Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Chromatography A, 1094 (2005) 118–121
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of atmospheric concentrations of inorganic anions by ion chromatography following ultrasonic extraction☆

Seyed Mortaza Talebi*, Mohammad Abedi

Department of Chemistry, The University of Isfahan, Hezar Jarib, Isfahan, Iran

Received 29 October 2004; received in revised form 21 July 2005; accepted 29 July 2005
Available online 26 August 2005

Abstract

The capability of the suppressed conductometric detection ion chromatography (IC) was investigated for the separation and determination of inorganic anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) in standard reference materials SRM-1648 urban particulate matter following ultrasonic extraction. The effects of the cationic surfactant (SDS) and the anionic surfactant (CTAB) on ultrasonic extraction efficiency of inorganic anions from complex matrix of airborne particulate matter were investigated. The results showed that surfactant can enhance the extraction efficiency. Finally, the concentrations of inorganic anions in the atmosphere of the city of Isfahan were determined. The results showed a trend of $SO_4^{2-} > NO_3^- > Cl^- > F^-$.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Airborne particulate matter; Ion chromatography; Inorganic anions; Surfactant; Ultrasonic extraction

1. Introduction

The chemical investigation of airborne particulate matter is of great importance in air pollutions studies. A combination of organic and inorganic compounds is adsorbed on the surface of airborne particulate matter [1]. During the last decades an extensive database has been published providing the determination of metals associated with airborne particulate matter [2–5], while there is less information about the atmospheric concentrations of inorganic anions [6]. The development of industries, the population of cities and metropolitans, and increasing the number of private and public automobile, caused the emission of high levels of primary air pollutants such as SO_2, CO, and NO_x into the urban atmosphere. These primary air pollutants in urban atmosphere can be converted to different anions such as SO_4^{2-}, HCO_3^-, NO_2^-, NO_3^-, etc. [7]. The determination of concentrations of inorganic anions is important, because these anions take part into the formation of acid rains [8].

There are several methods reported in the literature for determination of inorganic anions, include, spectrophotometry [9], ion selective electrode analysis [10], flow injection analysis [11], and capillary electrophoresis [12]. These methods almost are not able to determine the atmospheric concentration of anions simultaneously. Ion chromatography (IC) is known as an effective analytical method with higher sensitivity and lower detection limit for simultaneous determination of anions [13].

In this work, the capability of ion chromatography for separation and determination of inorganic anions such as F^-, Cl^-, NO_3^- and SO_4^{2-} associated with airborne particulate matter has been investigated. The efficiency of ultrasonic extraction method for extraction of inorganic anions from air particulate by using surfactant was also investigated.

2. Experimental

2.1. Collection of samples

Airborne particulate matter from the atmosphere of the city of Isfahan was collected on quartz fiber filter (20 cm × 25 cm) using a high volume air sampler (Greasby,

☆ Presented at the 17th International Ion Chromatography Symposium, Trier, Germany, 20–23 September 2004.

* Corresponding author. Tel.: +98 3116631855; fax: +98 3116689732.
E-mail address: smtalebi@yahoo.com (S.M. Talebi).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.07.118

PS2, USA). Samples were collected from five different stations at a height of 1.5 m above the ground level during the period of September 2003 to December 2003. Sampling flow rate and sampling period were 1 m^3 min^{-1} and 12 h, respectively. Each week a sample was collected from each station.

2.2. Chemicals and reagents

All chemicals used in this work were analytical grade or better.

N-Cetyl-*N*,*N*,*N*-triethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), potassium nitrate, potassium sulfate, potassium chloride, sodium fluoride, sodium hydrogen carbonate and sodium carbonate, were obtained from Merck (Darmstadt, Germany).

Standard sample of urban air particulate matter, SRM-1648 was purchased from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA).

Anion standard solutions were prepared by weighing and dissolving the appropriate amounts of each anion salt in deionized distilled water in order to prepare 1000 μg/l stock standard solution.

The working range standard solutions were prepared from the1000 μg/l stock standard solutions.

2.3. Instrumentation

A suppressed ion chromatograph (Metrohm Compact IC model 761, Switzerland) was used for the separation and determination of anions. The system was equipped with a conductometric detector. Introduction of the sample into the system was performed by a 25 μl injection loop. The analytical column was a 150 mm × 3.0 mm I.D., Metrosep Anion Dual 1 6.1006.020 (Metrohm). A Wifug centrifuge (Germany) with 3000 rpm (1920 × *g*) was used for separation of extracts. Ultrasonic extractions were carried out on a Bandelin Electronic (Germany) ultrasonic bath with frequency of 35 kHz.

2.4. Chromatographic conditions

The eluent was composed of 2.4 mM $NaHCO_3$ and 2.5 mM Na_2CO_3. The eluent flow rate was 0.75 ml min^{-1}. The column pressure and temperature were set up at 6.8 MPa and 20 °C, respectively. The suppressor was automatically regenerated by 20 mM H_2SO_4. The instrument was equilibrated for 30 min prior to use. The instrument was calibrated with standard solutions after minimizing the baseline drift. Blank solutions (deionized distilled water and the solutions of 2.5 mM of SDS and CTAB) were tested for anionic impurities before analysis.

2.5. Extraction procedure

For extraction of inorganic anions from SRM-1648 urban particulate matter, 10 mg portions of the standard sample were introduced into the centrifuge tubes. A 10 ml deionized distilled water, 2.5 mM SDS and 2.5 mM CTAB were added into the tubes, respectively. The tubes were put in an ultrasonic bath with frequency of 35 kHz for 25 min. The extracts were then separated from the solid phase by centrifuging at 3000 rpm (1920 × *g*) for 20 min. The supernatant phases were decanted into clean tubes and used for IC determination.

For extraction of inorganic anions from airborne particulate matter collected from the atmosphere of the city of Isfahan, circles with diameter of 67 mm were punched out from the exposed filters and transferred into the corresponding extraction tubes. A 20 ml 2.5 mM SDS was added into the tubes. The other steps of extraction were exactly the same as that earlier described for the SRM-1648.

3. Results and discussion

The solubility of F^-, Cl^-, $NO_3{}^-$ and $SO_4{}^{2-}$ compounds in water indicates that these anions can often easily be removed from solid matrices by aqueous extraction. The sample matrix and the nature of the cationic concomitant can affect on releasing efficiency of anions. The chemical composition of the solvent which is used for extraction has also appreciable effect on the extraction efficiency of anions. Therefore, water combined with a miscible solvent such as methanol and more dilute salt solutions is used for extraction of inorganic anions [13]. Ideally, when conductometric detection is used for determination of anions by ion chromatography, carrier solution should have no inorganic materials such as, strong acids, bases and soluble salts. From this point of view, many of the traditional methods used for extraction or digestion of samples are not compatible with IC method [14]. The present work, describes the effects of different variables on the extraction efficiency of inorganic anions.

3.1. Effect of surfactant on extraction of anions

Surfactants are made up of a water soluble (hydrophilic) and a water insoluble (hydrophobic) components. The hydrophilic head helps solubilization of polar species and the hydrophobic head dissolves organic species [15]. It seems that using a surfactant in extraction of anions from airborne particulate matter could increase the yield of extraction. In this work, the effect of a cationic surfactant (CTAB) and an anionic surfactant (SDS) on extraction of inorganic anions from airborne particulate matter were investigated. Fig. 1 shows the chromatogram of the inorganic anions in SRM-1648 urban particulate matter extracted with water. The results obtained from this investigation showed that the recovery of extraction is considerably increased in the presence of surfactants. The extraction efficiency of anions from airborne particulate matter with water and with water containing surfactant was investigated. The results of the latter investigations are shown in Fig. 2. It is obvious that using of surfactant has increased the efficiency of extraction. The

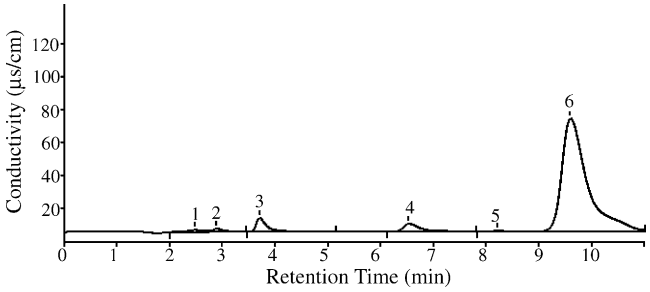

Fig. 1. Chromatogram of inorganic anions in SRM 1648 urban particulate matter. Extracted with water: (1) fluoride (0.43 mg/l), (3) chloride (4.07 mg/l), (4) nitrate (11.12 mg/l), and (6) sulfate (154.88 mg/l).

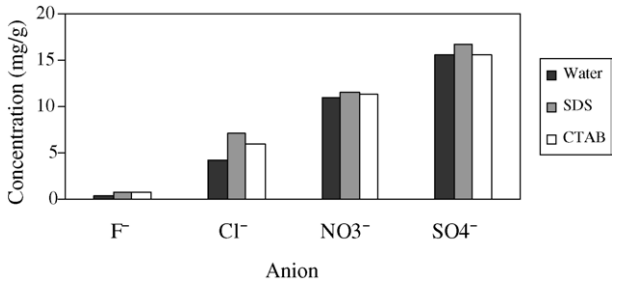

Fig. 2. Effect of 2.5 mM SDS and 2.5 mM CTAB on extraction of inorganic anions from SRM 1648 in comparison with water. Extraction time: 30 min, ultrasonic irradiation: 35 kHz, column: Metrosep Anion Dual 1 6.1006.020, column temperature: 20 °C, eluent: 2.4 mM $NaHCO_3$ and 2.5 mM Na_2CO_3, eluent flow rate: 0.75 ml min^{-1}, injection volume: 25 μl.

inorganic anions were extracted from SRM 1648 urban particulate matter with water, with a solution of 2.5 mM SDS and finally, with a solution of 2.5 mM CTAB using ultrasonic extraction. The concentrations of the inorganic anions were detected by ion chromatography. The results obtained from four replicates are summarized in Table 1. The comparison of the results obtained from the different extraction methods showed that surfactants effectively cause easier releasing of anions from matrix of airborne particulate matter especially in the cases of F^-, and Cl^-.

3.2. Effect of surfactant concentration on extraction

The effects of SDS and CTAB concentrations on the efficiency of ultrasonic extraction of F^-, Cl^-, NO_3^- and SO_4^{2-} from standard reference materials of urban particulate matter SRM-1648 were also investigated. The results are shown in Fig. 3 and indicate that efficiency of extraction of anions is increased by increasing the concentration of SDS and

Table 1
The comparison of concentrations of extracted anions from the 1648-SRM urban particulate matter (mg/g) by water, 2.5 mM SDS and 2.5 mM CTAB

Anion	Water	SDS	CTAB
Fluoride	0.42 ± 0.04	0.69 ± 0.13	0.74 ± 0.07
Chloride	4.09 ± 0.23	7.04 ± 0.31	5.89 ± 0.42
Nitrate	11.19 ± 0.19	11.68 ± 0.23	11.30 ± 0.82
Sulfate	154.40 ± 2.14	163.02 ± 4.99	153.67 ± 5.86

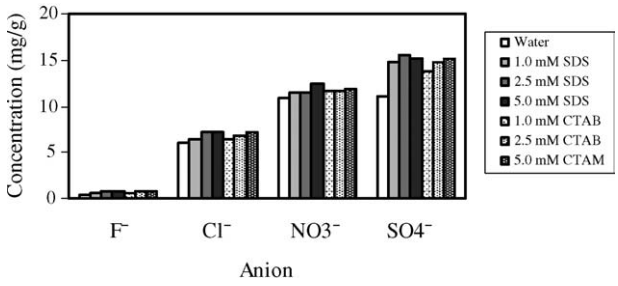

Fig. 3. The effect of surfactant concentration (SDS and CTAB) on ultrasonic extraction of inorganic anions from SRM 1648 in comparison with water. Extraction time: 30 min, ultrasonic irradiation: 35 KHz, column: Metrosep Anion Dual 1 6.1006.020, column temperature: 20 °C, eluent: 2.4 mM $NaHCO_3$ and 2.5 mM Na_2CO_3, eluent flow rate: 0.75 ml min^{-1}, injection volume: 25 μl.

CTAB. It should be noted that the rate of increasing of extract efficiency decreases at 5.0 mM concentration of surfactants. Considering these results, the optimum concentration of surfactants for ultrasonic extraction of inorganic anions from airborne particulate matter is 2.5 mM.

3.3. Effect of extraction time

The effect of extraction time on releasing of inorganic anions from airborne particulate matter was also investigated. Four series of samples were sonicated at times of 10, 20, 25 and 30 min and the concentrations of extracted anions were determined by IC. The results obtained from this investigation showed that the extraction efficiency is time dependent. Fig. 4 shows the relationship between the time of extraction and the concentration of anions released.

3.4. Determination of concentrations of inorganic anions in the airborne particulate matter collected from the atmosphere of the city of Isfahan

After optimizing of the extraction conditions, the concentrations of inorganic anions in airborne particulate mater of the city of Isfahan were determined by ion chromatography after ultrasonic extraction by 2.5 mM SDS. Fig. 5 shows the

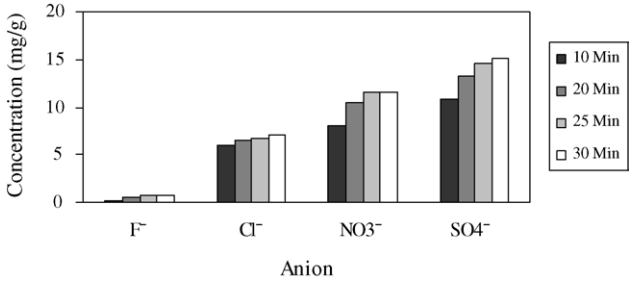

Fig. 4. Effect of time on extraction of inorganic anions from SRM 1648 by 2.5 mM SDS. Ultrasonic irradiation: 35 kHz, column: Metrosep Anion Dual 1 6.1006.020, column temperature: 20 °C, eluent: 2.4 mM $NaHCO_3$ and 2.5 mM Na_2CO_3, eluent flow rate: 0.75 ml min^{-1}, injection volume: 25 μl.

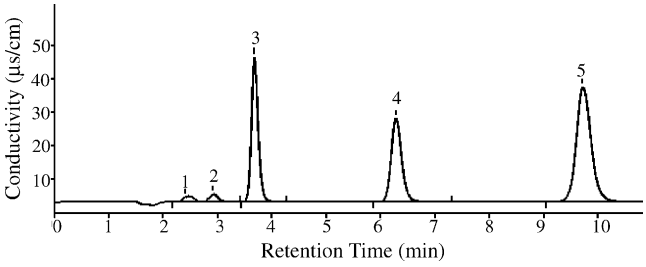

Fig. 5. Chromatogram of inorganic anions in urban particulate matter of the city of Isfahan extracted by 2.5 mM SDS: (1) fluoride (0.44 mg/l), (3) chloride (10.42 mg/l), (4) nitrate (36.73 mg/l), and (5) sulfate (34.75 mg/l).

Table 2
Mean atmospheric concentration of anions in the airborne particulate matter of the city of Isfahan ($\mu g/m^3$) in five different stations

Station	Fluoride	Chloride	Nitrate	Sulfate
1	0.26 ± 0.04	3.01 ± 0.31	4.58 ± 0.51	12.24 ± 1.12
2	0.40 ± 0.03	2.50 ± 0.36	6.36 ± 0.46	10.23 ± 1.08
3	0.34 ± 0.02	2.53 ± 0.35	7.01 ± 0.45	10.52 ± 1.23
4	0.12 ± 0.03	3.18 ± 0.33	10.62 ± 0.42	10.61 ± 1.20
5	0.05 ± 0.01	1.78 ± 0.18	4.08 ± 0.24	7.15 ± 0.40

Table 3
Mean concentration ($\mu g/m^3$) and percentage of inorganic anions in the atmosphere of the city of Isfahan (80 samples were collected from five different stations during the period of September 2003 to December 2003)

Anion	Fluoride	Chloride	Nitrate	Sulfate	Total
Mean	0.23 ± 0.15	2.61 ± 0.54	6.53 ± 2.58	10.14 ± 1.53	19.51
Percent	1.21	13.33	33.47	51.99	100

chromatogram of inorganic anions in the urban particulate matter. The atmospheric concentrations of inorganic anions were calculated by comparison with the standard curve. Table 2 summarizes the atmospheric mean concentrations of inorganic anions collected from five different sampling stations during the period of September 2003 to December 2003.

The average of total soluble anions in the airborne particulate matter of the city of Isfahan was 19.51 ($\mu g/m^3$) (Table 3). Among the inorganic anions, sulfate contributed maximum to the soluble anions mass (51.99%) followed by nitrate (33.47%), chloride (13.33%) and fluoride (1.21%). Therefore, the anionic balance of airborne particulate matter samples showed a trend of $SO_4^{2-} > NO_3^- > Cl^- > F^-$ in the atmosphere of the city of Isfahan.

An evidence for high concentration levels of sulfate and nitrate could be the oxidation of SO_2 and NO_x at the surface of airborne particulate matter. Temperature, relative humidity and atmospheric chemical composition may also affect these conversions.

Another source of sulfate is the dusts that transported from the deserts around of the city by wind. Nitrate can be originated from soils, particles emitted from the industrial plants and the nitric acid production factory located at the west of the city.

Chloride may be originated from transporting of dusts from desert, and of course from the industrial activities around the city by wind.

Fluoride may be contributed by emissions from industrial activities like metallurgical and chemical plants which are located very close to the city of Isfahan.

4. Conclusion

The extraction and analysis of anions in standard reference material SRM-1648 and different samples collected from the atmosphere of the city of Isfahan, showed that relatives high concentration of inorganic anions are associated with urban particulate matter. Ultrasonic extraction with water containing surfactants is a rapid and sensitive method for effective extraction of inorganic anions from airborne particulate matter. Ion chromatography is a sensitive and powerful technique for simultaneous determination of inorganic anions in air pollution studies, where a large number of samples should be analyzed in a short period of time.

References

[1] A. Clouter, D. Brown, D. Hohr, P. Borm, K. Donaldson, Toxicol. Sci. 63 (1991) 90.
[2] P. Bruno, M. Caselli, G. de Gennaro, P. Ielpo, A. Traini, J. Chromatogr. A 888 (2000) 145.
[3] S.M. Talebi, Environ. Res. 92 (2003) 54.
[4] K.X. Yang, K. Swami, L. Husain, Spectrochim. Acta B 57 (2002) 73.
[5] J. Hrsak, A. Sisoric, A. Skrbec, K. Sega, Atmos. Environ. 35 (2001) 3543.
[6] M. Khalifa, M. Hafez, Talanta 47 (1998) 547.
[7] A. Rahmalan, M. Zahari Abdullah, M. Marsin Sanagi, M. Rashid, J. Chromatogr. A 739 (1996) 233.
[8] Q. Xu, W. Zhang, C. Xu, L. Jin, Analyst 125 (2000) 1065.
[9] J.C. Martinez, J.V.M. Garcia, Analyst 123 (1998) 429.
[10] S. Matysik, F.M. Matysik, Electroanalysis 10 (1998) 181.
[11] L.M.B.C. Alvares-Ribeiro, A.A.S.C. Machado, Analyst 123 (1998) 653.
[12] P. Kuban, B. Karlberg, Anal. Chem. 70 (1998) 360.
[13] P.E. Jakson, in: R.A. Meyers (Ed.), Encyclopedia of Analytical Chemistry, Wiley, Chichester, 2000, p. 2782.
[14] S. Mou, J. Chromatogr. 546 (1991) 317.
[15] K.L. Mittal, B. Lindman, Surfactants in Solution, Plenum Press, New York, 1984.