

Application of ion chromatography to the determination of water-soluble inorganic and organic ions in atmospheric aerosols

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Abstract: A simple, sensitive and convenient ion chromatography(IC) method was established for the simultaneous determination of twelve water-soluble inorganic anions(F^- , Cl^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , PO_4^{3-}), and fifteen water-soluble organic ions(formate, acetate, MSA, oxalate, malonate, succinate, phthalates, etc.) in atmospheric aerosols. The linear concentrations ranged from 0.005 $\mu\text{g}/\text{m}^3$ to 500 $\mu\text{g}/\text{m}^3$ ($r = 0.999—0.9999$). The relative standard deviation(RSD) were 0.43%—2.00% and the detection limits were from 2.7 ng/m^3 to 88 ng/m^3 . The proposed method was successfully applied to the simultaneous determination of those inorganic ions and organic ions in $\text{PM}_{2.5}$ of Beijing.

Keywords: ion chromatography; water-soluble ions; aerosols; Beijing

Introduction

Atmospheric aerosols might affect the earth's radiation balance directly by backscattering and absorbing solar radiation, and indirectly by increasing cloud condensation nucleus(CCN) concentrations, which in turn increased cloud droplet concentrations and thus the cloud albedo (IPCC, 2001). The chemical composition of the aerosol particles is very important for better understanding their human health and climate effects. Atmospheric aerosol is composed of diverse chemical species. It contains rather a few inorganic species and a very complex mixture of organic compounds (Saxena, 1996). Until recently, the knowledges of inorganic constituents such as sulfate, nitrate, ammonium, sea-salt and element carbon of aerosols were relatively well established (Chow, 1999; He, 2001; Wang, 2002). But the information on the organic fraction was far less complete than the knowledge on the inorganic constituents because of its complexity and low atmospheric concentration of the individual organic compounds. Although hundreds of non-polar and semi-polar organic compounds have been identified by gas chromatography-mass spectrometry, total mass of all the individual compounds together accounted for only 10%—20% of the total organic carbon(Rogge, 1993). In contrast, other studies reported that water-soluble organic compounds (WSOC) account for a significant fraction(28%—77%) of the total organic compounds depending on the sampling sites (Sempere, 1994; Zappoli, 1999; Yao, 2002). In the past few years, evidence started to emerge, that is, WSOC may also have an effect on the hygroscopic behavior of atmospheric aerosol and play an important role in cloud condensation processes (Saxena, 1995; Hansson, 1998; Facchini, 1999). There was now a growing consensus that information on the inorganic and organic composition of aerosols must be integrated in order to understand and describe the physical and chemical process occurring in a multiphase atmospheric

system(Dick, 2000; Peng, 2001).

To date, most studies on water-soluble inorganic ions were performed by ion chromatography(IC) techniques, while water-soluble organic fraction of atmospheric aerosols were performed by use of GC-MS with relatively complex pre-treatment of esterification and organic solvent extraction (Grosjean, 1978; Rogge, 1993; Kawamura, 1999), which was incomplete for analysis of the high polar organics (Saxena, 1995). This paper conducted a study of simultaneous determination of water-soluble inorganic and organic ions of aerosols using ion chromatography technology, which would provide a simple, sensitive and convenient way of analysis of both water-soluble inorganic and organic species of aerosol. Based on this, the chemical compositions of $\text{PM}_{2.5}$ water-soluble ions in Beijing were characterized.

1 Experimental

1.1 Apparatus

A Dionex-600 IC system with ED50 detector and GP50 eluent gradient pump was used in this study. The anionic species was analyzed with a 4 × 250 mm separator column Ion Pac AS11 and a 4 mm anion self-regenerating suppressor ASRS-ULTRA. The column was protected upstream by a 4 × 50 mm guard column Ion Pac AG11. A 9 × 24 mm anion trap column ATC-32 were fixed between the gradient pump and the injection valve to strips trace anionic contaminants out of the eluent and prevents them from reaching the guard and analytical column. The cationic species were analyzed with a 4 × 250 mm separator column Ion Pac CS12A and a 4 mm cation self-regenerating suppressor CSRS-ULTRA. The column was protected upstream by a 4 × 50 mm guard column IonPac CG12A.

A $\text{PM}_{2.5}$ sampler (made in China) was used for the aerosol sampling in Beijing. The sampling flow rate was 77 L/min and the sampling period was 24 h.

1.2 Reagents and materials

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The 0.5–30 mmol/L gradient eluent of NaOH and 20 mmol/L isocratic eluent of MSA were used for the anion and cation analysis, respectively. All reagents and standard materials were of analytical grade from Sigma-Aldrich Inc., Germany. All solutions were prepared with water purified with a Milli-Q apparatus from waters.

2 Results and discussion

2.1 Water extraction efficiency

The aerosol filter sample was weighed before and after the sampling. And then, three-fourth of the filter was cut into pieces. In order to quantitatively determine the extraction efficiency of the filter samples by water, 5–7 samples were randomly selected and put into 20 ml test tubes individually. Then 10 ml of Milli-Q water was added into the tubes extracting in an ultrasonic bath for 20 min. The solution was filtered via a 0.45 μm pore size nylon filter and the filtrate was collected. Another 10 ml of fresh ultra-pure water was added into the tubes, extracting another 20 min and then filtered. The filtrate was collected. These procedures were repeated five times and the five filtrates were chemically analyzed individually. It was found that the ionic concentrations of the fourth and the fifth extraction filtrate of all samples were about the experimental blank levels. Some of the third extraction filtrate were a little beyond the blank levels, while those of the first and second extraction filtrate were far beyond the blank levels. One-time extraction efficiency and two-time accumulated extraction efficiency of the major water-soluble species are shown in Fig. 1. It indicated that most of the water-soluble species could be eluted from the filter samples via two-time extractions except calcium. The two-time accumulated extraction efficiencies were 98% for chlorate, 96% for nitrate, 97% for sulfate, 96% for oxalate, 98% for sodium, 96% for ammonium, 96% for potassium, 92% for magnesium, but 86% for calcium. Thus all the samples were extracted twice and the two filtrates were amalgamated for the chemical analysis.

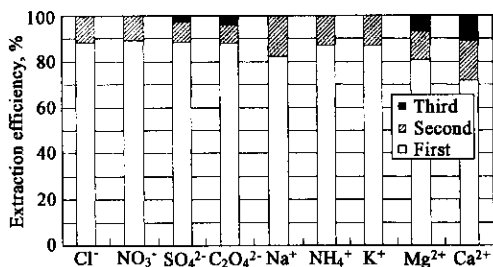


Fig.1 Extraction efficiency of the water-soluble ions

2.2 Analytical process

For the analysis of anions, 0.5–30 mmol/L gradient eluent of NaOH was used. The eluent concentration was originally set to be 0.5 mmol/L and remained 3 min, then was programmed increasing from 0.5 mmol/L to 5 mmol/L within 2 min, and then from 5 mmol/L to 30 mmol/L within 6 min, thereafter decrease from 30 mmol/L to 0.5 mmol/L within 0.1 min and remained 3 min. The total run time was approximately 14 min. The flow rate was 1.5 ml/min and the injection volume was 20 μl . Identification of the species was performed by a comparison of IC retention times with those of authentic standards. Quantification was based on the peak

area of the species. Via these methods, seven inorganic anions (F^- , Cl^- , NO_2^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , PO_4^{3-}) and sixteen water-soluble organic ions (formate, acetate, MSA, oxalate, malonate, succinate, phthalates, etc.) were separated and identified in the same run (Fig. 2).

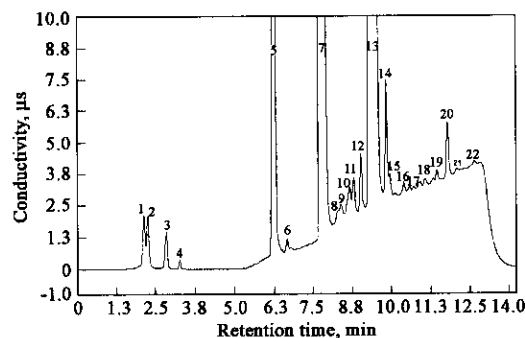


Fig.2 IC separation of the anions (1. fluoride; 2. acetate; 3. formate; 4. MSA; 5. chloride; 6. nitrite; 7. nitrate; 8. adipate; 9. glutarate; 10. succinate; 11. carbonate and malonate; 12. sulfite and suberate; 13. sulfate; 14. oxalate; 15. azelate; 16. sebacate; 17. undecanedioate; 18. dodecanedioate; 19. *o*-phthalate; 20. phosphate; 21. *p*-phthalate; 22. *m*-phthalate)

For the analysis of cations, 20 mmol/L isocratic eluent of MSA were used. The injection volume was 20 μl and the flow rate was 1.0 ml/min. The total run time was approximately 10 min. Five inorganic cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) were determined (Fig. 3).

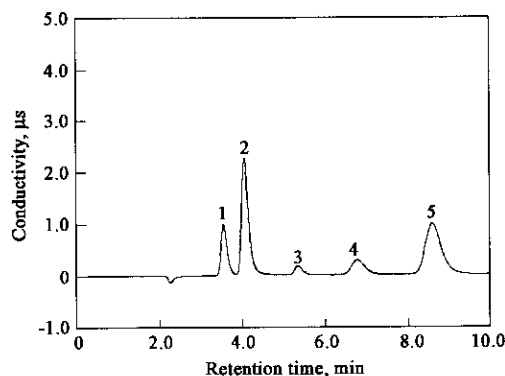


Fig.3 IC separation of the cations (1. Na^+ ; 2. NH_4^+ ; 3. K^+ ; 4. Mg^{2+} ; 5. Ca^{2+})

2.3 Calibration curves

Table 1 shows the parameters of the calibration curves of some major water-soluble ions. The retention times of the species are also listed in the table. The accuracy of the calibration curves could be evaluated by the correlation coefficient. It could be seen that the correlation coefficients of the major water-soluble ions were no less than 0.999 except that of ammonium ($r = 0.994$). The linear concentrations ranged from 0.005 $\mu\text{g}/\text{m}^3$ to 500 $\mu\text{g}/\text{m}^3$ for these inorganic and organic ions.

2.4 Detection limits and RSD

The detection limits at a signal-to-noise ratio of 2 were determined to be 88 ng/ml for chloride, 25 ng/ml for nitrate, 70 ng/ml for sulfate, 2.7 ng/ml for sodium, 4.5 ng/ml for ammonium, 5.3 ng/ml for potassium, 3.1 ng/ml for magnesium, 5.7 ng/ml for calcium, 34 ng/ml for oxalate, 50 ng/ml for succinate, 80 ng/ml for sebacate, and so on.

Table 1 The parameters of the calibration curves of the water-soluble ions

Peak name	Retention time, min	Calibration type	Points	Offset	Slope	Correlation coeff., %
F ⁻	2.65	Loff	4	-0.003	3.212	99.933
Cl ⁻	6.41	Loff	4	-0.003	1.698	99.961
NO ₃ ⁻	8.03	Loff	4	-0.007	0.956	99.962
SO ₄ ²⁻	9.28	Loff	4	-0.014	1.607	99.954
PO ₄ ³⁻	11.32	Loff	4	0.000	0.510	99.961
C ₂ O ₄ ²⁻	9.59	Loff	4	0.000	2.769	99.982
C ₄ H ₄ O ₆ ²⁻	8.66	Loff	4	0.001	1.351	99.954
C ₁₀ H ₁₆ O ₄ ²⁻	10.94	Loff	4	0.004	1.765	99.969
Na ⁺	3.75	Loff	5	0.018	0.279	99.975
NH ₄ ⁺	4.21	Loff	5	0.000	0.318	99.387
K ⁺	5.33	Loff	5	0.007	0.189	99.988
Mg ²⁺	6.84	Loff	5	0.007	0.541	99.992
Ca ²⁺	8.49	Loff	5	0.021	0.336	99.990

The relative standard deviations (RSD) of this method were determined to be 0.52% for chloride, 0.67% for nitrate, 1.32% for sulfate, 0.87% for sodium, 0.85% for ammonium, 0.43% for potassium, 0.55% for magnesium, 0.88% for calcium, 2.00% for oxalate, 1.02% for succinate, 0.92% for sebacate, and so on.

2.5 Application to PM_{2.5} in Beijing

The proposed method was applied to the simultaneous determination of the inorganic ions and organic ions in PM_{2.5} of Beijing. The measured concentrations of the water-soluble ions and their fractions in PM_{2.5} are listed in Table 2. The results showed that SO₄²⁻, NO₃⁻ and NH₄⁺ were the dominant ionic species of PM_{2.5} in Beijing, which were 8.56 μg/m³, 7.43 μg/m³ and 4.55 μg/m³ and accounted for 6.47%, 5.61% and 3.44% of the total PM_{2.5} mass, respectively. The sum of these three major ions accounted for about 15.5% of the total PM_{2.5} mass. The sum of other inorganic ions (F⁻, Cl⁻, NO₂⁻, SO₃²⁻, PO₄³⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺) accounted for about 6% of the total mass. Sixteen water-soluble organic ions (formate, acetate, MSA, oxalate, malonate, succinate, phthalates, etc.) exhibited a concentration range of 8–1060 ng/m³ and totally possessed about 1.6% of PM_{2.5} mass, among which oxalate was the most abundant, followed by acetate, formate, succinate, adipate and malonate.

Table 2 The concentrations and fractions of the water-soluble ions of PM_{2.5}

Species	Inorganics		Organics	
	Concentration, μg/m ³	Fraction, %	Species	Concentration, μg/m ³
PM _{2.5}	132.342		Formate	0.14
SO ₄ ²⁻	8.56	6.47	Acetate	0.14
NO ₃ ⁻	7.43	5.61	Oxalate	1.06
NH ₄ ⁺	4.55	3.44	Malonate	0.12
Cl ⁻	2.69	2.03	Succinate	0.27
K ⁺	2.23	1.68	Glutarate	0.08
Ca ²⁺	1.76	1.33	Adipate	0.14
Na ⁺	0.54	0.41	Suberate	0.03
Mg ²⁺	0.21	0.16	Azelate	0.09
F ⁻	0.18	0.14	Sebacate	0.02
NO ₂ ⁻	0.001	0.001	Undecanedioate	0.02
SO ₃ ²⁻	0.16	0.12	Dodecanedioate	0.02
PO ₄ ³⁻	0.08	0.06	<i>o</i> -phthalate	0.05
			<i>p</i> -phthalate	0.04
			<i>m</i> -phthalate	0.008
			MSA	0.05

3 Conclusions

A simple, sensitive and convenient ion chromatography (IC) method was established for the simultaneous determination of seven water-soluble inorganic ions and fifteen water-soluble organic ions in atmospheric aerosols. The linear concentrations ranged from 0.005 μg/m³ to 500 μg/m³ ($r = 0.999-0.9999$). The RSD were 0.43%–2.00% and the detection limits were from 2.7 ng/m³ to 88 ng/m³.

Sulfate, nitrate and ammonium were the dominant ionic species of PM_{2.5} in Beijing, which were 8.56 μg/m³, 7.43 μg/m³ and 4.55 μg/m³ and accounted for 6.47%, 5.61% and 3.44% of the total PM_{2.5} mass, respectively. Sixteen water-soluble organic ions exhibited a concentration range of 8–1060 ng/m³ and totally possessed about 1.6% of PM_{2.5} mass, among which oxalate was the most abundant, followed by acetate, formate, succinate, adipate and malonate.

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