Analysis of trace elements in air particulate matters by non-suppressed ion chromatography

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Abstract—The application of non-suppressed ion chromatography for monitoring of trace elements in air particulate matter was studied in the present investigation. The results indicate that the use of microwave acid digestion method is superior in comparison with the conventional thermal acid digestion method as it leads to higher recovery, better reproducibility, lower volatility loss, better protection against environmental contamination and much less digestion time (5 minutes vs. 24 hours). The use of eluent as extractant is shown to reduce the water dip problem in the chromatogram. The addition of chelating agent in the eluent coupled with UV detection is shown to provide satisfactory chromatographic separation and good sensitivity for the analysis of transition metals present in the air particulate matter. Using the U.S. National Bureau of Standards Reference Material 1648 Urban Particulate Matter as standard for checking, the analytical procedure is shown to give good recovery and reproducibility for the detection of the following cations and anions in air particulate matter: Fe, Cu, Mn, Pb, Zn, Mg, Na, HN_4^+, Cl^-, NO_3^- and SO_4^{2-}. Field test was also performed to check the applicability of the method and the results obtained were discussed in the present paper.

Keywords: non-suppressed ion chromatography; air particulate matter; trace metals analysis; anions analysis; microwave digestion.

INTRODUCTION

Due to the recent concern about the health implication of respirable particulate matter (Batterman, 1987; Brown, 1988; Schroeder, 1987) and the need to obtain the chemical elemental profile of air particulate matter for source apportionment studies, a large volume of analysis of trace elements in air particulate matter is required for monitoring purpose (Gordon, 1980; Hopke, 1976; Thurston, 1985). As heavy metals and chemical compounds of environmental interest are often present in trace amount in a rather complicated matrix (Friedlander, 1973;

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Kowalczyk, 1978), separation is needed before analysis. The recent advance in the ion chromatography (I.C.) provides an important tool for such analysis. I.C. is a liquid chromatographic technique that uses ion-exchange resins combined with conductivity detection for separation of anions and cations (Fritz, 1982; Pohl, 1980; Small, 1975; Smith, 1983). It is now possible to separate and determine low concentrations of cations (Fritz, 1980) and anions (Gjerde, 1979) up to 10 different ions in a single chromatographic run within a few minutes. Thus, although modern I.C. is only 14 years old, it is now being used routinely in many scientific and environmental laboratories as a result of the short analysis time and the capability of simultaneous determination of several elements after separation.

The non-suppressed ion chromatography (Matsushita, 1984) started as an alternative technique for ion analysis in competition with the expensive dual column I.C. technique which is currently under patent protection. The recent rapid pace of development of the non-suppressed I.C. technique indicates the improvement of the analytical methodology and illustrates the attraction of this technique for environmental monitoring, as it is cheap and conventional HPLC equipment can be used for the analysis. Thus, one set of equipment can be used for both organic and inorganic analysis.

The analytical problem facing the application of non-suppressed ion chromatography for monitoring trace elements in air particulate matter is the need for the dissolution of the air particles collected and the maintenance of a constant pH of the sample solution before injection into the I.C. column so as to reduce the disturbance of the ionic environment of the eluent. Another problem is the sensitivity of the conductivity detection system, especially for detecting transition metals having similar conductivity as compared to the eluent.

The conventional method of dissolution of urban particles prior to trace analysis is by thermal acid digestion. This method is very slow and time consuming. The recent development of microwave oven-based wet digestion technique (Barrett, 1978; Gilman, 1988) provides a promising alternative method for the dissolution of the air particulate matter. In addition to being quicker, it is less prone to suffer environmental contamination and less acid will be used during digestion inside enclosed vessel under pressure. This is particularly desirable for sample treatment for I.C., as the ionic strength of the sample obtained after digestion would be lower. In the present investigation, the applicability of the microwave digestion technique will be studied and compared with the conventional thermal technique.

As the use of complexing eluent coupled with UV detection was shown to enhance the sensitivity of the detection method (Matsushita, 1984), the application of this technique for analyzing transition metals in air particulate matter was also investigated in the present study. The recovery of Fe, Cu, Mn, Pb, Zn, Mg, Na, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} from the NBS standard urban particulate matter was determined and the analytical procedure developed was

verified in a field study at a selected site near the university.

EXPERIMENTAL

Apparatus and equipment

The chromatographic system comprised a self-constructed guard column, a high pressure pump (Rainin Rabbit HP), a pulse damper (SSI LO-Pulse), Rheodyne 7125 injection valve and a low capacity polystyrene-divinyl benzene copolymer anion exchange column (Hamilton PRP-X100). Two detectors were being used, with conductivity detection (ConductoMonitor III, Milton Roy) for simple anion and cations and UV detection (SpectroMonitor 3100, Milton Roy) for transition metals. The output from the detectors was fed simultaneously to a chart recorder (Hitachi, QPD54) and an integrator (HP3393A).

For microwave digestion of particulate samples, teflon vessels were used as the container, which were put inside a partially evacuated 2 litres plastic desiccator before introduced to the microwave oven (National NN-6507 model) with a timer, variable power setting (70–700 Watts) and a turn-table with inside cavity of dimensions 26cm × 35cm × 32cm.

Chemicals and materials

All chemicals used were analytical reagent grade (BDH) unless otherwise stated. All reagents were dried under vacuum before use. Doubly distilled water was used for making up the standard solution immediately before use. The standard sample (NBS standard reference material 1648 urban particulate matter) for recovery study was received from NBS and used directly without further treatment.

Analytical procedure

For sampling air particulate matter, air was drawn through 0.8μm millipore filter with air pumps at the entrance of the university with fairly heavy traffic. The particulate matter collected was determined in pre-conditioned filter papers gravimetrically using the Mettler AE163 electronic semi-micro analytical balance.

For the determination of anions and alkali metals in the particulate matter, they were extracted either using distilled water or using eluent for the I.C.. The extraction was carried out by immersing the filter paper with particulate matter in an ultrasonic bath for about 60 minutes (Smith, 1983). The eluent for the determination of anions was 1 mmol/L potassium hydrogen phthalate and the pH was adjusted to 4 using sodium tetraborate. The eluent for the monovalent cations determination was 1 mmol/L nitric acid which was diluted immediately before use from stock solution of doubly distilled concentration HNO_3 (70% w/w).

For the determination of divalent metals ions, the filter paper with dust loading was digested either by thermal or microwave heating. For thermal digestion, the sample was refluxed with concentration HNO_3 for 24 hours prior to evaporation to dryness. 10 ml of the eluent (1

mmol/L EDTA, pH 6 with adjustment using sodium tetraborate) was then added to recover the divalent metal ions in an ultrasonic bath. For microwave heating, 5 ml HNO_3 was added to the sample in a teflon beaker which was subsequently lowered into the digestion vessel with a screwed head. After tightening, the setup was placed inside a slightly evacuated plastic desiccator before introduced it to the microwave oven. The sample was then heated with Hi power for 5 minutes, air cooled for 10 minutes before opened up the digestion vessel. The acid was then evaporated to dryness and the metals extracted ultrasonically using 10 ml eluent (1 mmol/L EDTA, pH 6).

·For digesting the NBS standard sample, same procedures were followed with the omission of the sampling steps. The optimum chromatographic conditions for subsequent analysis will be discussed in the following section.

RESULTS AND DISCUSSION

Study of digestion methods

The recent application of microwave heating for sample digestion provides a promising sample preparation method for environmental monitoring. Theoretically, only polar molecules are affected by microwave radiation. The magnetron of the microwave oven produces a pulsing electromagnetic field at 2450 MHz in which the polar molecules in the sample first align with the field. When the field direction is changing, the molecules are forced to realign. The repetitive alignment and realignment results in the rapid oscillation of the molecules and subsequently the generation of heat by the frictional force.

Instant uptake of microwave radiation throughout the solution produces more efficient dissolution because of better contact between the acids and sample. As closed digestion vessels are normally used the enable higher temperature to be reached during digestion, the loss of acid is minimum. Thus, less acid will be used. Moreover, as the sample isolated from the atmosphere, there will be a decrease in the volatility loss of the analyze and the digestion method is protected from the entrance of contaminant from the laboratory environment.

For acid digestion of particulate samples, the boiling point of sample solution is usually limited to the boiling point of the digesting acid mixture. If heating is done in a sealed pressurized vessel, the maximum temperature will rise dramatically. In addition, substances that ordinarily would not be decomposed by the acids at their normal boiling points react at elevated temperature and pressure. The nitrogen dioxide generated during the digestion process from the decomposition of HNO_3 will increase the pressure inside the digestion vessel and this will enhance the chemical dissolution process by allowing higher sample-solution temperature.

The results for the application of microwave heating as compared to conventional thermal acid digestion method for the dissolution of the air particulate samples are shown in Table

1 using NBS urban particulate matter as the reference for computing the recovery of Zn, Mg, Mn, Pb, Cu and Fe. The average recovery for the above six metals are 97.1%, with good reproducibility (relative standard deviation varies from 2.1 to 3.4% for the six metals investigated). As compared to the use of the conventional thermal acid digestion method with average percentage recovery of 88.3% and relative standard deviation between 2.4 to 4.3%, the use of the microwave digestion method is shown to improve the recovery, reduce the analysis variance and shorten the digestion time from 24 hours to 5 minutes.

Table 1 Extraction of metals by microwave digestion as compared to conventional thermal acid digestion.

Analytical parameters	Metals investigated[‡]					
	Zn	Mg	Mn	Pb	Cu	Fe
Retention time,	8.6	9.3	10.3	11.8	13.5	15.3
min	(8.5)	(9.3)	(10.5)	(11.8)	(13.5)	(15.2)
Concentration stated[*],	0.476	0.80	0.0806	0.655	0.0609	3.91
%, w/w						
Concentration detected[+]						
mean, %, w/w	0.470	0.768	0.0772	0.646	0.0537	3.81
	(0.423)	(0.738)	(0.0774)	(0.509)	(0.0537)	(3.68)
RSD, %	3.0	2.6	3.2	3.4	3.0	2.1
	(2.6)	(3.0)	(4.3)	(3.5)	(3.4)	(2.4)
Recovery, %	98.7	96.0	95.8	98.6	96.1	97.4
	(88.9)	(92.3)	(90.0)	(76.3)	(88.2)	(94.1)
Average recovery,			97.1			
%, w/w			(88.3)			

[*] From specification of the NBS standard reference material 1648 urban particulate matter.

[+] The number of determination is 3 and 10 mg NBS sample was dissolved in 10 ml eluent solution before injection.

[‡] The results obtained by conventional thermal acid digestion are given in brackets.

Water vs eluent as extractant

The chromatogram for using water or eluent as the extractant is shown in Fig.1. Due to the difference in the conductivity of water and the eluent, a water dip (negative peak) was observed using water as the extractant, whereas a solvent peak (positive peak) appeared using eluent for extraction. As the water peak is rather pronounced compared to the solvent peak, it would affect the resolution of the chromatogram. Thus, eluent was used as the extractant for subsequent studies.

The results for the extraction of anions and the determination of their concentrations in the urban air particulate matter are given in Table 2 using eluent as compared to water as the extractant. The results of using water as extractant indicate good precision (0.83 to 4.9%) and
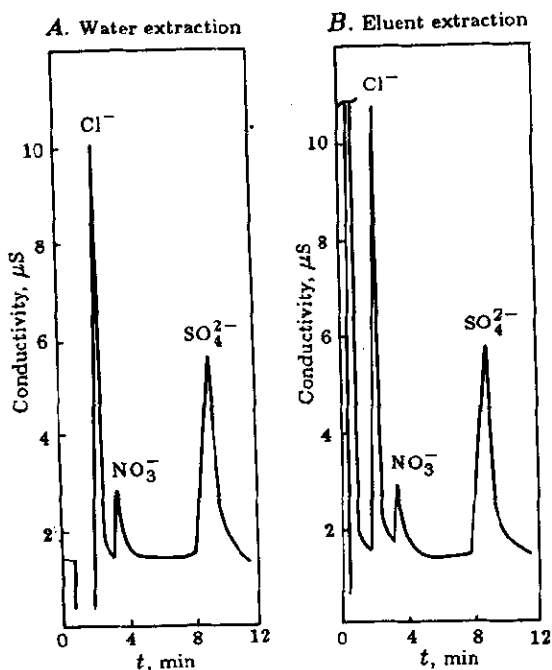
Fig. 1   The effect of using water and eluent as extractant

            Chromatographic conditions: column=Hamilton PRP-X100;

            flow rate = 1.5ml/min; mobile phase = 1mmol/L KHP; pH 4; detection

            = conductivity

high recovery (average 94.9%) of chloride, nitrate and sulphate from the standard NBS urban particulate matter.

     Comparing the results of the same anions using eluent as the extractant, the recovery is clearly improved for both chloride, nitrate and sulphate with average 99.4% in addition to a slight improvement in the precision of the data (1.0 to 3.7%). This may be due to the slightly acidic property of the eluent which make the extraction more complete. On the other hand, the retention time are the same for the three anions investigated independent of whether or not water or eluent are used as the extractant.

Table 2   The recovery of anions using water eluent as extractant

Analytical parameters	Anions[‡]		
	Cl^-	NO_3^-	SO_4^{2-}
Retention time,	2.2	3.5	9.8
min	(2.2)	(3.5)	(9.8)
Concentration stated[*],	0.45	1.07	15.42
%, w/w			
Concentration detected[+]	0.46	1.07	14.85
mean, %, w/w	(0.43)	(1.02)	(14.45)
RSD, %	2.2	3.7	1.0
	(2.3)	(4.9)	(0.83)
Recovery, %	102	100	96.3
	(95.6)	(95.3)	(93.7)
Average recovery,		99.4	
%, w/w		(94.9)	

[*] From specification of the NBS reference material 1648 particulate matter.

[+] The number of determination is 3 and 10 mg NBS sample was dissolved in 10 ml eluent solution before injection.

[‡] The results using water as the extractant are given in brackets.

Analysis of monovalent and divalent metal ions

The recovery of alkali metal ions and ammonium cation using eluent extraction is shown in Table 3. The corresponding chromatogram is shown in Fig.2. The high recovery (average 98.2%) and the good reproducibility (3.5 to 4.9%) of the results indicate that the analytical procedure is particularly suitable for the analysis of alkali metals and the ammonium ion.

Table 3   The recovery of cations using eluent as extractant

Analytical parameters	Cations		
	Na^+	NH_4^+	K^+
Retention time, min	5.6	8.0	10.2
Concentration stated[*], %, w/w	0.425	2.01	1.05
Concentration detected[+]			
mean, %, w/w	0.41	2.02	1.02
RSD, %	4.9	3.5	4.9
Recovery, %	96.5	101	97.1
Average recovery, %, w/w		98.2	

[*] From specification of the NBS reference material 1648 particulate matter.

[+] The number of determination is 3 and 10 mg NBS sample was dissolved in 10 ml eluent solution before injection.

For the analysis of divalent metals, their concentrations in the air particulate matter are very low and conductivity detection is not sufficient sensitive for the analysis. Thus, an indirect
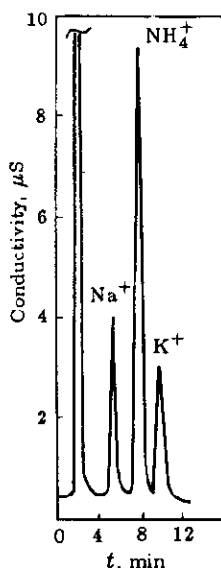
Fig. 2   Ion chromatogram for the analysis of cations
Chromatographic conditions: column=Vydac 400-IC405; flow rate =
1.0ml/min; mobile phase = 1.0 mmol/L HNO_3; detection = conductivity

detection method was used. EDTA is used as the eluent to separate metals ion being converted into metal chelate anions upon contact with the chelating agent. Divalent metal ion (M^{2+}) will form a chelate anion $MEDTA^{2-}$ immediately in contact with the EDTA eluent as shown in the following equation,

$$M^{2+} + H_2EDTA^{2-} \rightleftharpoons MEDTA^{2-} + 2H^+.$$
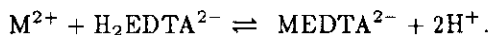
Many metal EDTA complexes exhibit strong absorption bands in the UV region at 220 nm and thus can be detected with an UV detector immediately after separation.

Table 1 and Fig.3 show the recovery and the corresponding chromatogram of the various divalent ions using NBS urban particulate matter as the sample. High recovery (97.1%) and good reproducibility (2.1 to 3%) of the results are obtained for the six metals investigated.

Applicability study

The applicability of the analytical procedures developed using the microwave acid dissolution technique and the non-suppressed ion chromatography for ions analyses in air particulate matter was investigated in the field study at a sampling site at Bonham Road near the East Gate of University of Hong Kong. 47 mm cellulose acetate membrane filters (0.45 μm) were used to collect the particulate matter at a pumping rate of 31.4 L/min over a period of 4 hours.
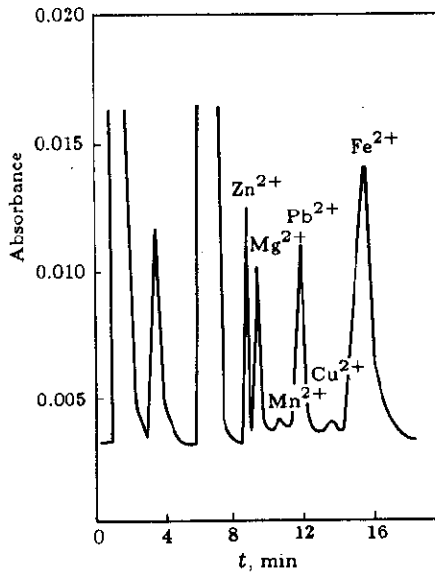
Fig.3 Ion chromatogram for the analysis of divalent metal ions

Chromatographic conditions: column = Hamilton PRP-X100; flow rate

= 1.0 ml/min; mobile phase = 1mmol/L EDTA; pH 6; detection

= UV, 220 nm

Totally, 5 samples were taken in June, 1988 and the results are shown in Table 4.

Table 4 Applicability study of the analytical methodology

Ion	Concentration in particulate matter, %, w/w					Mean*, %, w/w	RSD, %
	June 22	June 23	June 25	June 26	June 28		
Cl^-	3.93	3.90	4.02	4.01	3.98	3.97	1.3
NO_3^-	1.45	1.52	1.53	1.48	1.50	1.50	2
SO_4^{2-}	6.23	5.82	5.63	6.10	6.33	6.02	4.8
Na^+	3.10	3.08	2.98	3.12	3.03	3.06	2.0
NH_4^+	0.31	0.34	0.29	0.29	0.33	0.31	6.5
K^+	1.71	1.83	1.81	1.75	1.86	1.79	3.4
Fe^{2+}	1.20	1.28	1.32	1.36	1.25	1.28	4.7
Cu^{2+}	0.42	0.41	0.37	0.38	0.40	0.40	5.0
Pb^{2+}	1.01	0.97	0.94	0.98	1.03	0.97	4.1
Mg^{2+}	0.72	0.78	0.79	0.80	0.79	0.78	3.8
Zn^{2+}	0.75	0.72	0.77	0.80	0.84	0.78	6.4
Total weight of particulate matter, mg							
	0.93	0.83	0.82	0.94	0.87		

* The number of determination is 3.

In general, the concentrations of anions, cations and divalent metal ions are more or less the same over the 5 sampling days with standard deviation ranging from 1.3 to 6.5%. This may be due to the fact that the climate condition over the 5 days remains steady. This can be reflected by the constancy of the total weight of air particles collected in the 5 days. Moreover, the variation of the aqueous extractable ions (NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Na^+ and K^+) is more or less the same as those ions determined after acid digestion (Fe, Cu, Pb, Mg and Zn). Thus, the data obtained show that the analytical methodology developed is capable of covering the normal range of ions in the air particulate matter under the field condition.

CONCLUSIONS

The results obtained in the present study demonstrate the feasibility of using the non-suppressed ion chromatography for the analysis of trace elements in air particulate matter. The use of microwave heating for acid digestion of the air particulate matter is shown to improve the recovery and to obtain better reproducibility as compared to the conventional thermal acid digestion method. It also lowers the volatility loss, reduces the danger of contamination from the environment and shortens the analysis time from 24 hours to just 5 minutes. For the analysis of anions and simple cations, the use of eluent as extractant is shown to reduce the interference of the water dip, making the measurement of the data more reliable. The use of the UV detector coupled with chelating EDTA as the eluent is shown to give satisfactory chromatographic separation and to provide suitable sensitivity for the detection of six divalent metal ions present in the air particulate matter. Selected groups of cations and anions have been investigated in the present study and the analytical methodology developed certainly could be extended to the analysis of other metals and anions present in particulate matter collected in other locations.

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