Thermospray enhanced inductively coupled plasma atomic emission-spectroscopy detection for liquid chromatography

ARTICLE *in* ANALYTICAL CHEMISTRY · MARCH 1990

Impact Factor: 5.64 · DOI: 10.1021/ac00204a012

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for heavily overlapped bands, and leads directly to quantitative information.

We believe that these results can form the basis of a method for obtaining accurate quantitative information on the areas of unresolved components in real, complex spectra. In this procedure, spectra would be divided into regions in which all bands would be expected to have approximately the same width. A series of deconvolved spectra would then be computed with values of γ' equally spaced between 0 and the value causing the onset of side lobes. If each spectrum is then used as the input for a curve-fitting program, the best quantitative information (i.e. those values at which E is a minimum) would be found from the results of fitting the spectrum that was deconvolved by using the value of γ' just lower than that at which the deviation starts to increase rapidly.

This method has been applied to coal spectra (*33–35*) but has not yet been tested rigorously.

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RECEIVED for review June 15, 1989. Accepted November 6, 1989. This work was supported in part by Grant No. DE-FG22-87PC79907 from the U.S. Department of Energy and by Cooperative Agreement No. CR814909-01 from the U.S. Environmental Protection Agency.

Thermospray Enhanced Inductively Coupled Plasma Atomic Emission Spectroscopy Detection for Liquid Chromatography

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Thermospray sample introduction is studied as an interface between liquid chromatography and inductively coupled plasma atomic emission spectrometry for metal speciation studies. Detection limits for chromium species separated by ion chromatography or mobile phase ion-pairing chromatography are improved by factors of 24 and 36, respectively, for 50 and 25 μm aperture based thermospray systems, as compared to pneumatic sample introduction. For arsenic species separated by ion chromatography, relative response factors between the two sample introduction systems were species dependent. Lower enhancements for certain species with thermospray were thought to result from thermal decomposition to form volatile species which were lost during desolvation. For nonaqueous size exclusion studies of organoiron species, detection limits were improved by a factor of about 50 with thermospray compared to a pneumatic sample introduction system.

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The determination of the chemical forms (i.e. speciation) of trace metals is well-known to be important to a wide range of chemical systems (i.e. environmental, biochemical, etc.). One approach to such measurements is to separate the various metal species using liquid chromatography and employ a detector, such as inductively coupled plasma atomic emission (ICP-AES) or mass spectrometry (ICP-MS), for selective detection of the metal(s) of interest (*1*). These types of atomic spectrometers are particularly advantageous as high-performance liquid chromatography (HPLC) detectors since simultaneous multielement analysis is possible, and the speciation of more than one metal may be evaluated during a single chromatogram.

In many speciation applications, detection is required at extremely low levels (sub-nanogram-per-milliliter to nanogram-per-milliliter). The nature of the sample and the lability of the various species may preclude the reliable use of preconcentration techniques. Although ICP-AES and ICP-MS have low limits-of-detection (LOD's) for direct sample introduction (~ng/mL to sub-ng/mL, respectively), LOD's for

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chromatographically injected discrete samples are generally substantially higher based on the dilution and dispersion which unavoidably occurs during the chromatographic process and sometimes on matrix interferences resulting from the mobile phase. As an example of these effects, the commonly reported LOD for chromium by ICP-MS with direct aspiration is 0.02 ng/mL, while HPLC–ICP-MS LOD's were 50 ng/mL or greater, depending on chromatographic conditions (*2*). Consequently, improvements in the detection capabilities of ICP-AES or ICP-MS should be of advantage to the practical application of metal speciation studies employing HPLC–ICP detection.

One aspect of ICP methods that has long been considered to be a hindrance to detection is the sample introduction process (*3*, *4*). Conventional sample introduction systems involve the pneumatic generation of aerosols which are processed in a spray chamber prior to injection into the ICP. During the course of this processing, typically 98–99% of the analyte goes to waste and never reaches the ICP. In principle, this analyte loss corresponds to 99% of the potential signal, as well. Further, these pneumatic sample introduction systems are thought to introduce a substantial amount of noise to the measurement process, further degrading potential LOD's.

Recently, the alternative use of thermospray for aerosol generation (*5*) and sample introduction to ICP-AES (*6*) has been described. With thermospray, aerosols are generated by pumping liquids through an electrothermally heated capillary where partial vaporization occurs at appropriate temperatures, resulting in a jet of vapor and aerosol. Thermospray aerosol particles have been shown to be smaller on average than those for pneumatic aerosols, leading to higher analyte transport efficiencies (*7*). With a decrease in the capillary exit diameter, such as through the use of a limiting aperture (*8*), transport efficiency increases; with a 25 μm aperture based thermospray vaporizer, >60% of the input analyte may be transported to the plasma, resulting in a 20–25-fold signal enhancement (*9*). Further, background noise levels typically 2–3 times lower have been reported for our thermospray system (*6*, *7*) resulting in up to 50-fold signal-to-noise ratio (SNR) and LOD improvements for thermospray sample introduction compared to pneumatic sample introduction (*9*). Thermospray systems operated under optimum conditions for ICP-AES have also been shown to be surprisingly resistant to clogging even with high dissolved solids levels (*10*). Thermospray systems also have inherently low liquid dead volumes, minimizing dispersion effects in the liquid phase. An earlier study described the use of a thermospray interface for HPLC–ICP-AES of tin species (*11*).

In this report, we will describe the application of thermospray sample introduction as an interface between HPLC and ICP-AES for metals study with aqueous, mixed-phase, and nonaqueous chromatographies. The system will be described for ion exchange, reverse-phase (mobile phase ion pairing), and gel-permeation separations. The advantages of this system will be specifically discussed with regard to studies of chromium speciation in environmental aerosols.

EXPERIMENTAL SECTION

A detailed list of the various instrumental facilities is provided in Table I. For chromium speciation, a Leeman Labs (Lowell, MA) Model 2.5 ICP was used with a McPherson (Acton, MA) Model 270 monochromator. A Perkin-Elmer ICP/5500 was employed for arsenic speciation with the monochromator being purged with nitrogen during study. Wavelength modulation using a quartz refractor plate was used for dynamic background correction in both instrumental setups.

Pneumatic Nebulizer Interface. A Hildebrand grid (Leeman Labs, Lowell, MA) pneumatic nebulizer with a polyethylene spray chamber (Leeman Labs) was used for conventional sample introduction to the plasma. A jacketed, double-pass spray chamber

Table I. Instrumentation

A. HPLC system	
pump	Autochrom M500 dual piston
pump controller	Autochrom OPG/S
injector	Rheodyne Model 7125
pulse dampner	SSI Model LP-21
B. Leeman Labs ICP system	
torch box	Leeman Model 2.5
monochromator	McPherson Model 270 0.35 m focal length 2400 grooves/mm grating 30 μm slit width
preamplifier	Keithly Model 485 picoammeter
C. Perkin-Elmer ICP system	
torch box/monochromator	Model 5500 0.408 m focal length 2880 grooves/mm grating 30 μm slit width
preamplifier	Keithly Model 610B
D. wavelength modulation	
frequency generator	Wavetek Model 114 185 Hz
lock-in amplifier	Stanford Research Systems Model SR510
E. data acquisition/manipulation	
computer	Multitech 700 PC Compatible
interface	Metrabyte Dash-16
software	Assystant +

that was cooled to −4 °C followed by a cold-finger condenser cooled to −50 °C in a dry ice acetone slush bath was used for solvent vapor removal for chromatographic experiments employing tetrahydrofuran (THF) as the solvent.

Thermospray Nebulizer Interface. The aperture-based thermospray vaporizer begins with a capillary of 0.127 mm i.d. by 1.6 mm o.d. stainless steel obtained from Alltech (Deerfield, IL). J-type thermocouples were spot-welded 1.5 cm and 30 cm from the vaporizer tip. The assembly of the exit aperture was identical with that described elsewhere (*8*), except that the apertures were of slightly smaller diameter (3.125 mm) and were placed into a cup-shaped back ferrule which was used instead of the supporting washer described previously. This back ferrule was of appropriate size to slide over the ferrule, sandwiching the aperture in place. This arrangement was found to reduce mechanical wear to the aperture during tightening and simplified the process of centering the exit hole of the aperture upon the exit hole of the 1.6-mm nut. The apertures (0.13 mm thick) were laser drilled (25 or 50 μm) and were obtained from National Aperture, Inc. (Windham, NH). A heated spray chamber (145 °C) and Friedrich's condenser (0 °C) were employed with thermospray for desolvation and were identical with those described previously (*6*). For experiments with THF, the condenser was followed by the cold-finger condenser described above for the pneumatic nebulizer.

Both nebulizers were connected to the sample source (i.e. injector for flow injection analysis or column exit for chromatographic analysis) using a 10 cm length of 0.13 mm i.d. tubing.

With the pneumatic nebulizer, the exit of this tube was butted against the inlet tube of the nebulizer and joined by means of a Tygon sleeve to minimize dead volume. Flow systems were connected with the thermospray probe by means of a 1.6-mm Kel-F union (Upchurch Scientific Model U-402K, Oak Harbor, WA) which also provided electrical isolation. The assembled probe was used with a Vestec (Houston, TX) triac-controlled thermospray power supply (*5*).

HPLC–ICP-AES. The mobile phase was metered with a high-pressure liquid chromatography pump (Auto Chrom OPG/S system with an M 500 dual-piston pump). A Rheodyne Model 7125 injector with a 200 μL injection loop was used for analyte injection. Dionex HPIC AS4 and HPIC AS4A columns were used for ion chromatography separations of chromium and arsenic species, respectively. An Adsorbosphere (Alltech, Deerfield, IL) C-18 column was used for mobile-phase ion pair (MPIP) separations. A Phenogel 100 Å (Phenomenex, Palos Verdes, CA) column was used for gel permeation chromatography (GPC).

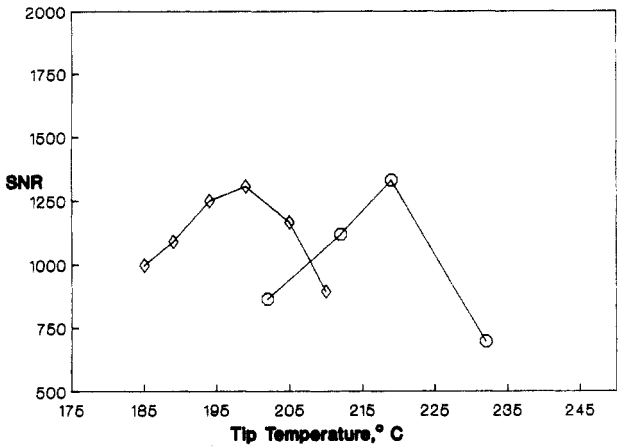

Figure 1. Effect of thermospray tip temperature on SNR for 2 μg/mL Cr(VI) after ion chromatography (◇) and mobile phase ion-pairing chromatography (○), 50-μm thermospray.

The plasma operating parameters were optimized following standard procedures. The nebulizer flow was controlled by a Tylan (Carson, CA) Model FC280 mass flow controller. The rest of the plasma operating gases were controlled by the standard rotameters. For experiments with THF, 0.15 L/min of O_2 was metered into the aerosol carrier/nebulizer flow with a Tylan FC 260 mass flow controller. The pneumatic and also the thermospray nebulizers were operated at the liquid flow rate employed for the HPLC separation, i.e. at a carrier flow rate of 1.0 mL/min. Further, with THF mobile phases a low-flow ICP torch operating at 12 L/min and 1.2 kW was employed.

Reagents. All the chemicals used were reagent grade. Standard solutions were prepared freshly from chromium nitrate and potassium dichromate for chromium speciation studies. The solutions for arsenic speciation were prepared from sodium arsenite, sodium arsenate, dimethylarsinic acid (DMA), and phenylarsonic acid (PhAs). The Conostan S-21 nonaqueous multielement standard was obtained from Conoco (Ponca City, OK) and diluted with THF as required.

The eluent used for ion chromatography of Cr species was potassium hydrogen phthalate (KHP) at a concentration of 5×10^{-4} M. The pH was adjusted to the desired value with either hydrochloric acid or potassium hydroxide solutions.

The eluent in mobile phase ion-pairing chromatography (MPIP) was prepared from the sodium salt of pentanesulfonic acid (Aldrich). The sodium salt of pentanesulfonic acid was ion exchanged with Amberlite CG-120 (200–800 mesh) (Mallinckrodt) to replace sodium with magnesium. This procedure was conducted to reduce the suppression effect of sodium on the Cr II 283.563 nm emission line. Magnesium acetate was added to this solution at a concentration of 0.01 M. Acetic acid (1% by volume) and methanol (10% by volume) were also added. The pH of the eluent was adjusted to the value of 3.5 with dilute acetic acid.

The anion chromatography of arsenic species was carried out using a linear gradient from 100% distilled deionized water to 100% 0.05 M ammonium carbonate containing 0.2% methanol. Ammonium salts were chosen to minimize easily ionizable element effects within the plasma once again.

RESULTS AND DISCUSSION

Flow Injection Analysis (FIA) and HPLC–ICP-AES for Cr. The optimization of the thermospray nebulizer was carried out in a flow injection mode by using the intended chromatographic solvent as the carrier stream, prior to the study of separation of the species. Figure 1 shows the effect of probe tip temperature on signal to noise ratio (SNR) obtained for 2 ppm Cr(VI) with a 50 μm aperture-based thermospray vaporizer using two different solvent systems. The probe tip temperature influences the degree of vaporization of the carrier fluid through the thermospray capillary and is dependent on the composition and flow rate of the carrier fluid (7). Optimum temperatures may vary somewhat from vaporizer to vaporizer. Operating tip temperatures were chosen

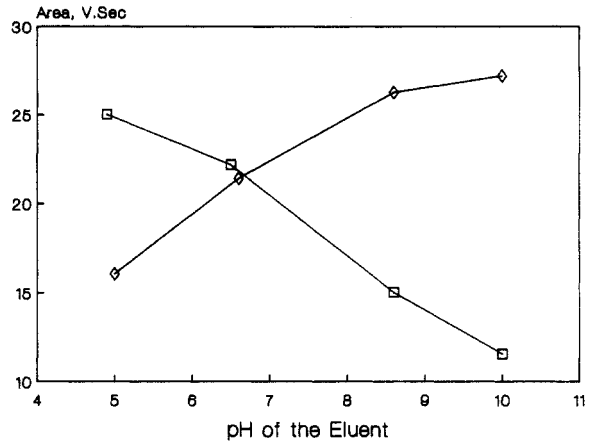

Figure 2. Peak area versus pH for Cr(III) (□) and Cr(VI) (◇) after ion chromatography.

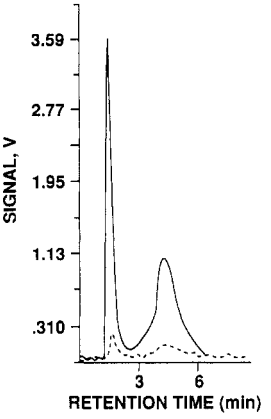

Figure 3. Separation of chromium species by ion chromatography with 50-μm thermospray (—) and pneumatic (---) sample introduction.

to optimize SNR. At excessively higher temperatures, nonvolatile species may deposit inside the probe and may eventually clog the probe. The optimum tip temperatures chosen for chromium were 200 °C for anion chromatography and 220 °C for MPIP At these temperatures, capillary clogging was extremely rare and could be alleviated via short-term ultrasonication of the aperture.

For anion exchange chromatography, Cr(III) was complexed with ethylenediaminetetraacetic acid (EDTA) to form the anionic complex of Cr(III) with EDTA. The pH values of the sample and the eluent were important to the separation and response observed. Figure 2 shows the effect of eluent pH on peak area for Cr(III) and Cr(VI) species with the Dionex HPIC AS4 column. A pH of 6.5 was chosen for subsequent studies. The retention time and the peak profile for Cr(III)–EDTA were not affected by the pH of the eluent, but the retention time and the peak profile of Cr(VI) were strongly influenced by the pH of the eluent. Figure 3 is a chromatogram for the separation of Cr(III) and Cr(VI) which also compares the response obtained with a pneumatic sample introduction system to that with a 50-μm thermospray system. In this chromatographic mode, Cr(III) eluted early (1.4 min) while Cr(VI) eluted at 4.2 min. Clearly indicated is the much higher response for chromium species obtained with the thermospray system. The broad peak for Cr(VI) was likely due to an oxidative interaction of this species with the column. Peak areas per unit mass were identical for the two species, however.

Figure 4 indicates the separation of Cr(III) and Cr(VI) by MPIP and also compares the response obtained for the two sample introduction systems. Once again, the response obtained with the 50-μm thermospray system was substantially higher than that obtained with the pneumatic system. With

Table II. Limits of Detection (ng/mL)[a]

species	nebulizer	FIA[b]	IC[c]	FIA[d]	MPIP	FIA[d]	GPC
Cr(III)	25-μm thermospray				7 (1.4)		
	50 μm thermospray	2 (0.4)	10 (2)		10 (2)		
	pneumatic	48 (9.6)	244 (48.8)		252 (50.4)		
Cr(VI)	25-μm thermospray			2 (0.4)	7 (0.4)		
	50-μm thermospray	2 (0.4)	30 (6)	3 (0.6)	10 (2)		
	pneumatic	48 (9.6)	526 (105)	71 (14.2)	254 (50.8)		
As(III)	25-μm thermospray		1170 (234)				
	pneumatic	63 (12.6)	250 (50)				
As(V)	25-μm thermospray	3 (0.6)	17 (3.4)				
	pneumatic	63 (12.6)	306 (61.2)				
DMA	25-μm thermospray	47 (9.4)	155 (31)				
	pneumatic	63 (12.6)	253 (50.6)				
PhAs	25-μm thermospray	4 (0.8)	12 (2.4)				
	pneumatic	63 (12.6)	254 (50.8)				
ferrocene	50-μm thermospray					39 (7.8)	120 (24)
	pneumatic					2000 (400)	5600 (1120)
Conostan S-21	50-μm thermospray					13.5 (2.7)	39 (7.8)
	pneumatic					630 (126)	1791 (358)

[a] Absolute LOD's in nanogram are listed in parentheses. [b] Flow injection analysis using ion chromatographic mobile phase as carrier stream. [c] Flow injection analysis using ion-pairing mobile phase as carrier stream. [d] Flow injection analysis using THF as carrier stream.

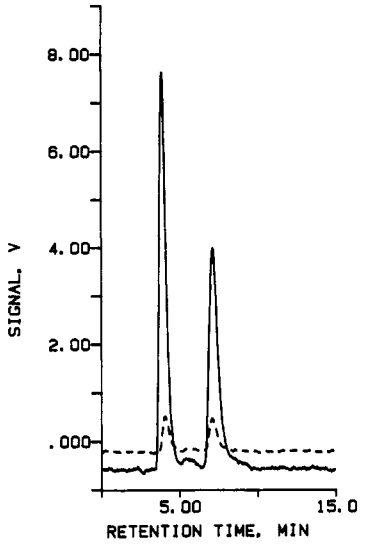

Figure 4. Separation of chromium species by MPIP with 50-μm thermospray (—) and pneumatic (---) sample introduction.

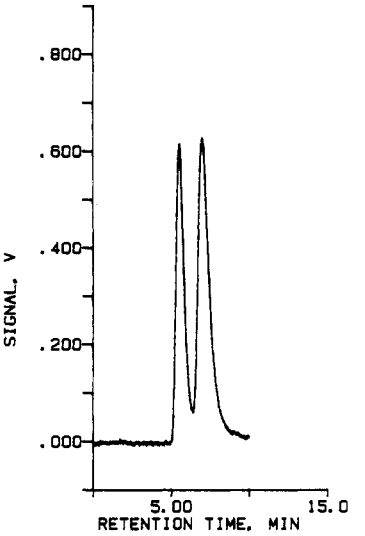

Figure 5. Ion-pairing chromatogram for 1 μg/mL Cr(III) after 12 h of aging, 50-μm thermospray interface.

this separation, Cr(VI) was now the early eluting species. The retention of Cr(III) was substantially affected by the age and matrix of the solution. The chromatogram in Figure 4 was obtained for a mixture of freshly prepared solutions. Figure 5 shows a chromatogram obtained for a Cr(III) standard solution which had been aged for 12 h. In this case, a second peak has appeared at a shorter retention time. This peak was still well-resolved from the Cr(VI) peak, however. With samples derived from extracts of environmental aerosol samples, as many as five different peaks for Cr(III) have been observed, with three additional minor species having retention times from 7 to 10 min (*12*). These multiple peaks for Cr(III) likely result from the fact that coordination complexes for Cr(III) are highly kinetically stable (*13*). In aqueous solutions where they are not chelated, a variety of hydrolysis species are possible (*14*), to include: $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5OH^{2+}$, $Cr(H_2O)_4(OH)_2^{+}$, and $Cr(H_2O)_4(OH)_4^{-}$. These species are stable enough to survive the MPIP chromatographic process with different retention times. This feature of MPIP–ICP-AES with Cr(III) may be used to advantage for providing detailed information concerning the distribution of Cr(III) among these various complexes.

The peak widths at half height obtained with both the nebulizers were equivalent for each chromatographic system. The large difference in nebulizer spray chamber dead volumes (118 mL for the pneumatic nebulizer and 570 mL for the thermospray system) did not appear to contribute to peak broadening.

The slopes of the calibration curves were equivalent for the two different Cr species studied in a flow injection mode and with MPIP chromatography with either nebulizer; a difference in slope for Cr(III) and Cr(VI) with ion chromatography was attributed to the broadened peak shape for Cr(VI). The equivalent slopes indicated the independence of the sensitivity of the measurement process for the two different Cr species with either mode of aerosol generation. The process of heating within the thermospray did not have an effect on the Cr analyte. With the thermospray nebulizer, the slopes of the calibration curves were over an order of magnitude superior to those with the pneumatic nebulizers. The reduced noise level with the thermospray nebulizer also enhanced the detection capability for the analyte (*6*).

Detection limits, based on 3σ values, were estimated by using the slope method (*15*). The detection limits obtained for Cr in FIA–ICP-AES and HPLC–ICP-AES are listed in Table II. In FIA, the detection limit was determined with a carrier stream consisting of the chromatographic mobile phase. The 50- and 25-μm thermospray nebulizers offered

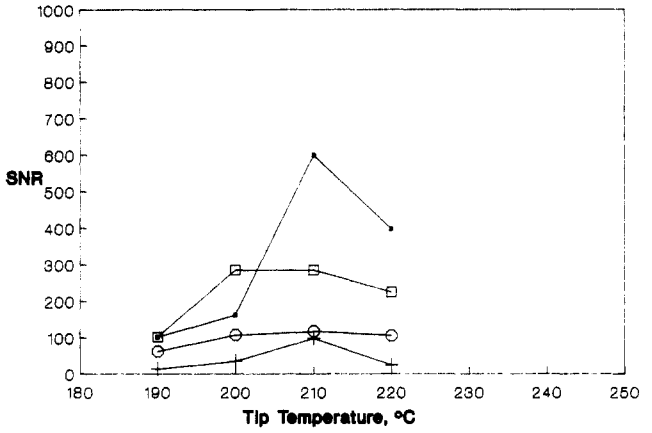

Figure 6. The effects of thermospray tip temperature on SNR for 5 μg/mL of PhAs (■), arsenate (□), DMA (O), and arsenite (+), 25-μm thermospray.

improvements in detection limit of factors of 24 and 36, respectively, compared to the conventional pneumatic nebulizer. The detection limits obtained with the 25-μm thermospray (7 ng/mL or 1.4 ng) for Cr(III) and Cr(VI) in the HPLC studies are comparable to the best reported detection between 5 and 15 ng/mL (0.5–1.5 ng) for HPLC–DCP-AES (*16*), 20 ng/mL (4 ng) for HPLC–ICP-AES (*17*), and 50 ng/mL (1 ng) for HPLC–ICP-MS (*2*). The moderate resolution spectrometer employed in these studies was likely a substantial hindrance to the generation of lower absolute limit of detection values (*18*); the relative LOD's for the conventional and thermospray nebulizers are considered to be of greater relevance. The poorer detection limit for Cr(VI) with ion chromatography was also attributed to the broad peak observed for this species. The superior LOD for Cr(VI) obtained with MPIP chromatography made this separation the method of choice for studies with chromium aerosols which are described elsewhere (*12*).

FIA and HPLC–ICP-AES for As. The thermospray nebulizer was optimized for arsenic compounds at an analytical wavelength of 193.7 nm in an analogous fashion to that employed for chromium (i.e. flow injection). The plot of SNR vs probe tip temperature is shown in Figure 6. The optimum temperature was found to be 215 °C. The responses for various arsenic compounds with the thermospray probe were not identical. As in the case of chromium, the slopes of calibration data obtained with the thermospray nebulizer generally were much higher than those for the pneumatic nebulizer. The detection limits obtained in flow injection analysis for the arsenic species are listed in Table II. Negative intercepts of the calibration curves for DMA and arsenite in the case of the thermospray nebulizer suggested a possible sample loss within the sample introduction system. This resulted in an apparently lower sensitivity of the thermospray nebulizer ICP-AES system for these two compounds. This lower sensitivity was also observed for the chromatographic analysis. The loss of arsenite was thought to arise from a thermal disproportionation within the thermospray vaporizer or heated spray chamber, forming arsenite and free arsenic (*19*). Although the fraction of arsenite converted to arsenate would be likely to be transported to the plasma, arsenic sublimes at 100 °C and the resultant vapors would likely be trapped by the condenser employed with the desolvation system. The comparable calibration data for DMA suggest that a thermal decomposition process may also account for the lower response for DMA, althouth no similar mechanism can be rationalized. The responses for DMA and arsenite however, were still comparable to or better than those provided by the pneumatic sample introduction system. The precision of analysis for the individual arsenic compounds with both

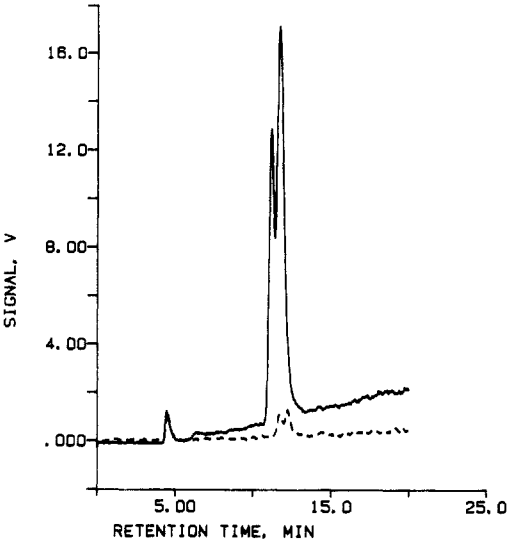

Figure 7. Separation of arsenic species by ion chromatography with 25-μm thermospray (—) and pneumatic (---) sample introduction.

the nebulizers was within 2%, except for DMA which was 6% with the thermospray.

The separation of the arsenic species on the Dionex HPIC AS4A column using a linear gradient from distilled deionized water to 0.05 M $(NH_4)_2CO_3$ containing 0.2% methanol in 20 min was established by using the pneumatic nebulizer. The order of elution of the different arsenic compounds was as expected, with the singly charged arsenic and DMA eluting before the doubly charged arsenate and PhAs.

A chromatogram of DMA, arsenate, and PhAs comparing the response for the thermospray and the pneumatic nebulizers is shown in Figure 7. The detection limits obtained on a 3σ basis are shown in Table II. The thermospray nebulizer offered superior detection for DMA, arsenate, and the PhAs species. The improvement factors in detection with the thermospary nebulizer were 1.6, 18.5, and 20.7 for DMA, arsenate, and PhAs, respectively. The detection limit for arsenite was higher with the thermospray nebulizer. The response for arsenate and PhAs compounds with the thermospray nebulizer was also hindered by the sloping base line which arose from the spectral broadening of the carbon emission line at 193.09 nm due to the increasing concentration of the carbonate in the mobile phase. The effect was greater with the thermospray nebulizer and attributed to the higher transport efficiency of this sample introduction system for not only the analyte but also the nonvolatile matrix components. The detection limits obtained for arsenite (234 ng or 1171 ng/mL), DMA (31 ng or 155 ng/mL), and arsenate (3.4 ng or 17 ng/mL) with the thermospray were superior to the 2σ LOD values of 390 ng (arsenite), 60 ng (DMA), and 126 ng (arsenate) as reported for anion exchange chromatography ICP-AES by Spall et al. (*20*).

Nonaqueous FIA and HPLC–ICP-AES. Evaluation of the thermospray interface for nonaqueous applications was conducted with THF as the mobile phase for gel permeation chromatography. As before, response for iron at 259.9 nm was optimized in a flow injection mode. For a 50-μm thermospray, a tip temperature of 200 °C was found to be optimum for both ferrocene and the Conostan S-21 standard. Figure 8 depicts the relative response obtained for a 5 μg/mL solution of the Conostan standard injected on to the GPC column. As before, the response obtained with thermospray sample introduction was substantially higher than that obtained with pneumatic sample introduction. LOD's for ferrocene and the Conostan standard in FIA and GPC modes are listed in Table II. The relative improvements in LOD with thermospray ranged from 46 to 51. Of particular note was the high response for ferrocene

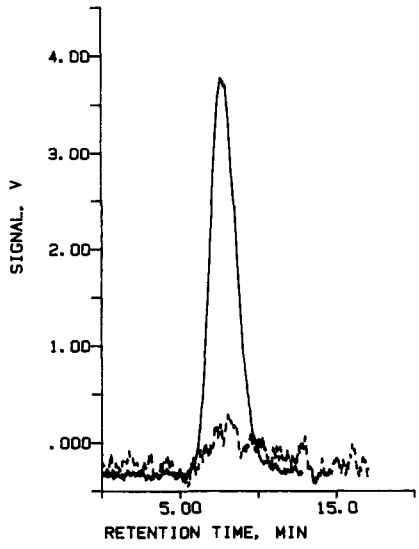

Figure 8. Gel permeation chromatography of 5 μg/mL Fe via Conostan S-21 organometallic standard with 50 μm thermospray (—) and pneumatic (---) sample introduction.

despite its substantial volatility (sublimes above 100 °C).

CONCLUSION

The use of thermospray sample introduction as a means for interfacing HPLC with ICP-AES offers substantial improvement in detection for most of the elemental species described herein. Limits of detection for chromium species are better than HPLC–ICP-AES values reported elsewhere and generally as good as or better than those reported for other plasma methods (DCP-AES or ICP-MS). These improvements in detection can be used to advantage for aqueous samples containing low concentrations of chromium or to reduce the collection time for samples such as atmospheric aerosols. In the latter case, for example, the collection time for aerosols required for reasonable measurements can be reduced by a factor equivalent to the LOD improvement. In our case, sampling times could be reduced from up to 24 h to 1 h, or less (*12*). For chromium, similar improvements were observed for aqueous (IC) and mixed phase (MPIP) separations. For arsenic species separated by ion chromatography, LOD's were improved by a factor of about 20 for some compounds but were only comparable to those obtained with pneumatic sample introduction for species which are apparently thermally labile. The thermospray sample introduction system also provided substantial LOD improvements (~50 times) for organometallic species in nonaqueous systems.

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RECEIVED for review September 18, 1989. Accepted November 22, 1989. Partial support of this work was provided by Vestec Corp. and the U.S. Department of Energy through Grant DE-FC22-87PC 79863.

Application of the Hollow Cathode Discharge Emission Source to the Determination of Nonmetals in Microsamples

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The use of the hollow cathode discharge source for the excitation of nonmetals in volume-limited samples is discussed. The effects of breakdown voltage, fill-gas composition, electrode composition, hollow size, sample deposition mode, current, and fill-gas pressure on the emission signal from phosphorus and chlorine are reported. Instrumentation, operation, and sample preparation procedures are described. Temporal profiles of the emission signal from very small samples deposited in the hollow are given for P, Cl, and Se. Detection limits of 9 and 20 pg are reported for P and Cl, respectively.

INTRODUCTION

The hollow cathode discharge (HCD) has been successful as a source of radiation for atomic spectroscopy for a very long time. It provides a spectrum with very narrow emission lines, which contributes significantly to its sensitivity and selectivity as an atomic emission source (*1*, *2*). As compared to metals, there are many fewer reports of determination of nonmetallic elements using the hollow cathode emission source. The nonmetals, P, Se, and Cl, have many known functions in life processes; thus, analytical methods, including trace analysis of small samples and analysis of nanoliter-size samples of physiological fluids, are needed. The HCD source fills the need for nonmetal determination in volume-limited samples. The analysis is very important because renal physiologists typically employ either micropuncture or microperfusion obtaining tubule fluid samples ranging from picoliters to nanoliters. Common physiological fluids contain Na, K, Ca, Mg, Cl, and P, which frequently must be determined in very

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