor, Mich., 1978.

19. Kuwana, T., ed., Physical Methods in Modern Chemical Analysis, Vols. 1 and 2, Academic Press, Inc., New York, 1978, 1980.

20. Schwedt, G., Chromatographic Methods in Inorganic Analysis. Separation Methods and Systems, Detection Methods, Applications in Inorganic Trace Analysis, A.H. Verlag Publishers, Heidelberg, 1981.

21. Schwedt, G., in Topics in Current Chemistry, Boschke, F.L., ed., Vol. 85, Springer-Verlag Publisher, Berlin, 1981, p. 160.

22. Cassidy, R.M., in Trace Analysis, Lawrence, F.J., ed., Academic Press, New York, in press, 1981.

23. Kahn, N. and Van Loon, J.C., J. Liq. Chrom., 2, 23 (1979).

24. Brinckman, F.E. and Blair, W.R., in National Bureau of Standards Special Publications No. 556. National Bureau of Standards, Wash., D.C., 1979, p. 25.

25. Grabinski, A.A., Anal. Chem., 53, 966 (1981).

26. Woolson, E.A. and Aharonson, N., J. Assoc. Off. Anal. Chem., 63, 523 (1980).

27. Slemer, D.C., Koleel, P., Haworth, D.T., Taraszewski, W.J., and Lawson, S.R., Anal. Chem., 51, 575 (1979).

28. Uden, P.C., Bigley, I.E., and Walters, F.H., Anal. Chim. Acta, 100, 555 (1978).

29. Uden, P.C., Paper presented at the International Winter Conference on Developments in Atomic Plasma Spectrochemical Analysis, Puerto Rico, January, 1980, in press, Heyden & Son, New York, 1981-2.

30. Gast, C.H., Kraak, J.C., Poppe, H., and Maesen, F.J.M.J., J. Chrom., 185, 549 (1979).

31. Koropchak, J.A. and Coleman, G.N., Anal. Chem., 52, 1252 (1980).

32. Cassidy, R.M. and Elchuk, S., J. Chrom. Sci., 18, 217 (1980).

33. Mulik, J.D. and Sawicki, E., eds., Ion Chromatographic Analysis of Environmental Pollutants, Ann Arbor Science, Inc., Ann Arbor, Mich., 1979.

34. Girard, J.E., Anal. Chem., 51, 836 (1979).

35. MacDonald, J.C., American Laboratory, 45 (January, 1979).

36. Wetzel, R.A., Anderson, C.L., Schleicher, H., and Crook, G.D., Anal. Chem., 51, 1532 (1979).

37. Smith, F.D., Jr. and Chang, R.C., CRC Critical Reviews in Anal. Chem., 197 (August, 1980).

38. Pohl, C.A. and Johnson, E.L., J. Chrom. Sci., 18, 442 (1980).

39. Gjerde, D.T., Schmuckler, G., and Fritz, J.S., J. Chrom., 187, 35 (1980).

40. Valenty, S.J. and Behnken, P.E., Anal. Chem., 50, 834 (1978).

41. Chiu, G., Anal. Chem., 52, 1157 (1980).

42. Brinckman, F.E., Blair, W.R., Jewett, K.L., and Iverson, W.P., J. Chrom. Sci., 15, 493 (1977).

43. Reeve, R.N., J. Chrom., 177, 393 (1979).

44. Kamiura, T. and Tanaka, M., Anal. Chim. Acta, 110, 117 (1979).

45. Molnar, I., Knauer, H., and Wilk, D., J. Chrom., 201, 225 (1980).

46. Snyder, L.R. and Kirkland, J.J., Introduction to Modern Liquid Chromatography, Second Edition, J. Wiley & Sons, Inc., New York, 1979, Chapter 11.

47. Bidlingmeyer, B.A., Deming, S.N., Price, W.P., Sachok, B., and Petrusek, M., J. Chrom., 186, 419 (1979).

48. Bidlingmeyer, B.A., J. Chrom. Sci., 18, 525 (1980).

49. Krull, I.S., Bushee, D., Young, D., and Smith, S.B., Jr., Paper presented at the 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., March, 1981. Abstract No. 580.

50. Krull, I.S., Bushee, D., Smith, S.B., Jr., Savage, R.N., and Schleicher, R., Anal. Letters, submitted for publication (1981).

51. Morita, M., Uehiro, T., and Fuwa, K., Anal. Chem., 53, 1806 (1981).

52. Boorn, A.A. and Browner, R.F., Anal. Chem., in press (1982).