Determination of Anions and Carboxylic Acids in Urban Fine Particles ($PM_{2.5}$)

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Key Words

Inorganic Anions, Organic Acids, Urban Ambient Particles, Fine Particulate Matter ($PM_{2.5}$), Conductivity Detection, Environmental Analysis, Ion Chromatography (IC), Air Analysis

Goal

To develop an efficient IC method for the sensitive determination of inorganic anions and carboxylic acids (fluoride, acetate, formate, mesylate, chloride, nitrate, succinate, malonate, sulfate, and oxalate) in airborne $PM_{2.5}$

Introduction

Identifying the composition of ambient $PM_{2.5}$ plays an important role in air quality management. The chemical composition of $PM_{2.5}$ includes a large number of mineral oxides, sulfate, nitrate, polycyclic aromatic hydrocarbons, organic acids, and organic chlorine that directly impact atmospheric quality and influence human health.[1–3] Although the simultaneous determination of water-soluble anions and carboxylic acids such as fluoride, acetate, formate, mesylate, chloride, nitrite, nitrate, succinate, malonate, sulfate, oxalate, and phosphate in $PM_{2.5}$ is difficult to accomplish by other analytical methods, it has already been demonstrated using IC.[4] Standard methods (e.g., U.S. Environmental Protection Agency [EPA] Method 26A and ASTM International's Standard Test Method ASTM D5085-02) can be used to determine chloride, nitrate, and sulfate in the air; however, limitations in the number of analytes and method sensitivity are inadequate when compared to newer technologies and current knowledge of air contaminants.[5,6]

Equipment

- A Thermo Scientific™ Dionex™ ICS-5000⁺ Reagent-Free™ HPIC™ system, capable of supporting high-pressure IC, including:
  - – DP Dual Pump
  - – EG Eluent Generator
  - – DC Detector/Chromatography Compartment
- Thermo Scientific Dionex AS-AP Autosampler
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082540)
- Thermo Scientific Dionex EGC 500 Potassium Hydroxide (KOH) Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific Dionex CRD 200 Carbonate Removal Device (optional)
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2

Consumables

- Thermo Scientific™ Target2™ Nylon Syringe Filters, 0.45 µm, 30 mm (P/N F2500-1)

Reagents and Standards

- Deionized (DI) water, 18.2 MΩ-cm resistivity
- Sodium Fluoride (Fisher Scientific P/N S299-100)
- Sodium Acetate Trihydrate (Fisher Scientific P/N S608-500)
- Sodium Formate (Fisher Scientific P/N S648-500)
- Methanesulfonic Acid (Fisher Scientific P/N AC43297-0010)
- Sodium Chloride (Fisher Scientific P/N S671-500)
- Sodium Nitrate (Fisher Scientific P/N S343-500)
- Sodium Nitrite (Fisher Scientific P/N S347-250)
- Sodium Succinate Hexahydrate (Fisher Scientific P/N S413-500)
- Malonic Acid (Fisher Scientific P/N A170-100)
- Sodium Sulfate (Fisher Scientific P/N S429-500)
- Sodium Phosphate Tribasic Dodecahydrate (Fisher Scientific P/N S377-500)
- Sodium Oxalate (Fisher Scientific P/N S487-500)

Chromatographic Conditions

Column:	Thermo Scientific™ Dionex™ IonPac™ AS11-HC Guard, 4 × 50 mm (P/N 052962) Dionex IonPac AS11-HC Analytical, 4 × 250 mm (P/N 052960)
Eluent:	KOH
Eluent Source:	Dionex EGC 500 KOH Eluent Generator Cartridge
Gradient:	0–5 min, 1 mM; 28 min, 15 mM; 32–36 min, 50 mM; 36.1–46 min, 1 mM
Flow Rate:	1.5 mL/min
Injection Volume:	25 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 Anion Electrolytically Regenerated Suppressor, in recycle mode, 186 mA
System Backpressure:	2046 psi
Background Conductance:	0.3 µS

Preparation of Standard Solutions

Working Standard Solutions for Calibration

Stock standard solutions

To prepare stock standard solutions, weigh 100 mg of sodium fluoride, sodium acetate trihydrate, sodium formate, methanesulfonic acid, sodium chloride, sodium nitrate, sodium nitrite, sodium succinate hexahydrate, malonic acid, sodium sulfate, sodium phosphate tribasic dodecahydrate, and sodium oxalate into 12 separate volumetric flasks; then dilute each to 100 mL with DI water. The concentration of each stock standard solution will be 1000 mg/L.

Standard Mix for Method Development

For method development, prepare a mixed standard solution that contains the 12 analytes using different concentrations that will yield a similar peak height for each analyte. Complete the preparation by diluting the proper amounts of the stock standard solutions with DI water. The volume of each stock standard solution needed and the final concentration of each analyte in the standard mix are shown in Table 1.

Table 1. Preparation of the standard mix for method development.

Analyte	1000 mg/L Stock Std Solution Vol (mL)	DI Water Vol (mL)	Std Mix Final Vol (mL)	Final Concn of Each Analyte (mg/L)
Fluoride	0.50	79.75	100	5.0
Acetate	3.0			30
Formate	0.80			8.0
Mesylate	2.2			22
Chloride	0.75			7.5
Nitrite	1.2			12
Nitrate	2.5			25
Succinate	3.5			35
Malonate	3.0			30
Sulfate	0.60			6.0
Oxalate	1.0			10
Phosphate	1.2			12

Stock Standard Mix

To prepare a mixed stock standard solution that contains chloride and nitrate (both with a concentration of 24 mg/L) and the other 10 analytes (each with a concentration of 20 mg/L), dilute proper amounts of the stock standard solutions with DI water. The volume of each stock standard solution needed and the final concentration of each analyte in the stock standard mix are shown in Table 2. Use this stock standard mix for preparation of the working mixed standard solutions for calibration.

Table 2. Preparation of the stock standard mix.

Analyte	1000 mg/L Stock Std Solution Vol (mL)	DI Water Vol (mL)	Std Mix Final Vol (mL)	Final Concn of Each Analyte (mg/L)
Fluoride	2.0	75.2	100	20
Acetate	2.0			
Formate	2.0			
Mesylate	2.0			
Oxalate	2.0			
Nitrite	2.0			
Phosphate	2.0			
Succinate	2.0			
Malonate	2.0			
Sulfate	2.0			
Chloride	2.4			24
Nitrate	2.4			

Table 3. Preparation of working mixed standard solutions for calibration.

Analyte	Stock Std Mix Vol (mL)	DI Water Vol (mL)	Working Mixed Std Solution Final Vol (mL)	Final Concn of Each Analyte (mg/L)
Chloride, Nitrate	0.012	9.978	10	0.024
Other 10 Analytes*	0.010			0.02
Chloride, Nitrate	0.030	9.945		0.06
Other 10 Analytes*	0.025			0.05
Chloride, Nitrate	0.06	9.89		0.12
Other 10 Analytes*	0.05			0.10
Chloride, Nitrate	0.12	9.78		0.24
Other 10 Analytes*	0.10			0.20
Chloride, Nitrate	0.30	9.45		0.60
Other 10 Analytes*	0.25			0.50
Chloride, Nitrate	0.60	8.9		1.2
Other 10 Analytes*	0.50			1.0
Chloride, Nitrate	1.2	7.8		2.4
Other 10 Analytes*	1.0			2.0
Chloride, Nitrate	3.0	4.5		6.0
Other 10 Analytes*	2.5			5.5

*The 10 analytes are fluoride, acetate, formate, mesylate, oxalate, nitrite, phosphate, succinate, malonate, and sulfate.

Working Mixed Standard Solutions for Calibration

For calibration, prepare eight working mixed standard solutions with different concentrations by diluting proper amounts of the stock standard mix with DI water. The volume of each stock standard mix needed and the final concentration of each analyte in the working mixed standard solutions for calibration are shown in Table 3.

Air Sample Extraction

The airborne PM$_{2.5}$ sample was supplied by the Department of Environmental Science and Engineering, Fudan University, Shanghai, People's Republic of China. The procedures for extraction were based on those specified in publications noted in the Reference section of this work.[7–9]

Using an air sampler, collect PM$_{2.5}$ in the air for 48 h on a quartz membrane at a flow rate of 77.49 L/min.* Extract the ions of interest using 10 mL of DI water in an ultrasonic bath for 40 min, then cool to room temperature. Filter the extract through a 0.45 µm Target2 nylon syringe filter prior to analysis.

*In this study, a URG-3000K Versatile Air Pollutant Sampler (URG Corporation, Chapel Hill, NC, USA) PM$_{2.5}$ located at the top of Building No. 4, Fudan University, was used for air sampling.

Prepare the spiked sample using 10 mL of the stock standard mix solution that contains appropriate amounts of analytes (instead of the 10 mL of DI water) to extract the analytes from the quartz membrane. Other procedures are the same as described above. The spiked concentrations are included in Table 4.

Table 4. Sample analysis results.

Analyte	Detected (mg/L)	Spiked Sample		
		Added (mg/L)	Found (mg/L)	Recovery (%)
Fluoride	0.23	0.23	0.24	103
Acetate	0.22	0.15	0.15	101
Formate	0.14	0.086	0.071	83
Mesylate	0.10	0.10	0.12	121
Chloride	2.4	2.0	1.9	95
Nitrate	44	44	46	104
Succinate	0.15	0.15	0.16	107
Malonate	0.11	0.10	0.083	80
Sulfate	30	28	27	96
Oxalate	1.1	1.0	1.0	100

Results and Discussion

Column Selection

The Dionex IonPac AS11-HC column—designed to resolve a large number of inorganic and organic acid anions in a single run—has been successfully used for the determination of organic acids and inorganic anions in cranberry and bilberry extracts, fruit juices, fermentation broths, and drugs.[10–13] Therefore, the Dionex IonPac AS11-HC column was selected for this analysis of $PM_{2.5}$ for organic acids and inorganic anions.

Figure 1 shows that fluoride, acetate, formate, mesylate, chloride, nitrite, nitrate, succinate, malonate, sulfate, oxalate, and phosphate are baseline separated, all with peak resolutions exceeding 2.0 except for malonate, Peak 9. The small peak observed before malonate is undoubtedly carbonate, as that is its known elution position and it was expected and found in the injection blank. Peak resolution between carbonate and malonate is 1.2 and, therefore, does not impact the quantification of malonate. If desired, the Dionex CRD 200 Carbonate Removal Device can be used to remove carbon dioxide from the suppressed eluent.

Reproducibility, Linearity, and Detection Limits

Method precision was estimated by making seven consecutive 25 µL injections of a calibration standard with concentrations of 1.2 mg/L for chloride and nitrate and 1.0 mg/L for the other 10 analytes. Retention time reproducibilities (RSDs) were all ≤0.03 and peak area reproducibilities RSDs were all ≤0.87, demonstrating good short-term precision for this method.

Calibration linearity of the analytes was investigated by making three consecutive 25 µL injections of the working mixed standard solutions prepared at eight different concentrations (i.e., 24 total injections). Linearity was observed when plotting concentration versus peak area. Detailed calibration data calculated by Chromeleon CDS software are shown in Table 5.

Five consecutive 25 µL injections of a calibration standard with concentrations of 6.0 µg/L for chloride and nitrate and 5.0 µg/L for the other 10 analytes were used to estimate the method detection limit (MDL) using a signal-to-noise ratio = 3. The calculated MDLs are listed in Table 5.

Sample Analysis

Figure 2 shows the chromatograms of an air sample and Table 4 shows the analysis results. Ten ions—fluoride, acetate, formate, mesylate, chloride, nitrate, succinate, malonate, sulfate, and oxalate—were found. The results show that chloride, nitrate, and sulfate have the highest concentrations in this sample, and the detected mesylate suggests the sample has been impacted by the ocean. Method accuracy was investigated by determining the recoveries in the spiked air sample. The recoveries ranged from 80 to 121%, demonstrating that this IC method provides good selectivity and is suitable for the determination of anions and carboxylic acids in $PM_{2.5}$.

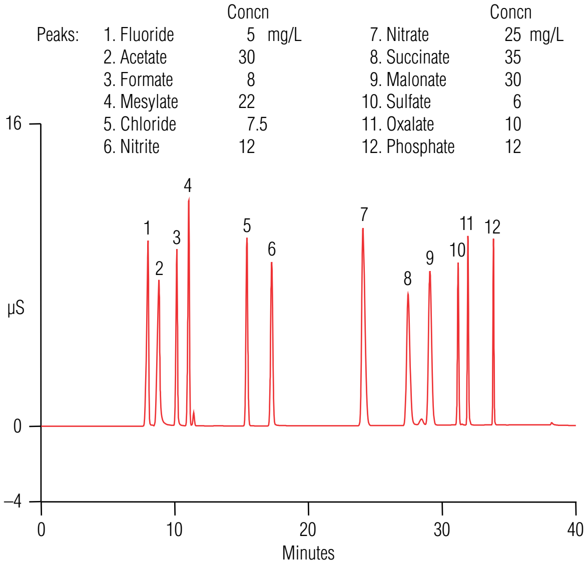

Figure 1. Separation of a standard anion mix.

Table 5. Calibration data and MDLs.

Anion	Regression Equation	r^2	Range (mg/L)	MDL (µg/L)
Fluoride	A = 0.3498c – 0.0054	1	0.02–5	6
Acetate	A = 0.0794c + 0.0034	0.9985	0.02–5	12.5
Formate	A = 0.1678c + 0.0024	0.9999	0.02–5	7
Mesylate	A = 0.072c – 0.0038	0.9994	0.02–5	18
Chloride	A = 0.206c – 0.0015	0.9999	0.024–6	4.5
Nitrite	A = 0.1398c – 0.0049	0.9999	0.02–5	14
Nitrate	A = 0.1197c – 0.0045	0.9995	0.024–6	13
Succinate	A = 0.076c + 0.0028	0.9987	0.02–5	17
Malonate	A = 0.089c + 0.0039	0.9983	0.02–5	18.5
Sulfate	A = 0.1554c + 0.0313	0.9999	0.02–5	10.5
Oxalate	A = 0.1072c – 0.0013	1	0.02–5	11
Phosphate	A = 0.0685c – 0.0012	0.9999	0.02–5	12

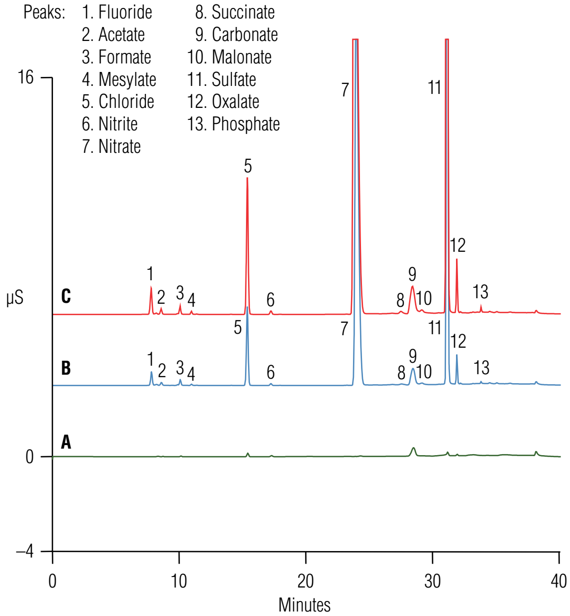

Figure 2. (A) A blank, (B) an air sample, and (C) the same sample spiked with a mixed anion standard solution.

Conclusion

This work describes an IC method with suppressed conductivity detection for sensitive determination of inorganic anions and carboxylic acids in urban $PM_{2.5}$. The determination is performed using a Dionex ICS-5000$^+$ Reagent-Free HPIC system controlled by Chromeleon CDS software and equipped with a Dionex IonPac AS11-HC column. This study demonstrates that this new method can determine more analytes relevant to air contamination than either of the standard methods currently in use (i.e., EPA Method 26A and ASTM D5085-02).

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