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# Determination of trace elements in airborne $PM_{10}$ by inductively coupled plasma mass spectrometry

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Abstract Airborne particulate matter, in particular fine fraction, is accompanied by many harmful trace elements. The method for determining heavy metals in suspended particulate matter (PM10) by inductively coupled plasma mass spectrometry was established. Atmospheric particulate matter was sampled from urban area in Baoding of North China. Sampling was performed for a period of 72 h between August 2011 and July 2012 using a sequential PM<sub>10</sub> air monitor. Microwave-assisted acid digestion method was applied to the sample pretreatment. The concentration of several trace elements namely Mn, Ni, Mo, Cd, Cu, V and Co collected on nitrocellulose filters was analyzed in per sample by the proposed method in 1-year period. An assessment of air quality was performed. It is important to study the air quality in this area since significant releases of metal to the environment due to energy production could represent a threat to local communities.

**Keywords** Metal elements · Airborne particulate · Air quality · Simultaneous determination

## Introduction

The research of toxic air pollutants has been the subject of interest and concern for many years. Airborne particulate matter (PM), one of major air pollutants, contributes to visibility reduction, climate change, cardiopulmonary and respiratory disease, and decreased life expectancy (Jahn

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Key Laboratory of Analytical Science and Technology of Heibei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, People's Republic of China e-mail: liangsx168@126.com et al. 2011; Rohr and Wyzga 2012). Particulate matter is usually divided into different categories depending on the size of the particles (aerodynamic diameter). Total suspended particles include all particles, of whatever size.  $PM_{10}$  (thoracic particles) are particles <10  $\mu$ m in diameter, and PM<sub>2.5</sub> are particles <2.5 µm in diameter. Particles which are 2.5-10 µm in diameter are called coarse particles, also known as respirable particulates (RP), which distinguishes them from the smaller airborne particulate matter referred to as fine particulates with diameters of 2.5 µm and smaller (Satsangi and Yadav 2013). The coarse fraction is found to consist mainly of organic material, silicates and larger soot aggregates (Ormstad 2000). It has received considerable attention as it is easily inhaled and deposited within the respiratory system (Wang et al. 2006). The fine fraction typically contains a mixture of particles resulting from different kinds of combustion processes (e.g., exhaust particles) and secondary particulates generated by chemical reactions in the atmosphere (Lowenthal et al. 2013). PM is particularly important because of their potential for deposition on human respiratory system, while accompanied by many harmful trace elements.

Heavy metals present in the atmosphere in trace amounts may pose a serious risk to human health in urban populations (Taner et al. 2013). Multiple studies show that short-term exposure to  $PM_{10}$  results in small increases in cardiovascular mortality (Jesus and Andre 2009). Quantification and characterization of metal composition in PM have significant associations with decline in lung function, respiratory and cardiovascular diseases deaths (Toscano et al. 2011; Pavlík et al. 2012; Sysalová et al. 2012). Additionally, particulate metals can be used to identify sources and develop control strategies. Trace elements (TEs) are released into the atmosphere both from natural and anthropogenic sources, namely resuspended surface



dust, combustion of fossil fuels and traffic (Carvalho and Freitas 2011). The examination of heavy metal and trace element concentration is a useful tool for the evaluation of health risk and apportionment of the sources of particulate matter. Hence, establishing the elemental composition of atmospheric particles is essential to quantify the sources and health impacts of particulate air pollution (Danadurai et al. 2011). However, the inherent variability and heterogeneity of airborne particulate matter coupled to the very low sampled mass of metals complicate their reliable measurement.

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful and sensitive tool for the accurate trace element determinations required for environmental science studies. It has been used successfully for the direct determination of trace elements in environmental samples including PM (Carvalho and Freitas 2011; Niu et al. 2010; Valbona et al. 2010; Veguería et al. 2013; Hetzinger et al. 2011). This technique are most often called upon to determine total metal content in samples and thus are required to use sample preparation methods that result in the total dissolution of the sample. Microwave sample preparation method shows significant improvement in chemical reaction rates (Perämäki et al. 2000). ICP-MS combined with microwave-assisted digestion has become the preferred methodology for the analysis of metals.

The choice of digestion reagents is an important consideration for measurement of multiple elements in samples. In this study, acid solution of HNO<sub>3</sub>, HCl and HF was chosen for sample decomposition. The instrument operating parameters of ICP-MS were optimized. The purpose of this investigation was to develop a digestion and simultaneous determination method for the several ultratrace-level elements of interest in airborne particulate matter. In this study, measurements of 8 trace elements were conducted on airborne PM<sub>10</sub> samples collected in the urban air at Baoding in Hebei province of North China. This area was of special significance for its important geographical location, known as the southern gate of the capital. To the best of our knowledge, metal composition in airborne particulate matter is reported for the first time for this city. Sampling was performed for a period of 72 h between August 2011 and July 2012 using a sequential  $PM_{10}$  air monitor. The present study provided useful information for the assessment on the risk to human health in urban populations.

## Materials and methods

Chemicals and equipments

The standard stock solutions of  $1 \times 10^3$  mg/L Mn, Ni, Mo, Cd, Cu, V, Co, Bi, In, Ge and Be were purchased from



National Analysis Center for Iron and Steel. The standard working solutions of the metal ions were prepared by step dilution of standard stock solutions with high-purity deionized water.

Ultrapure HNO<sub>3</sub> and analytical reagent-grade HCl and HF were used. The high-purity deionized water was used (18.2 M $\Omega$ ) throughout this work. In order to eliminate the blank of trace analytes and other contaminants, all containers were dipped in 10 % HNO<sub>3</sub> over 24 h and rinsed by high-purity deionized water prior to use.

A model of X Series ICP-MS (Thermo Fisher Scientific Corporation) was used for the measurements. MARS microwave oven (CEM Corporation) was used for the pretreatment of samples. TH-16A ambient particulate sampler (Wuhan Tianhong Instruments Co. Ltd) was used as sampling device. The sampler is equipped with computer control and multi-parameter data-logging systems.

#### Procedure

Particulate matter with aerodynamic diameter  $<10 \ \mu m$  (PM<sub>10</sub>) was sampled at the top of the second floor (9 m high from the ground) of a local university building in urban area, from August 2011 to July 2012. Each sampling lasted 7 days to minimize the influence of short-term weather condition changes. The meteorological parameters such as atmospheric pressure, temperature and wind speed and direction (optional) was recorded by TH-16A all day long meanwhile.

Each sample was collected on 47-mm fibrous cellulose filter paper at a flow rate of 16.7 L/min. Total volume of air passed through a filter was computed using a flow recorder for each sampling period. The collected samples were prestored for 24 h in a controlled atmosphere (20 °C, 50 % relative humidity) and transferred into polyethylene vials after weighing.

A closed vessel microwave-assisted reaction system (Mars, CEM Corporation) was used. All digestions were performed in Teflon digestion vessels. The pressure inside the liners and the internal temperature of the vessels were monitored in a control vessel assembly, which is equipped with pressure and temperature sensor units.

Atmospheric particle samples in filter paper were weighed and placed it into the microwave digestion vessels. Seven milliliters of  $HNO_3$ , 2 mL HCl and 1 mL HF were added to each vessel, immersing the sample. The vessels were closed and heated in the microwave oven following a three-step digestion program. Temperature program is listed in Table 1.

Determination was carried out using quadrupole inductively coupled plasma-mass spectrometry (ICP-MS). Calibration of the ICP-MS instrument was performed with  
 Table 1
 Digestion program of microwave-assisted acid digestion method

Step	Temperature (°C)	Ramp-heating rate (°C/min)	Dwell time (min)
1	120	5	2
2	160	3	3
3	180	4	15

Table 2	Operation condition of
ICP-MS	

Parameters Setting value Pa		Parameters	Setting value	
Power (W)	1,400	Measurement method	peaking	
Atomizer gas flow (L/min)	0.8	Sampling points	3	
Radiator gas flow (L/min)	13.0	Repetition	3	
Auxiliary gas flow(L/min)	0.7	Sampling time/s	50	
Sampling depth	130	Mode	Xt standard mode	

standard multi-element solutions. Mixture of In, Ge and Be was used as internal standard.

The digestate was cooled and then diluted to 50 mL. The diluted solution was analyzed for metal elements by ICP-MS.

All instrument operating parameters are given in Table 2.

## **Results and discussion**

## Correction of isobaric interferences

Isobaric interferences occur for equal-mass isotopes of different elements. Isobaric interferences are easily corrected by measuring the intensity of another isotope of the interfering element and subtracting the appropriate correction factor from the intensity of the interfered isotope. In this work, the isobaric interferences occurred to the following isotopes: <sup>64</sup>Ni, <sup>92</sup>Mo, <sup>94</sup>Mo, <sup>96</sup>Mo, <sup>98</sup>Mo, <sup>100</sup>Mo, <sup>106</sup>Cd, <sup>108</sup>Cd, <sup>110</sup>Cd, <sup>112</sup>Cd, <sup>113</sup>Cd, <sup>114</sup>Cd, and <sup>116</sup>Cd. They were avoided by choosing alternative non-interfered analyte isotopes <sup>62</sup>Ni, <sup>95</sup>Mo and <sup>111</sup>Cd, respectively.

# Molecular/polyatomic interferences

Molecular/polyatomic interferences are due to the recombination of sample and matrix ions with Ar or other matrix components in the cooler regions of the plasma. The interferences are caused by atomic or molecular ions that have the same mass-to-charge as analytes of interest (May and Wiedmeyer 1998). Polyatomic interferences are probably the largest class of interferences in ICP-MS. Molecular interferences could be avoided by using alternative, non-interfered analyte isotopes. In some cases, they can be reduced in severity or even eliminated completely by using more appropriate sample introduction systems or optimizing instrument operating conditions. Recent advances in collision cell technology (CCT) have led to dramatic improvements in the analysis of interfered elements which previously proved difficult or impossible to measure at required levels in certain sample matrices. Almost all current quadrupole ICP-MS systems use collision/reaction cell technology to reduce polyatomic interferences (McCurdy et al. 2010).

Comparative determination results of normal mode and CCT mode are shown in Table 3. These results revealed that there is no obvious molecular/polyatomic interference in the determination; thus, normal mode was used in the following work.

## Analytical performance

Maintaining low limits of detection (LOD) is crucial in the analysis of trace elements in  $PM_{10}$  samples. The presence of metals in blank samples is highly affected by several factors such as cleaning procedures, purity of reagents/filter media and conditions of sample manipulations during digestion. All these factors, in addition to instrumental noise and interferences, affect analytical performance and consequently were carefully controlled.

Under the optimized conditions, the LODs, precision and recoveries were determined. Linearity was obtained with  $r^2 > 0.99$ . Table 4 is the analytical performance data for the developed method. The recoveries were in the range of 89.5–115.5 %.

Determination results	V	Mn	Со	Ni	Cu	Мо	Cd
				1.1			
Normal mode							
Concentration (µg/L)	5.72	16.70	1.05	14.47	3.32	17.04	2.33
RSD(%)	0.78	0.77	0.83	0.67	1.26	0.42	1.15
CCT mode							
Concentration (µg/L)	5.87	17.04	0.99	14.65	11.03	16.87	3.23
RSD(%)	0.99	2.01	0.83	0.76	1.23	0.66	1.13

Table 3 Comparison results of normal mode and CCT mode

**Table 4** Analytical performance of the proposed method

Element	V	Mn	Co	Ni	Cu	Мо	Cd
LOD (µg/L)	0.056	0.024	0.024	0.045	0.026	0.033	0.043
RSD (%)	1.25	1.85	1.23	2.11	1.45	1.44	2.12
Recovery (%)	93.0	95.0	89.5	91.5	90.5	115.5	87.5
Correlation coefficients	0.999991	0.999954	0.999989	0.999920	0.999948	0.999989	0.999997

Table 5	Determination results
of standa	rd soil samples

Element	Certified value (µg/g)	Analyzed value (µg/g)		
Mn	$1,097 \pm 27$	1,072		
Co	$14.8 \pm 0.7$	13.8		
V	$77.5 \pm 3.1$	71.6		
Cd	$0.083 \pm 0.011$	0.10		
Ni	$29.6 \pm 1.8$	34.2		
Cu	$20.9 \pm 0.8$	19.2		
Мо	$0.54\pm0.08$	0.61		

## Validation of the method

In order to validate the developed method, a standard reference material of soil (GSBZ 50011-88) was employed. Fifty milligrams of dried soil was accurately weighed into a digestion vessel. Seven milliliter of HNO<sub>3</sub>, 2 mL HCl and 1 mL HF were added. The soil was then digested by microwave-assisted reaction system with the same program as described above and finally diluted to 50 mL for determination. Blank experiment was carried out using the same procedure without soil.

Table 5 lists the determination values by the developed method and the certified values. As could be seen, a good agreement between the determined values and the certified values was obtained.

Analysis of ambient PM<sub>10</sub> samples

For sample analysis, the calibration was obtained using a standard solution. Blank experiments were carried out using the same procedure without samples. The analytical results are listed in Fig. 1.

Heavy metal measurements in  $PM_{10}$  in the urban area showed that the ambient concentration of Mn in the  $PM_{10}$ was the highest (4.14–6.34 µg/m<sup>3</sup>), following with high concentration for Ni and V in  $PM_{10}$ , reflecting the importance of anthropogenic inputs. Concerning Cu and Cd, representative toxic heavy metal, relatively high mean values of 0.64 and 0.42 µg/m<sup>3</sup> in  $PM_{10}$  were obtained.

Correlation coefficient of elements in  $PM_{10}$  and Fig. 1 revealed V–Ni and Cu–Cd were significantly correlated,





Fig. 1 Analytical results for elements in PM<sub>10</sub>

suggesting that V and Ni, Cu and Cd have the same pollution source, respectively. This result provided scientific basis for environmental management.

#### Conclusion

The method described in this paper for digestion and analysis of trace elements in atmospheric suspended particulate samples is suitable for routine analysis of the large number of samples commonly generated in air quality monitoring studies. Sample preparation by microwave digestion minimizes contamination and allows for digestion of silicate materials with the use of nitric/hydrochloride acid and hydrofluoric acid. Results suggest that only a trace amount of HF is required for essentially complete digestion. The results could be used as the baseline data for analysis of health risks due to inhalation of suspended aerosols and to provide scientific evidence for setting up an air pollution control strategy. This fact may well raise some concern and should stimulate the planning of long-term monitoring campaigns.

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Conflict of interest None.

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