

Simultaneous Determination of Trace Heavy Metals in Ambient Aerosols by Inductively Coupled Plasma Atomic Emission Spectrometry after Pre-Concentration with Sodium Diethyldithiocarbamate

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The simultaneous determination of heavy metals associated with airborne particulate matter in the atmosphere of the city Isfahan (Iran) was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES) after pre-concentration with sodium diethyldithiocarbamate. The pre-concentration procedure developed found instrumental to determine the trace heavy metals associated with ambient aerosols collected at a short sampling period or collected from rural areas where the concentrations of these metals are much less than those in urban areas. Several samples were analyzed by both flame atomic absorption spectrometry (FAAS) as a conventional method and the proposed method. The results obtained by the two methods were found in good agreement. The method was applied to the determination of atmospheric level of heavy metals in rural area and also for study of variation in levels of heavy metals in urban atmosphere during the days and nights.

Key words : *Trace heavy metals, ambient aerosols, inductively coupled plasma atomic emission spectrometry, pre-concentration, sodium diethyldithiocarbamate*

Introduction

Heavy metals occur in the urban atmosphere mainly in particulate form originating from the mixing of finely divided materials from various sources^{1,2}. Although both natural and anthropogenic sources contribute to distribution of heavy metals into the urban atmosphere, but the role of human activities is more important^{3,4}. The major anthropogenic sources responsible for releasing heavy metals into urban atmosphere include metallurgical processes, power plants, garbage incineration, and consumption of fossil fuels in automobile engines^{5,7}.

The determination of heavy metals associated with airborne particulate matter in urban areas is very important because of their adverse effects on human health, continuous nature of exposure of the residents, and the size of population at risk in industrialized areas and mega cities. During the last decades, an extensive database has been published providing different methods for the determination of heavy metals in environmental samples^{8,11}. Among different techniques, flame atomic absorption spectrometry (FAAS) is the most frequently used and the popular one. FAAS technique is classified as a single-elemental method and requires long time for analysis of several elements in a sample. In air pollution studies, several

metals have to be determined in a huge number of samples and in a short period of time. FAAS is time-consuming and tedious. Multi-elemental techniques such as x-ray fluorescence (XRF)¹², neutron activation analysis (NAA)^{13,14}, and inductively coupled plasma atomic emission spectrometry (ICP-AES)^{15,16} have been reported for simultaneous determination of heavy metals in environmental samples. Among different techniques, ICP-AES is the most popular technique for simultaneous and sensitive determination of heavy metals and offers reliable results. When the concentrations of heavy metals are too low to detect sensitively, it is necessary to perform a pre-concentration before determination.

In the present work, ICP-AES as a multi-elemental technique, has been used for the determination of trace heavy metals associated with airborne particulate matter following pre-concentration with sodium diethyldithiocarbamate.

Materials and methods

Sample collection

Airborne particulate matter from the atmosphere of the city Isfahan (Iran) was collected on quartz fiber filter (Whatman QM-A) using a conventional high-volume air sampler. Samples were collected from both urban and rural

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areas. Samples were collected from a height of 1.5 m above the ground level. Sampling flow rate and sampling period were $1 \text{ m}^3 \text{ min}^{-1}$ and 12 hours respectively. A continuous sampling was carried out for 8 days. Samples were collected in days and at nights, in order to investigate day to day and also day and night variations in concentrations of heavy metals in urban atmosphere.

Reagents

All chemicals were of analytical grade or equivalent. Aristar HNO_3 and HF (Merck Chemical Co.) were used for digestion of filters. Standard stock solutions (1000 mg/L) of Pb, Cd, Cr, Cu, Ni, Zn and Fe for atomic absorption spectrometry (BDH, Ltd.) were used. Standard solutions in the working range were prepared from the stock standard solution by proper dilution with 5% v/v nitric acid. 0.1M solution of sodium diethyldithiocarbamate was prepared by dissolving 2.253 g of the reagent in doubly distilled de-ionized water and the volume of the solution was then made to 100 mL. Distilled de-ionized water was used for preparation of standard solutions. It was prepared by a Wters, Milli Q water purification system. Standard reference material SRM-1648 was prepared from National Bureau of Standard Certificate of Analysis (USA). All glasswares were placed into 25% (v/v) nitric acid for 24 hours before use. Then the vessels were rinsed with distilled de-ionized water and dried.

Sample preparation

The exposed filter was folded several times, placed in a PTFE beaker and moisturized with a few mL of de-ionized distilled water. 15 mL of nitric acid was then added to it. The lid of the beaker was screwed, the beaker was heated on a hot plate and refluxed for 8 hours till all organic material got oxidized. The PTFE lid was then unscrewed and the beaker was heated at 90°C . When the volume was reduced to half, 10 mL nitric acid and 6 mL hydrofluoric acid were added and the mixture was refluxed again to dissolve the material completely. The lid of the beaker was then removed and the mixture evaporated to near dryness. After removing the remainder of HF (by adding concentrated HNO_3 and heating), the digest was extracted in nitric acid 1:1 (v/v), transferred into a 100 mL volumetric flask and made to the volume by deionized distilled water.

Pre-concentration of heavy metals

The digest was transferred to a pyrex beaker and its pH was adjusted to 5. 100 mL 0.1 M of sodium diethyldithiocarbamate solution was then added with continuous stirring. The solution was allowed to stand for 45 min. 1 mL of 1% H_2O_2

was then added and allowed to stand for 5 hours. The precipitate was then filtered on a narrow pore filter paper and washed with distilled de-ionized water. The precipitate was finally dissolved in a few mL of concentrated nitric acid and the solution was transferred to a 10 mL volumetric flask and diluted to the volume with deionized distilled water. Heavy metals were not detected in the filtrate, so it was discarded.

Instrumentation

ICP-AES determinations were carried out on a Maxim system (Applied Research, Fisons Instruments) fitted with an axial viewing of torch. Control of the Maxim ICP-AES spectrometer was performed by a software program called Plasma Vision. The system was linked to a DECP 450, D2LP computer and IBM 238 printer. The ignition, shut down, and sample uptake rate were computer-controlled. The instrumental conditions and the wavelengths used for the determination of heavy metals are listed in **Table 1**. The background correction was performed using two different positions, i.e. position No. 1 in negative offset and position No. 2 in positive offset from the analytical wavelength of the element of interest.

The flame atomic absorption spectrometric determinations were carried out on a Varian atomic absorption, Model AA-220. The system was equipped with D2 lamp for background correction. Standard Varian hollow cathode lamps and air-acetylene pre-mixed burner were used for the determinations.

Table 1 : ICP-AES scanning measurement parameters

Starting mirror	-60°
Ending mirror	$+60^\circ$
Step size	4
Pre-integration time	0 (s)
Integration time	1 (s)
Plasma flow	0.8 (L/min)
Forward power	1100 (W)
Carrier flow	0.4 (L/min)
Analysing pump speed	2.0 (L/min)
Transport pump speed	20.0 (L/min)
Transport time	30 (s)
Sample type	aqueous

The following analytical lines were used for analysis Pb 220.35 nm, Cd 228.80 nm, Cr 267.72 nm, Cu 324.75 nm, Ni 231.60 nm, Zn 213.86 nm, and Fe 259.94 nm

Results and discussion

Optimization of pre-concentration procedure

The pre-concentration is necessary especially where the concentrations of the metal ions are very low or in air pollution, where the samples are collected in a short period of time. There are different parameters affecting pre-concentration efficiency with any procedure. Among them, pH and amount of the reagent are most important. So, the effects of pH and amount of sodium diethyldithiocarbamate on the pre-concentration of heavy metals were investigated.

The effect of pH

The effect of pH on the pre-concentration efficiency of heavy metals with sodium diethyldithiocarbamate was investigated. 100 mL of the standard solution containing 3 mg/L of each element was transferred to a beaker and its pH was adjusted to a certain value (between 2 to 6). The pre-concentration was carried out according to the procedure and the pre-concentration efficiency was determined. **Fig.1** shows the pre-concentration efficiency percentages at different pH which are obtained from this investigation.

The relatively good pre-concentration efficiencies were obtained even at acidic pH, but it is obvious that the efficiencies are higher at pH near to neutral area.

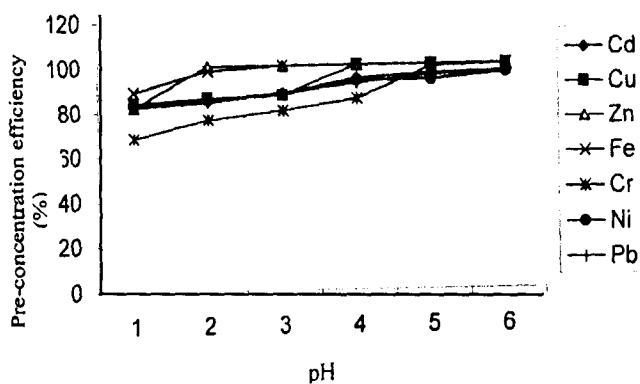


Fig. 1: Effect of pH on the pre-concentration efficiency of heavy metals

Effect of amount of sodium diethyldithiocarbamate

The effect of sodium diethyldithiocarbamate on the pre-concentration efficiencies of heavy metals was also investigated by adding different amounts of the reagent on 100 mL of the solution containing 3 mg/L of each element. The results obtained from this investigation are shown in **Fig. 2**.

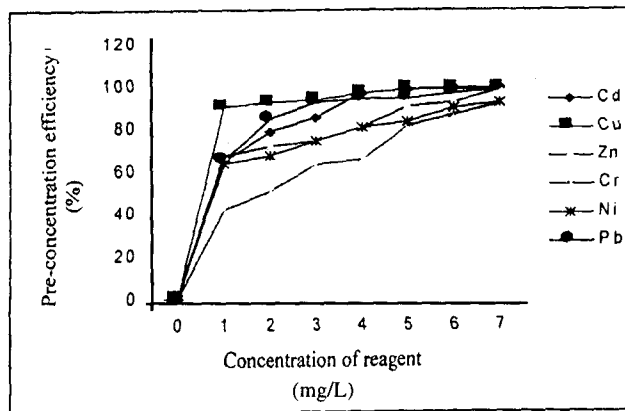


Fig. 2: Effect of the concentration of sodium diethyldithiocarbamate on the pre-concentration efficiencies of heavy metals

Recovery efficiency of pre-concentration of heavy metals

The recovery efficiency of pre-concentration stage was determined by spiking known amount of each element into the solution obtained from leaching of airborne particulate matter. pH of the solution was adjusted and the concentration of the element was determined. **Table 2** summarizes the results obtained from this investigation and indicates that all the heavy metals studied here show excellent recovery percentage and the method is reliable for pre-concentration.

Table 2 : Recovery of heavy metals from the pre-concentration procedure

Element	Concentration (µg/mL)		Recovery (%)
	added	found	
Pb	-	1.010	97
	2.0	2.920	
Cd	-	0.029	98
	2.0	1.989	
Cr	-	0.238	97
	2.0	2.171	
Ni	-	0.209	98
	2.0	2.165	
Zn	-	4.033	102
	2.0	6.154	
Cu	-	2.021	98
	2.0	3.941	
Fe	-	5.546	103
	2.0	7.772	

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Comparison of metal concentration determination by AAS and ICP-AES

Several samples of airborne particulate matter were digested and analyzed for heavy metals by both FAAS and the proposed method. The results obtained by the two methods were compared and good agreement was found between the results. The regression equations between the concentrations of different elements analyzed by two techniques are summarized in **Table 3**. Although FAAS is a conventional and popular method for determination of heavy metals, but it is time-consuming and tedious, while ICP-AES is a multi-elemental technique which offers the same results as FAAS in short time. Analysis of heavy metals by ICP-AES after pre-concentration can be used in air pollution studies, especially where the samples are collected from rural areas or in such cases where variations of atmospheric levels of heavy metals are being studied during day time and sampling period is limited.

Table 3 : Comparison of FAAS and ICP-AES by a linear regression analysis

Element	Regression equation	X, Y pairs
Pb	$Y = 1.221 + 0.998 X$	32
Cd	$Y = 0.132 + 1.054 X$	32
Cr	$Y = 0.021 + 1.014 X$	32
Cu	$Y = 0.387 + 0.990 X$	32
Ni	$Y = 0.042 + 1.014 X$	32
Zn	$Y = -0.110 + 1.002 X$	32

Comparison of heavy metal concentration in urban and rural areas

The method was applied for the determination of atmospheric levels of heavy metals in urban and rural areas. The rural area is located about 140 km away from the city of Isfahan in the east. The atmospheric concentrations of heavy metals in these areas are summarized in **Fig 3**.

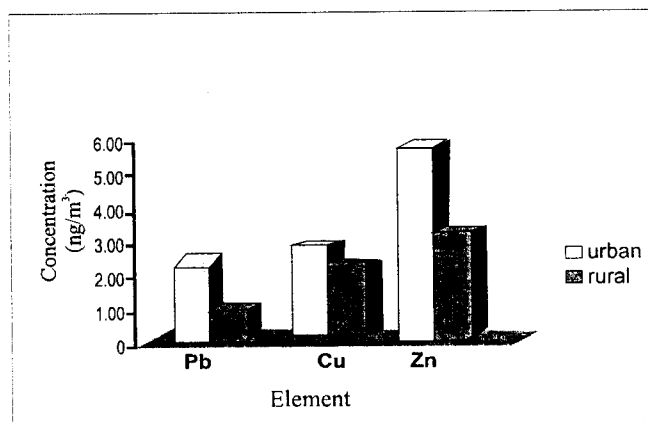
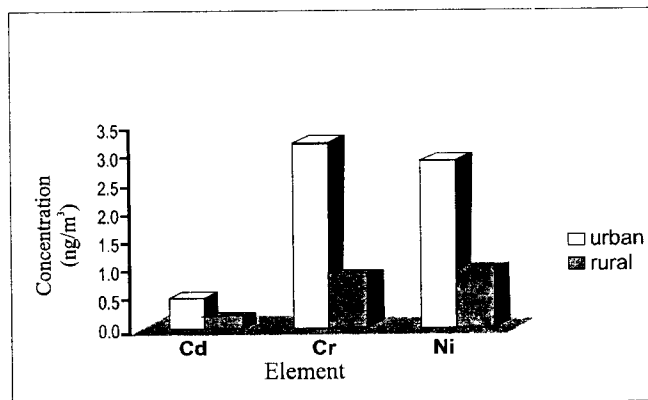


Fig 3 : Mean concentrations of heavy metals in rural and urban areas

Day and night variations in atmospheric levels of heavy metals

In order to investigate the variations in concentrations of heavy metals in day and night periods in urban area, a continuous sampling was carried out. Sampling period was 12 hours. Day samples were collected from 7 am to 7 pm, and night time samples were collected from 7 pm to 7 am. The results obtained from this investigation are shown in **Fig 4**, which indicate that at nights with lower traffic density the concentrations of heavy metals are much less than those in days. The results also indicate that traffic in the city is a major source responsible for introducing heavy metals into the atmosphere.

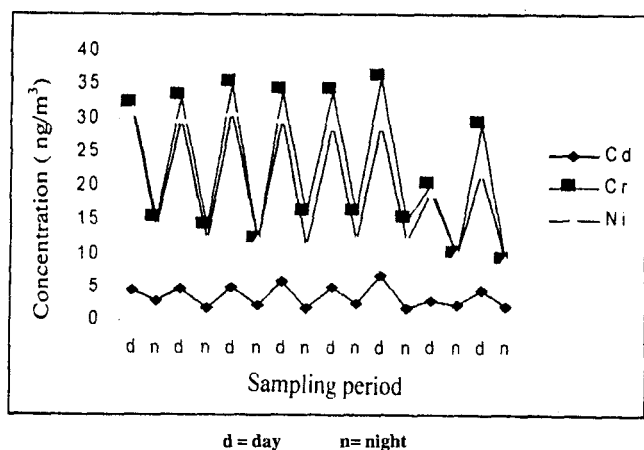
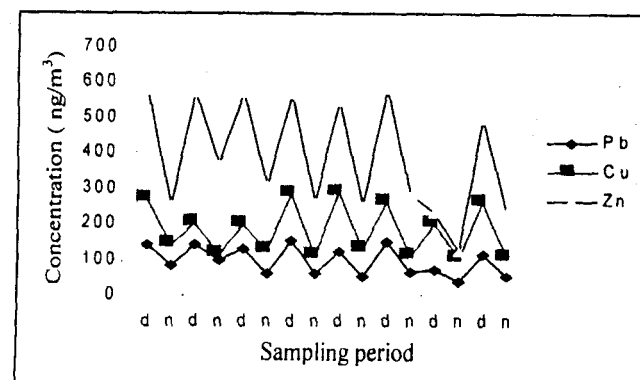


Fig. 4 : Day and night time variations in concentrations of heavy metals

References

1. R. Chester, F. J. Lin and K. J. T. Morphy, A three stage sequential leaching scheme for the characterisation of the sources and environmental mobility of trace metals in the marine aerosol, *Environ. Technol. Lett.*, **10**, 887-900 (1989)
2. S. Landsberger, M. Kamiski, M. Basunis and F. Y. Iskander; Multielemental analysis of solid wastes and leachates, *J.of Radioanal. & Nuclear Chem.*, **244**, 35-40 (2000)
3. M. A. Al-Rajhi, S. M. Al-Shayeh, M. R. D. Seaward and H. G. M. Edwards, Particle size effect for metal pollution and analysis of atmospherically deposited dust, *Atmos. Environ.*, **30**, 145-153 (1996)

4. G. W. VanLoon and S. J. Duffy, *Environmental Chemistry: A Global Perspective*, Oxford University Press Inc., p. 117, 2000
5. K. F. Ho, S. C. Lee, J. C. Chow and J. G. Watson, Characteristic of PM₁₀ and PM_{2.5} sources profile for fugitive dust in Hong Kong, *Atmos. Environ.*, **37**, 1023-1032 (2003)
6. S. M. Talebi and M. Abedi, Concentration of heavy metals in the atmosphere of the city of Isfahan, *Poll.Res.*, **23** (2), 211-214 (2004)
7. G. B. Wiersma and C. I. Davidson, in (J. O. Nriagu and C.I. Davidson ed.), *Toxic metals in the atmosphere*, Wiley, New York, p. 201, 1986
8. B. Ye, X. Ji, H. Yang, X. Yao, C. K. Chan, S. H. Cadle, T. Chan and P. A. Mulawa, Concentration and chemical composition of PM_{2.5} in Shanghai for one year period, *Atmos. Environ.*, **37**, 499-510 (2003)
9. I. Narin, M. Soylak, L. Elci and M. Dogan, Determination of trace metal ions by atomic absorption spectrometry in natural water samples after pre-concentration of pyrocatechol violet complexes on an activated carbon column, *Talanta*, **52**, 1041-1046 (2000)
10. P. Vinas, M. Pardo-Martinez and M. Hernandez-Cordola, Rapid determination of Se, Pb, and Cd in baby food samples using electrothermal atomic absorption spectrometry, *Anal. Chim. Acta*, **412**, 121-130 (2000)
11. A. M. H. Shabani, S. Dadfarnia and N. Nasirzadeh, Speciation analysis of mercury in water samples by CVAAS after pre-concentration with dithizone immobilized on microcrystalline naphthalene, *Anal. Bioanal. Chem.*, **378**, 1388-1391 (2004)
12. S. M. Talebi, Determination of lead associated with airborne particulate matter by flame atomic absorption and wave-length dispersive X-ray fluorescence spectrometry, *Environ. Anal. Chem.*, **72**, 1-9 (1998)

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- 13 L. Ortiz, N. Apelbeza, C. Campson, S. Zleszi and M. Prendez, *Atmos. Environ.*, **27A**, 397 (1993)
 - 14 S. Tokalioghu, S., Kartal and L. Elci, *Anal. Chim. Acta*, **413**, 33 (2000)
 - 15 V. Bruder, F. Lgrade, M. J. F. Lerosy, C. Coughanower and F. Enguehard, Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash, *Anal. Chim. Acta*, **451**, 285-295 (2002)
 - 16 J. L. NI, C. C. Liu and S. J. Jiang, Determination of Ga, As, Ge, Se, and Sb in fly ash samples by ultrasonic slurry electrothermal vaporization ICP-MS, *Anal. Chim. Acta*, **550**, 144-150 (2005).
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