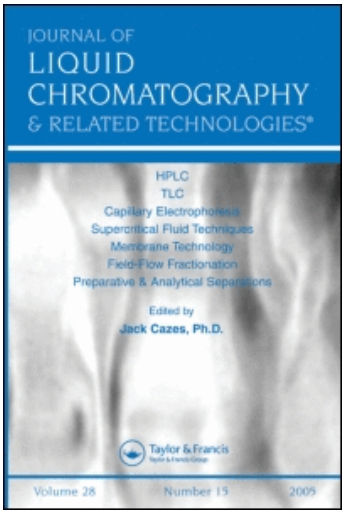

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Ion Chromatographic Analysis of Anions Based on Solid-Phase Extraction

Liu Kailu[a]; Liu Jin[a]; Yuan Siming[a]
[a] Beijing Research Institute of Chemical Engineering and Metallurgy, Beijing, The People's Republic of China

To cite this Article Kailu, Liu , Jin, Liu and Siming, Yuan(1993) 'Ion Chromatographic Analysis of Anions Based on Solid-Phase Extraction', Journal of Liquid Chromatography & Related Technologies, 16: 14, 3083 — 3092
To link to this Article: DOI: 10.1080/10826079308019634
URL: http://dx.doi.org/10.1080/10826079308019634

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(14), 3083-3092 (1993)

ION CHROMATOGRAPHIC ANALYSIS OF ANIONS BASED ON SOLID-PHASE EXTRACTION

LIU KAILU, LIU JIN, AND YUAN SIMING
Beijing Research Institute of Chemical Engineering and Metallurgy
P.O. Box 234
Beijing 101149, The People's Republic of China

ABSTRACT

Two kinds of solid phase extraction columns for sample preparation in ion chromatographic analysis of anions were developed. Anion SPE-1 Column was packed with a polymer sorbent and a cation exchanger. Anion SPE-2 Column was packed with the same sorbent and an anion exchanger. With SPE-1 Column, metal cations and lipophilic compounds were adsorbed on the column while anions remained in the mobile phase (deionized water). This procedure, coupled with IC, was used for analysis of anions in waste and industrial cooling water, in some solutions from hydrometallurgical process, in plating solutions and in radioactive samples. The analytical recoveries of anions were greater than 95%. With SPE-2 Column and deionized water as mobile phase, the anions were retained on the column to free them from impurities; then anions were eluted by changing the composition of mobile phase. The analysis of anions in biological matrices and food was successfully performed by IC-SPE method on SPE-2 Column.

INTRODUCTION

Now ion chromatography has come to be the most effective method for determining inorganic anions [1,2]. However, a wide variety of samples contains organic compounds, heavy metal ions and the anions

irreversibly adsorbed on anion exchangers. The column packing will be fouled by these substances and the analytical performance will be interrupted. Therefore, sample preparation is neccessary for determining anions in complex samples. Two kinds of solid phase extraction columns (SPE-1 column and SPE-2 column) are described in this paper. These columns have been widely used for sample preparation in ion chromatographic analysis of anions and very good results have been obtained.

MATERIAL

Reagents

All the reagents were analytical grade. Deionized water was used. The polymer sorbent and ion exchange resins were synthesized in our laboratory, including A05 polystyrene sorbent (50-70 μm) with the surface area of 300 m^2/g, the mean pore diameter of 150 Å; Y2*8 strongly acidic cation exchange resin (40-50 μm), a capacity of 5 meq/g; and 40 μm pellicular anion exchange resin with a capacity of 0.02 meq/g. The samples of "Brightblue" were obtained from National Research Center for CRM.S. (No.7 District 11, Hepinglie, Beijing 100013, P.R.China). The samples of human plasma were obtained from the hospital of our institute.

SPE Columns

1. SPE-1 Column, shown in Figure 1, consisted of a glass tube with a capillary outlet. The upper layer of the bed (15 mm) was packed with A05 polystyrene sorbent. The sorbent was purified by washing with methanol, followed with deionized water to remove methanol, the lower layer (40 mm) was packed with Y2*8 cation exchange resin. The purification steps included rinsing with methanol, 5% HCl and deionized water successively.
2. SPE-2 Column, with the same polymer sorbent in the upper layer. The lower layer was packed with 40 μm pellicular anion exchange resin. The column was successively washed with 5% HCl,

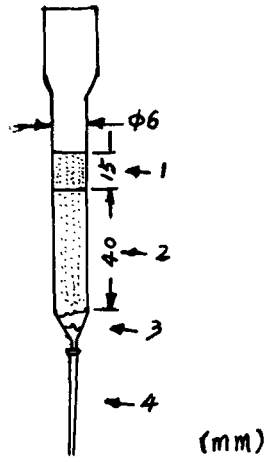

Fig.1 SPE Solid Phase Extraction Column of glass
1. upper layer 2. lower layer 3. glass wool
4. rubber tube

deionized water and 0.1 mol/l NaOH, followed by deionized water to remove Cl^-.

METHODS

IC Instrumentation

ZIC-2A ion chromatograph, equipped with a five-electrode conductivity detector, an electrodialysis suppressor (patent, CN 87106951), a model YS2 pump and a recorder (designed in our institute).

YSA-2 Separator Column, 250*4 mm ID, grain size 15 μm (made in our laboratory).

IC Condition

Eluent consisted of 2.9 mM Na_2CO_3 and 3 mM $NaHCO_3$ solutions. Flow rate of 2.0 ml/min were used. Injection volume was 100 μl.

Performance of Using SPE-1 Solid Extraction Column

An aliquot of sample solution (0.2-15 ml) was applied to the SPE-1 column and washed with deionized water. The sample and rinsing solution from the column was collected into a 25 ml volumetric flask. The CO_3^{2-} concentration of this flask was adjusted to 5.9 mM by addition of the concentrated Na_2CO_3 solution. The total volume was diluted to 25 ml with deionized water and 100 ul of such solution was injected into the IC system.

Performance of Using SPE-2 Solid Phase Extraction Column

An aliquot of sample solution (0.1-15 ml) was applied to the column. Then the column was rinsed with 6 mM Na_2CO_3 / 10 mM NaOH solution and all of the eluate was collected in a 25 ml volumetric flask. The total volume was diluted to 25 ml with deionized water and 100 ul of this solution was injected into the IC system.

RESULTS AND DISCUSSION

1. Analytical Result of Using SPE-1 Column

A05 polystyrene sorbent effectively adsorbed organic compounds from water, such as bezene, toluene, phenol and chlorophenols etc. With removal rates of more than 95%, Y2*8 cation exchange resin removed heavy metal ions effectively. Table 1 showed the varietions of concentrations of several heavy metal ions and organic compounds by passing through a SPE-1 column. It was shown that impurities were effectively removed.

The precision and accuracy of the method were evaluated by analysing a quality control sample over a six-day period. Its mean recovery was 100 +/- 5%; overall relative standard deviations were less than 5%, the low detection limits of seven anions were in the range of 0.005-0.05 ug/ml. (See Table 2,3,4)

TABLE 1
The Varietion in Concentration of Heavy Metal Ions and Organic Compounds by Passing Through SPE-1 Column (sample volume: 5 ml)

Impurity	Added (ug/ml)	Added (ug/ml)	Removal rate %
Gd	1	n.d.	100
Cu	4	n.d.	100
Zn	4	0.07	99.2
Cr^{3+}	8	n.d.	100
Pb^{2+}	8	n.d.	100
Fe^{3+}	8	n.d.	100
Ni^{2+}	8	0.1	98.7
Ce^{2+}	200	n.d.	100
Lubrication oil	10	less than 0.1	more than 99
Benzene and naphthalene	10	less than 0.01	more than 99.9
CH_3Cl	10	less than 0.01	more than 99.9
Phenols	10	less than 0.1	more than 99

TABLE 2
Evaluation of Recoveries of Anions

	F^-	Cl^-	NO_2^-	HPO_4^{2-}	Br^-	NO_3^-	SO_4^{2-}
Waste water ug/ml (Diluted to 1/2)	0.21	1.83				6.45	24.6
Added ug/ml	1	1	0.5	5	5	5	5
Found ug/ml	1.23	2.49	0.49	4.9	5.05	10.95	29.5
Recovery %	101.6	104.0	98.0	98.0	101.0	95.6	99.6

TABLE 3
The Precision and Accuracy for Determining Anions in Quality Control Sample from EPA

	F^-	Cl^-	NO_3^-	SO_4^{2-}
Given ug/ml	1.30	7.43	6.26	18.76
Measure number	7	7	7	7
Found ug/ml	1.27 ± 0.01	7.10 ± 0.10	6.26 ± 0.055	18.61 ± 0.108
R.S.D. %	0.12	1.5	0.90	0.58

TABLE 4
The Detection Limits of Anions Using SPE-1 Column

	F^-	Cl^-	NO_2^-	HPO_4^{2-}	Br^-	NO_3^-	SO_4^{2-}
Detection limits ug/ml	0.005	0.008	0.02	0.090	0.04	0.04	0.05

TABLE 5
The Result of Analysis of Anions in Complex Sample (ug/ml)

	F^-	Cl^-	NO_2^-	HPO_4^{2-}	Br^-	NO_3^-	SO_4^{2-}	N_3^-
Waste water 1	1.0	3.0	800			10.5	57	17
Waste water 2	1.7	46.0				10.0	50.0	
Liquid of uranium ore extraction	50.0	156.0				10.0	$1.27*10^4$	
Radioactivity sample						$1.5*10^4$	5	
Industrial cooling water	2	28.2		2		22.2	43.1	
Liquid of a vegetable extract	76.7	126.4	41.0	$1.17*10^3$		$2.61*10^2$	$6.08*10^2$	

This method has been widely applied in many fields. It was successfully used for determination of anions in waste water, in injected water of oil fields, in industrial circulated cooling water in hydrometallurgical liquor, in paper processing liquor, in radioactive samples, as well as in food, medicines, beer and wine. Some results are shown in Table 5 and Figure 2.

2. Performance of Using SPE-2 Column

With SPE-2 column and suitable composition of mobile phase, organic impurities and strong-retaining anions were adsorbed on the column, common anions were eluted in rinsing solution. It was important to select the composition of the rinsing solutions. On one hands, concentrated eluent would be used to accelerate elution rate; on the other hand, component identity between rinsing solution and analytical

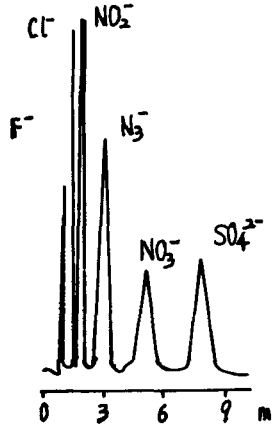

Fig.2 The chromatogram of anions in waste water sample using IC-SPE method based on Anion SPE-1 Column

TABLE 6

The Relationship between Elution Volume and Anion Recovery

Composition of eluent	Elution volume: ml	Recovery %				
		F^- 0.3 μg	Cl^- 0.4 μg	HPO_4^{2-} 2.5 μg	NO_3^- 1.5 μg	SO_4^{2-} 2.5 μg
2.4 mM	5	90	90	45.0		
Na_2CO_3/	10	100	102	100	92.6	2.7
3.0 mM	15	100	105	100	100	54.0
$NaHCO_3$	20	100	105	100	100	92.3
	25	100	105	100	100	100
6.0 mM	5	90	90	90	35	36
Na_2CO_3/	10	100	105	100	100	88
1.0 mM	15	100	105	100	100	100
NaOH						

TABLE 7

The Determination of Anions in "Brightblue" (%)

	Cl^-	HPO_4^{2-}	Br^-	NO_3^-	SO_4^{2-}
Sample 1	1.0	n.d.	n.d.	n.d.	1.14
Sample 2	1.0	n.d.	n.d.	n.d.	1.20
Sample 3	0.9	n.d.	n.d.	n.d.	1.08
Sample 4	0.9	n.d.	n.d.	n.d.	1.08

TABLE 8

The Determination of Cl^-, HPO_4^{2-}, NO_3^-, SO_4^{2-} in Human Plasma (ug/ml)

	Cl^-	HPO_4^{2-}	NO_3^-	SO_4^{2-}
Sample 1	$4.02*10^3$	102	47.0	103
Sample 2	$4.02*10^3$	120	67.0	53.0
Sample 3	$4.70*10^3$	110	51.4	96

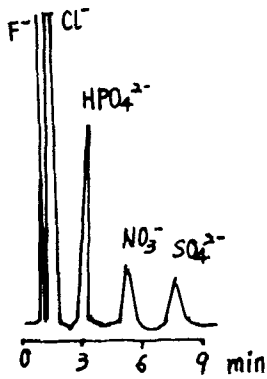

Fig.3 The chromatogram of anions in human plasma sample using IC-SPE method based of Anion SPE-2 Column

eluents must be considered. Table 6 shows the relationship between the recoveries of five anions and the volumes of different eluents.

It was observed, from Table 6, that common anions could be extracted by using the eluent of 6 mM Na_2CO_3 / 10 mM NaOH solution, with recoveries of 100%.

This procedure has been used for the determination of anions in "Brightblue", a kind of pigment (Table 7).

Because of interference of impurities, the background value in determining the chloride ion was too high to analyze accurately. The R.S.D. in determining the sulfate ion was +/- 1.1 %. Recovery of SO_4^{2-} in addition to the standard samples was 100.3 %. (determined six times)

It has been also applied to analysis of anions in human plasma.(See Table 8, Figure 3)

SUMMARY AND CONCLUSION

Two kinds of solid phase extraction technique were developed in this work. The methods successfully solved the problem of determining anions in complex substances. By these methods, the recoveries were 100 +/- 5%; the low detection limit of seven anions were in the range of 0.005-0.05 ug/ml, and the accuracy was better than +/- 5%. However, using a SPE-2 column in the analysis of the trace of F^-, Cl^-, the reproducibility was poor because of the interference of impurities in reagents.

REFERENCE

Journal:

1. H.Small, T.S.Stevens and W.C.Bauman Anal. Chem., 47, 1801 (1975)

Book:

1. Mu Shifen, Liu Kailu "Ion chromatography" Science Publishing House of China, Beijing, 1986.

Received: July 10, 1992
Accepted: February 17, 1993