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Note

Ion chromatography with direct and indirect spectrophotometric detection*

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Ion chromatography (IC) is a fast, efficient method for the separation of charged species[1,2]. Atomic spectroscopy is an efficient and sensitive method for the detection of most metal cations[3]. The combination of the two techniques provides a means for the separation of species based upon their ion-exchange characteristics and detection based upon atomic spectroscopy. Work combining IC and atomic spectroscopy has been reported in the past. Downey and co-workers[4,5] reported on the use of replacement IC to convert the analyte ions into a single atom suitable for atomic absorption spectroscopy (AAS). Other work has been performed by Chakraborti *et al.*[6] involving Zeeman graphite furnace as a selenium specific detector for IC. Additional selenium work has been performed by Roden and Tallman[7] using hydride generation after IC separation of the selenium species. Ricci *et al.*[8] used IC coupled with AAS to measure arsenic species. Chromate in lignosulfonate dispersants has been determined by IC–AAS by Pettersen[9]. The previous work tended to use either a replacement column (with the problems of regeneration or refilling which go with this type of column) or as a specific element system. The system described here is a simpler system than many of the previously described systems and can be used in a variety of methods thus providing a more versatile technique. The preliminary results reported here use the principles of direct and indirect photometric detection to accomplish the quantitation[10].

The following discussion and figures illustrate the type of work which has been performed in our laboratory using direct and indirect AAS for cation analysis and indirect absorption spectroscopy for anion analysis. It should be noted at this time that this work was performed on equipment which was not functioning at optimum efficiency. The purpose of this work was to determine the feasibility of the concepts and to determine whether or not there was sufficient reason for obtaining better equipment and pursue the research further. It is our opinion that further research is warranted based upon these preliminary findings.

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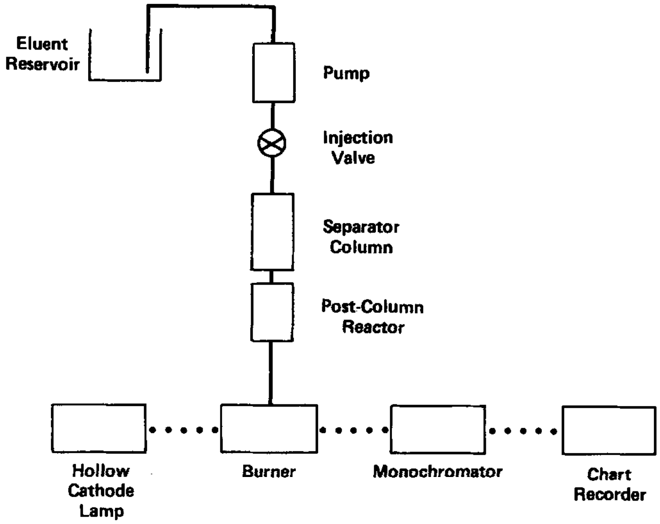


Fig. 1. Schematic of ion chromatography–atomic absorption system used in this research. See Table I for complete description of components.

EXPERIMENTAL

Equipment

Fig. 1 shows the flow schematic for the IC–AAS system employed in this research. The exact type of equipment used is described in Table I. The post-column reactor, which in this work is used as an auxiliary flow controller, is used to increase the rate of solution flow (by the addition of distilled-deionized water) into the atomic absorption spectrophotometer to just match the aspiration rate. By using the auxiliary flow controller (as we will call it in this paper), the chromatographic eluent flow does not have to match the aspiration rate providing more flexibility in the chromatographic portion of the system.

The Varian AA6 used in this research is an old instrument which had not been in use for several years. The stability of the signal obtained from this instrument was significantly less than the stability one would expect from a new, properly functioning instrument. Consequently, the detection limits are not low enough to warrant much excitement. We believe that with better equipment the detection limits can be brought down to acceptable, desirable, and useful levels.

TABLE I

INSTRUMENTAL CONDITIONS

Pump	Tracor Instruments, Model 955
Eluent and columns	See individual chromatograms
Injection volume (ml)	0.020
Auxiliary flow controller	Dionex reagent delivery module (post-column reactor)
Drip-aspirator interface	Laboratory made
Atomic absorption spectrophotometer	Varian AA6
Recorder	Linear Instruments 1200 chart recorder

Procedure

The ion chromatograph and the atomic absorption spectrophotometer were connected by the drip aspirator described below. The instrumental set-up was allowed to equilibrate for approximately 30 min to allow sufficient time for the chromatographic system to become fully stable. Solutions were then injected into the ion chromatograph and the results were monitored on the chart recorder attached to the Varian AA6. Various controls and standards were run to verify our results. All solutions and standards were prepared using distilled-deionized water. All chemicals used in this research were reagent grade chemicals.

Drip-aspirator

One of the main problems initially encountered in this work involved the baseline noise in the IC–AAS system. In direct IC–AAS, the noise is relatively small although it was larger than in AAS alone. In indirect IC–AAS, the magnitude of the noise increases dramatically. This increase can partially be explained by the fact that a small change is measured in a large signal (which is inherently less accurate than measuring a small change in a small signal). Another problem involves the method of introduction of the sample into the AA6. Direct coupling of the eluent line into the aspirator leads to inefficiency in the nebulization process with a corresponding increase in the noise. By using the drip interface, Fig. 2, the aspirator efficiency could be increased and the noise significantly decreased. With the drip aspirator it is essential that the drip rate equals the aspiration rate to minimize peak broadening due to mixing in the drip chamber. The auxiliary flow controller eases the problem of matching these two rates. (The 30-min equilibration time mentioned earlier can be used to adjust the auxiliary flow controller flow-rate such that the total flow-rate and the aspiration rate are equal.)

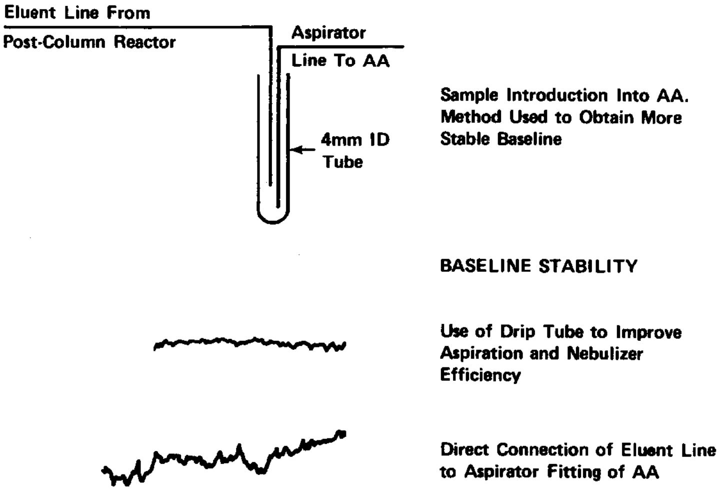


Fig. 2. Diagram of the drip aspirator interface used to connect the ion chromatograph to the atomic absorption spectrophotometer. The bottom tracings show the improvement in baseline stability which resulted when using this system.

Fig. 2 shows the design of the drip aspirator interface. It is essential that the inside diameter of the drip chamber be minimized to avoid mixing and peak broadening. The bottom portion of Fig. 2 shows examples of the baseline stability of the IC–AAS system with direct connection and with the drip aspirator interface. It is obvious that the noise level is significantly reduced using the drip aspirator interface. The drip aspirator interface was used in all work reported here.

RESULTS AND DISCUSSION

Direct IC–AAS

The easiest mode in which to operate the IC–AAS system is in the direct mode. In this mode of operation, the element of interest is determined using a hollow cathode lamp or electrodeless discharge lamp of that same element. The direct IC–AAS system is a specific detection system and has the advantages of sensitivity and selectivity which accompany the use of a specific detector. This system would be most effective in determining trace levels of different oxidation states of the same metal.

Fig. 3 shows several examples using the direct IC–AAS system. The separation observed is a function of the chromatography portion of the instrument and can be altered with changes in the eluent concentration and the eluent flow-rate. The handmade cation column referred to in Fig. 3 was prepared by surface sulfonating a polystyrene-divinyl benzene resin (Bio-Beads S-X2, 200–400 mesh; Bio-Rad Labs.,

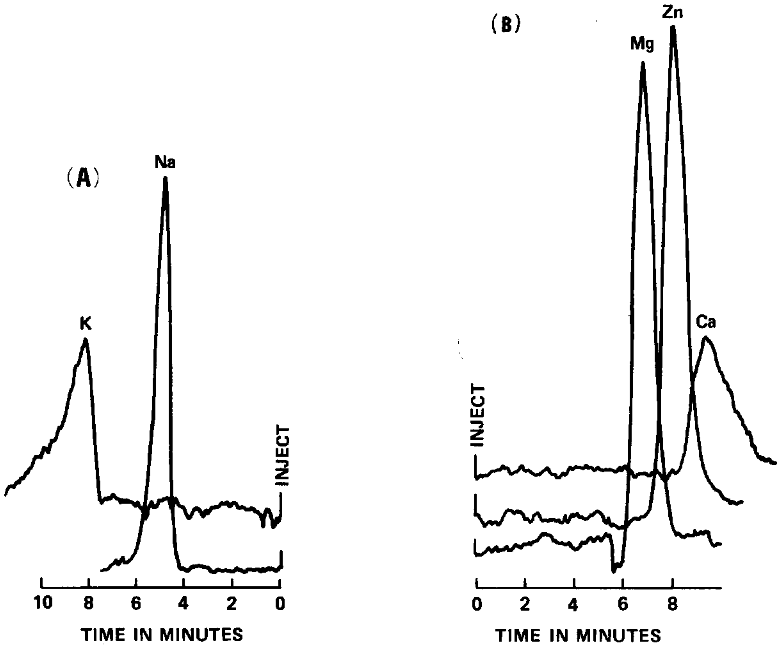


Fig. 3. Separation and detection of sodium and potassium (A) and some divalent cations (B) using direct IC–AAS and a lithium based eluent. Eluent, 5 m*M* lithium nitrate; flow-rate, 2.5 ml/min; columns, (A) hand-made cation column (see text), (B) Dionex CS-1 column; sodium lamp, 579.0 nm potassium lamp, 766.5 nm; zinc lamp, 213.9 nm; magnesium lamp, 285.2 nm; calcium lamp, 852.1 nm.

Richmond, CA, U.S.A.) followed by the hand packing of the dried resin into a 250 mm × 4 mm I.D. chromatographic column. Fig. 3A shows the analysis of sodium and potassium while Fig. 3B shows the analysis of magnesium, calcium and zinc. Detection limits for this procedure were at or below 1 ppm.

Indirect IC–AAS

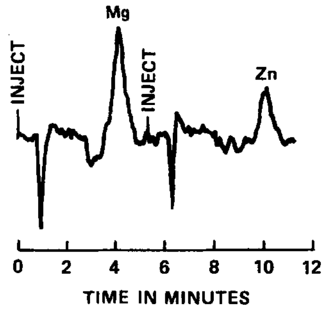
Indirect IC–AAS is a universal detection system with the general applicability of this type of system. The main advantage of the indirect IC–AAS system is that a wide range of analyte ions can be measured. The disadvantage is that the detector signal observed is a decrease in a large initial absorbance due to the relatively high concentration of the eluent ion used.

A wide variety of analytical concentrations are possible using indirect IC–AAS. A lithium based eluant (using a lithium hollow cathode lamp) is suitable for monovalent cation analysis, including the ammonium ion. A copper based eluant (using a copper hollow cathode lamp) has been successfully used for divalent cations, both the alkaline earths and the divalent transition metal cations.

Fig. 4 shows an example of magnesium and zinc using a copper based eluant. Table II lists a series of retention times for various transition metals using this copper based eluent system. The detection limits for this portion of the research were around 50 ppm. The detection limits were governed by the electronic noise in the AA6.

Indirect IC–AAS of anions

One of the more interesting applications of indirect IC–AAS is that the analyte ions do not have to be measurable using AAS (as in the analysis of ammonium in the preceding example). With this in mind, a system was tested for the analysis of anions using a copper based eluent and indirect photometric detection. The eluent is actually a solution of the EDTA complex of copper. The eluent is prepared by mixing powdered copper metal and fully protonated EDTA (approximately 0.05 mol each) in 50 ml of water and heating gently for several hours (keeping the volume of



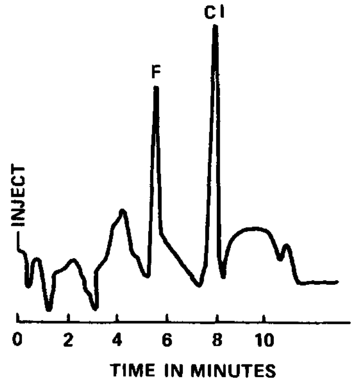


Fig. 4. Indirect IC–AAS of magnesium and zinc. Eluent, 1 mM Cu^{2+}; flow-rate, 2.1 ml/min; Column, Dionex CS1; copper lamp, 324.8 nm.

Fig. 5. Indirect IC–AAS of anions, preliminary results. Eluent, 0.004 M Cu(EDTA); flow-rate, 3.0 ml/min; column, Vydac 302IC; copper lamp, 324.8 nm.

TABLE II

RETENTION TIMES USING INDIRECT IC–AAS DETECTION WITH A COPPER-BASED ELUENT

Conditions as in Fig. 4.

Ion	*Retention time (min)*
Mn^{2+}	3.0
Mg^{2+}	3.2
Co^{2+}	3.4
Ni^{2+}	3.7
Zn^{2+}	4.0

water constant). The resulting solution of the copper–EDTA complex is filtered to remove unreacted copper metal and undissolved EDTA. The solution is then diluted to a volume of 1 l and is standardized using AAS. The copper–EDTA complex is a negatively charged complex and as such is capable of acting as an eluent for anion analysis. The analyte anion concentration can be determined by monitoring the copper–EDTA complex via indirect AAS.

Fig. 5 shows some preliminary results using this scheme. The separation of fluoride and chloride is illustrated. Obviously, this copper–EDTA eluent is not sufficiently strong to elute divalent anions in a reasonable time. This chromatogram illustrates the verification of the concept of indirect IC–AAS analysis of anions using indirect photometric principles. As above, the detection limits are governed by the electronic noise in the AA6.

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