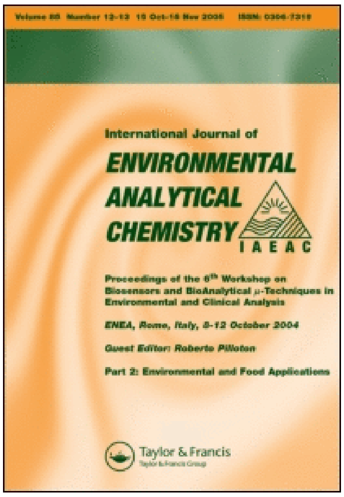

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Ion Chromatographic Determination of Soluble Anions Present in Coal Fly Ash Leachates†

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The advent of ion chromatography has provided an extremely useful tool for the rapid, precise and sensitive determination of inorganic anions. This capability can be put to excellent use in the determination of soluble anions associated with coal fly ash. Methodology applicable to determination of F^-, Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-} is described. Both the element solution concentration and pump pressures were varied to achieve optimal conditions in terms of resolution and speed of analysis. The precision of this method of analysis was determined to be ±3% and the accuracy ±5%. Replicate analysis of these coal fly ash leachate samples varied by less than 3%. In all cases % relative standard deviations were better than 3%.

INTRODUCTION

With coal becoming an increasingly important world energy source, the anion species present in coal fly ash represent a potentially large, and expanding, contribution to the environmental burden. Of particular im-

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portance are those anions which become available by leaching since rainfall water runoff from land fill sites or water within holding ponds all provide means for appreciable amounts of anions to enter the environment. Since some ionic species are present at some level in fly ash, all will appear in the process stream. For initial characterization purposes, therefore, an argument can be made for determining as many anions as possible so as to best delineate behavioral patterns and partitioning among them.

Because of the considerable complexity of environmental samples, a technique capable of analysing these types of samples must meet a number of criteria; (i) it must ideally provide a simultaneous multielement capability to minimize operator time and effort, (ii) it must provide low detection limits for the elements with a high degree of accuracy and precision, (iii) finally, it must be free from interferences and avoid matrix effects as much as possible. The technique which meets the above criteria is Ion Chromatography. This multielemental technique provides considerable savings in time over more traditional techniques in terms of preconcentration and/or separation procedures yet still provides the accuracy and precision which are so important in the analysis of environmental samples.

Ion chromatography (IC) is a recently developed technique that can separate and quantititatively analyse many ions in a variety of matrices.[1] Since the initial publication of the technique[2] in 1975, IC has been used in air and water pollution analyses,[3–6] boiler blow-down water,[7] sediment extract,[8] pickle liquors and fresh acids,[9] environmental pollutants such as copper and lead smelter flue dusts,[10,11] and clinical chemistry.[12] Basically, the system consists of a suppressor column, which removes unwanted background, and an analytical column which separates the ions by ion exchange. Detection is accomplished by use of a conductivity meter which provides a universal detection system for both anions and cations. An extensive comparison of IC to other methods of anionic analysis is reported in the literature.[1,13,14]

The purpose of this communication is to describe the successful application of ion chromatography to the analysis of water soluble carbonate, chloride, fluoride, nitrate and sulfate ions in coal fly ash leachates. The feasibility of rapid, simultaneous, multiion analyses is also demonstrated.

EXPERIMENTAL

Solutions and reagents

All chemicals were of analytical grade quality or better (J. T. Baker Co.

Ltd., U.S.A.). High-purity water from a Mili-Q water purification system (Milipore Corporation) was used throughout.

Mixed anion calibration standards were prepared by dissolving the appropriate sodium salts in water.

All glassware was cleaned by leaching with 3 M HNO_3 for 48 h, then in deionized water for 24 h and finally rinsed with deionized water prior to use. Similarly, membrane filters (Millipore HA, 0.45 μm) were leached for 3 h in a gently stirred solution of 1 M HNO_3 and for 3 h in deionized water before use.

Apparatus

A Model 10 Ion Chromatograph (Dionex Corp., U.S.A.) was used for the analysis of water soluble anions in coal fly ash leachates with the following instrumental settings:

Sample:	Water coal fly ash leachate
Eluent:	0.0030 M $NaHCO_3$/0.0024 M Na_2CO_3 in deionized water
Flow rate:	92 ml/hr (20%)
Analytical column:	Chromex anion exchange resin, 250 mm × 3 mm (ID)
Suppressor column:	Chromex cation exchange resin, 500 mm × 6 mm (ID)
Injection volume:	100 μl
Conductivity meter setting:	Variable, 3–1000 μmho full scale
Regenerant:	1 M H_2SO_4 in deionized water
Air stream:	Purified in a column of molecular sieve (Linde 13x) and a 10-μm mesh metallic filter
Recorder:	1 cm/min

The columns were supplied by the instrument manufacturer.

A Model W 200 R (Heat Systems-Ultrasonics Inc., U.S.A.) Sonicator Cell Disruptor was used for leaching of coal fly ash.

Sampling

The coal fly ash studied was obtained from the cyclone precipitator in the stack of the Corrette Plant of the Montana Power Corporation (Billings, U.S.A.).

Coal fly ash leaching procedure

22.5 g of fly ash were immersed in 90 ml of deionized water and sonically agitated for three hours using a sonic cleaning bath. The solution was then filtered through a 0.45 μm membrane filter. Blank solutions were prepared by these procedures without fly ash. This procedure was chosen as representative of the type of conditions which might occur when fly ash is discharged into a turbulent drain and thence into a river or impoundment pond.

Determination of anions

The anions present in each sample were measured using a Model 10 Analytical Ion Chromatograph. Chromatographic conditions for each analysis are shown previously. No pretreatment of leachates was found necessary. Each sample was loaded into a 5-ml plastic syringe, which contained a disposable 0.45-μm membrane filter (Millipore SLGSO-250-S) to filter out particulates upon injection. Samples were injected directly into the ion chromatograph. External standards were prepared from a stock solution containing 50 ppm F^-, 100 ppm Cl^-, 20,000 ppm CO_3^{2-}, 100 ppm NO_3^- and 10,000 ppm SO_4^{2-}. This standard solution was injected into the system prior to the analysis of each set of samples. The sample-ion peaks were compared to standard peaks of an external standard, for identification based on retention times, and concentrations were derived from comparison of either peak heights or areas. Blank filters are run with each set of samples, and all components rinsed with deionized water between samples.

RESULTS

Samples of aqueous coal fly ash leachates were analysed for five different anions (F^-, Cl^-, CO_3^{2-}, NO_3^- and SO_4^{2-}) using ion chromatography. Both the element solution concentration (a mixture of Na_2CO_3 and $NaHCO_3$) and pump pressures were varied to achieve optimal conditions in terms of resolution and speed of analysis. Sampling time varied slightly, but was consistently less than ten minutes. The results of the anion analysis are presented in Table I. In spite of the concentrated nature of the leachates, the separator column capacity and resolution were not observed to change during the course of the experiments. The suppressor column was regenerated at recommended intervals of 3 to 4 hours whenever background conductivity appear to be affecting the results.

Figure 1 shows a typical chromtogram of the anions in coal fly ash leachate. The precision of this method of analysis was determined to be

TABLE I

Aqueous extraction of anions from coal fly ash for three hour sonic extraction

	Standard	Concentrations		Detection limit
Anions	(μg/ml)	μg/ml	μg/g[1]	(μg/ml)
F^-	0.05–2.5	1.17	46.8	0.05
Cl^-	0.05–5.0	0.44	17.6	0.07
CO_3^{2-}	150–500	190	7600	150
NO_3^-	0.1–5.0	0.38	15.2	0.10
SO_4^{2-}	1.0–150	32.3	1292	0.10

[1] Concentration expressed as μg of anions extracted per gram of coal fly ash.

±3% and the accuracy ±5%. Replicate analysis of these coal fly ash leachate samples varied by less than 3%. In all cases % relative standard deviations were better than 3%.

DISCUSSION

Ion chromatography offers a method of direct anion analysis where other methods have interferences or are cumbersome and time consuming. It is possible to analyse many anions in a reasonably short time if all can be eluted and separated from one another. The conductivity detector makes multicomponent analyses highly practical. However, while the ion chromatograph is uniquely suited for the determination of anions in coal fly ash leachates, there are several problems which hinder optimal analyses. First, high ionic strength in a sample will affect anionic retention times. To correct this problem it is necessary to match standard and sample concentrations as closely as possible such has been done in Table I. Second, the columns can be affected by chemicals used in the preparation. The presence of BH_4^-, used to neutralise excess hydrochloric acid used in a related elemental analysis of coal fly ash digests, was found to seriously decrease the column's resolution. Third, all sulfur present is apparently in the form of sulfate; however detailed investigations indicate that rapid oxidation of sulfate occurs due to catalytic oxidation by the highly alkaline mobile phase in the presence of metal ions in solution.[15] This oxidation process makes the detection of SO_3^{2-} extremely difficult. Fourth, the water peak (peak A in Figure 1), a reproducible peak caused by the conductivity difference between the sample (in deionised water) and the eluent (a carbonate-bicarbonate solution) can interfere with the detection

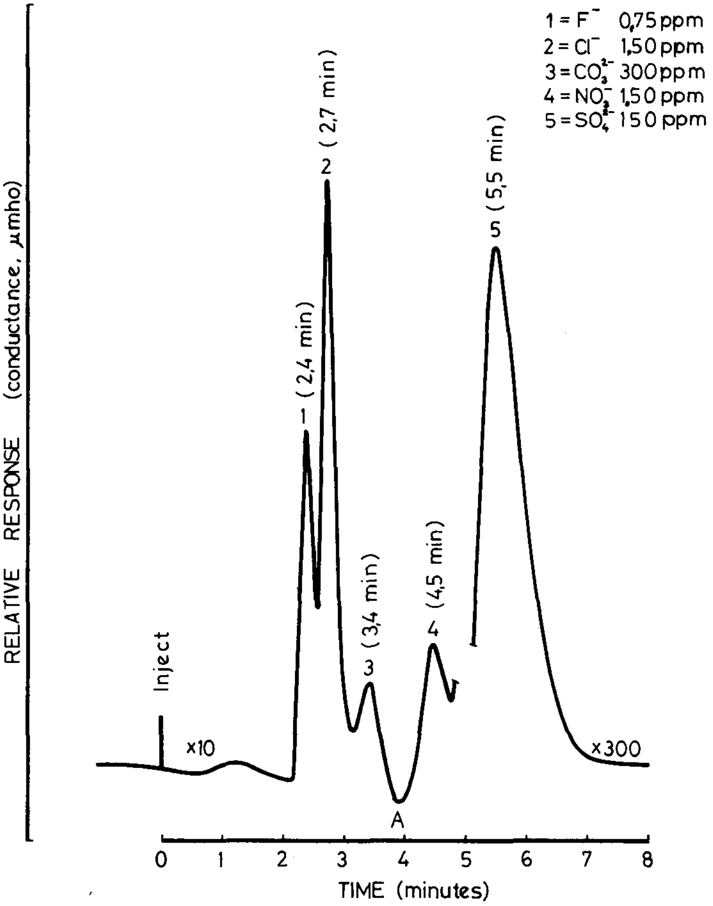

FIGURE 1 Determination of anions by ion chromatography in coal fly ash leachate. Retention times in brackets above each peak.

of some anions especially chloride and nitrate. In general, no problems were noted except when the suppressor column required regeneration.

One final IC related problem was the inability to detect phosphate (PO_4^{3-}). Unfortunately, the highly alkaline and high calcium content of the leachate medium caused spontaneous precipitation of phosphate. This precipitation has been examined in other environmental systems.[16,17]

The relatively high concentrations of the aforementioned anions are not surprising in view of the vigorous leaching conditions used in this study. Under those circumstances, a much larger amount of the matrix would be expected to dissolve than would be the case without sonication. Aside from the problems listed earlier, no problem was encountered with the complex high salt matrix which characterises fly ash leachates.

CONCLUSION

Ion chromatography is a technique that provides considerable information in a short period of time. It has no apparent difficulty with the complex fly ash leachate matrix, but the highly alkaline eluent may oxidise sulfur species and prevent other species such as phosphate from being solubilised. However, the use of IC provides a considerable advantage in anionic analyses since no other technique can both separate and quantitate complex mixtures as effectively.

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