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DETERMINATION OF LEAD ASSOCIATED WITH AIRBORNE PARTICULATE MATTER BY FLAME ATOMIC ABSORPTION AND WAVE-LENGTH DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

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The lead content of airborne particulate matter was determined by flame atomic absorption spectrometry (FAAS) following digestion with a mixture of nitric acid and hydrogen peroxide and also by wave-length dispersive x-ray fluorescence (WDXRF). The extraction procedure was checked by analyzing a standard reference material of airborne particulate matter (NIST, SRM -1648). It was concluded that lead can quantitatively (98%) be extracted from airborne particulate matter by the leaching process. A five-stage sequential extraction was performed to assess the potential mobility of lead associated with airborne particulate matter. Comparison of the airborne particulate lead measured by WDXRF to that measured by FAAS showed a good agreement. The WDXRF method requires no time-consuming sample preparation or use of environmentally unfriendly solvents. The technique is suggested for direct determination of lead in airborne particulate matter in air pollution studies.

Keywords: Lead; air pollution; flame atomic absorption spectrometry; wave-length; dispersive x-ray fluorescence spectrometry

INTRODUCTION

Airborne particulate matter is one of the most important atmospheric pollutants containing organic and inorganic material. The sources of particulate matter in the atmosphere are sub-divided into two groups: 1) natural sources, and 2) anthropogenic sources^[1-3]. During recent years much more attention has been paid to the anthropogenic emissions, because social and industrial activities can release large amounts of materials into the atmosphere^[4,5]. Lead is an important

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component of airborne particulate matter and in varying concentrations is an ubiquitous component of the lower atmosphere. Lead is emitted into the atmosphere from the combustion of fossil fuels, incineration of wastes, smelting of ores, and combustion of leaded petrol in automobile engines^[2,6,7].

The determination of lead associated with urban airborne particulate matter is important in order to clarify its adverse health effect and also to estimate the source and trend of air pollution. The conventional method for analysis of lead in airborne particulate matter involves acid digestion followed by quantitative determination of lead by flame atomic absorption spectrometry (FAAS)^[8-11]. Although FAAS is a sensitive and accurate technique, it is labor intensive, time-consuming, and acid digestion can introduce impurities into the sample.

Analysis of lead associated with airborne particulate matter by x-ray fluorescence spectrometry can be an alternative method to FAAS. This technique requires minimal sample preparation, and does not introduce any impurities into the sample during the sample preparation stage. In this work, a wave-length dispersive x-ray fluorescence technique has been studied as a means of the determination of lead in urban urban airborne particulate matter.

EXPERIMENTAL

Collection of airborne particulate matter

Sampling was performed from the atmosphere of an industrial city (Isfahan). The city was located in an area close to the desert and in the central part of Iran. Airborne particulate matter were collected on ultra pure quartz fibre filters (Whatman QM-A) using a high-volume sampler (Graseby) with an average flow rate of $1 \text{ m}^3 \text{ min}^{-1}$. The sampling stations were close to the commercial area of the city. The sampling period was 12 hours in order to collect sufficient material for sensitive analysis.

Reagents

All chemicals were analytical-reagent grade or better.

Working standard solutions of Pb for AAS were prepared by diluting from $1000 \mu\text{g ml}^{-1}$ stock solution for atomic absorption spectrometry (BDH, Ltd.) with 0.1 M nitric acid.

Standard filters for WDXRF analysis

Standard filters for WDXRF were prepared by spiking 50 l of various concentrations of Pb (prepared from the stock solution) onto the ultra pure quartz filter discs (d = 40 cm). The discs were fixed on aluminium discs (d = 40 cm) and dried for 15 min. at 70 °C in an oven before analysis.

Sample preparation

For the analysis of lead by WDXRF, five 40 mm filter discs were punched from the original exposed filter; two near the ends, one near the middle, and the other two at a location midway between the middle and the end. The filter discs were fixed on aluminium plates (40 mm, diameter), covered with a mylar film and analysed by WDXRF.

For analysis of lead by FAAS, a 4 × 18 cm section was cut from each exposed filter, digested with a mixture of nitric acid and hydrogen peroxide.

Wet digestion

Leaching with nitric acid and hydrogen peroxide

The filter was folded and placed in a 100 ml conical flask. 10 ml nitric acid 1:1 (v/v) was added and the flask was then placed on a hot plate for digestion at a temperature below the boiling point of the mixture. When the volume was reduced to a half, a further 10 ml (1:1) nitric acid and 5 ml of 30% hydrogen peroxide were added to oxidise any organic compounds, and mixture was then heated at sub-boiling temperature to reduce the volume down to about half. The digest was filtered on a Whatman 451 filter paper into a 25 ml volumetric flask and made up to 25 ml with deionised distilled water with rinsing.

Sequential extraction

To 0.2 g of sample, a series of five-stage sequential extractions was carried out sequentially according to the procedure developed by Tessier et al^[12] as follows:

Fraction 1: exchangeable metals

The sample was placed in a 50 ml glass test tube and 15 ml of 1 M, (pH = 7) of ammonium acetate was added and the mixture was shaken for 20 min. by a mechanical shaker. The tube was then centrifuged at 3000 rpm for 20 min. to

separate the two phases. The supernant was transferred into a 25 ml volumetric flask and made up to the volume with 0.1 M nitric acid.

Fraction 2: metals bound to carbonates

The residue from the fraction 1 was leached with 15 ml of 1 M, (pH = 5) sodium acetate for 5 hours. The same procedure as fraction 1 was followed for separation and preparation of supernant.

Fraction 3: metals bound to Fe, Mn oxides

The residue from fraction 2 was leached with 15 ml, 1 M hydroxylamine hydrochloride in 25% (v/v) acetic acid. After shaking for 16 hours the mixture was centrifuged and prepared for analysis.

Fraction 4: metal bound to organic matter

The residue from fraction 3 was leached with a mixture of 5 ml (pH = 2) of 30% hydrogen peroxide at 85 ± 2 °C for 3 hours. After centrifuging the supernant was prepared for analysis.

Fraction 5: residue

The residue from fraction 4 was transferred into a PTFE beaker, 10 ml of Aristar nitric was added and the beakers lid was closed carefully and heated on a hot plate for 1 hour. The PTFE lid was then removed and the beaker was heated at a temperature below the boiling point of the mixture. When the volume was reduced to a half, 5 ml of hydrofluoric acid was added, the lid was closed and the mixture refluxed for 12 hours at 100 °C. After cooling, the excess HF was driven off from the mixture by adding nitric acid and heating close to dryness. The residue was taken up in nitric acid, transferred into a 25 ml volumetric flask and made up to 25 ml.

Atomic absorption spectrometry

A Varian-Techtron Model AA-10 spectrometer with an air-acetylene burner using single hollow cathode lamp was used for analysis of lead in the digests. The instrument had a simultaneous deuterium background correction system. A wavelength of 217.0 nm was used for analysis and the flame was set in the oxidizing (lean blue) position. The analysis carried out using a standard addition method. Operating conditions of the instrument are shown in Table I.

TABLE I Operating conditions of AAS during the analysis for lead

Instrument Mode	Absorption
Sample Injection	Manual
Measurement Mode	Integration
Calibration Mode	Concentration
Lamp Position	2
Lamp Current	5 mA
Delay Time	3 sec.
Measurement Time	3 sec.
Replicates	3
Background Correction	On
Wavelength	217.0
Expansion Factor	1.0

Wavelength dispersive x-ray fluorescence spectrometry

Measurement of lead by WDXRF technique was made on a Philips spectrometer Model 1400, equipped with an automatic sample changer and Philips X41 software. The operating conditions of the instrument are shown in Table II. Background correction was used during the analysis and the averaged background intensity was then subtracted from the measured peak intensity.

TABLE II Operating conditions of WDXRF during the analysis for lead

Peak position	28.24 °
Tube voltage	80 KV
Tube current	30 mA
Tube target	Cr
Special line	Pb, L- β
Sample rotation	Yes
Detector	Scintillation counter
Fixed time count	80 s.
Channel mask	Large
Analyzing crystal	LiF 200

RESULTS AND DISCUSSION

In order to check the efficiency of extraction procedure the standard urban particulate matter (SRM-1648) was leached with a mixture of nitric acid and hydrogen peroxide and showed that 98% of lead is extractable (Table III), so using hydrofluoric acid and following a time-consuming and tedious procedure for extraction of lead from air particulates by wet digestion method is not necessary.

TABLE III Determination of lead in standard sample (NIST, SRM-1648) using different decomposition methods. (n = 5)

<i>Decomposition Method</i>	<i>Conc. of Pb as g g⁻¹</i>	<i>Standard Deviation</i>
HF, HNO ₃ , HCl	6506	62
HF, HNO ₃ H ₂ O ₂	6510	70
HNO ₃ H ₂ O ₂	6400	54

The sequential extraction scheme based on the Tessier, et al^[12] method has widely been used by geochemists for the study of trace metals associated with particulate material in aquatic samples and in sediments^[13]. However modified sequential extraction procedures have been reported for fractionation of metals from air particulate by Lume et al^[14] and Dreetz and Lund^[15]. In this study, Tessier method was followed in order to obtain the concentration of lead in each fraction individually.

The results obtained from the sequential extraction of lead associated with airborne particulate matter are shown in Figure 1. The lead concentration in each fraction is given as the percentage of the total concentration extracted from each sample. Substantial amounts of lead are present in the carbonate, Fe-Mn oxides, and residual fractions. The concentration of lead in residual fraction is in agreement with those reported by Harrison et al^[16] for roadside soils. It is expected that some part of atmospheric lead is related to the road dust and introduced into the atmosphere via a resuspension process.

In order to evaluate the ability of WDXRF technique for the determination of lead in airborne particulate matter, several exposed filters were analysed by both WDXRF and FAAS methods. The results showed that there is a good agreement between the two techniques (Table IV).

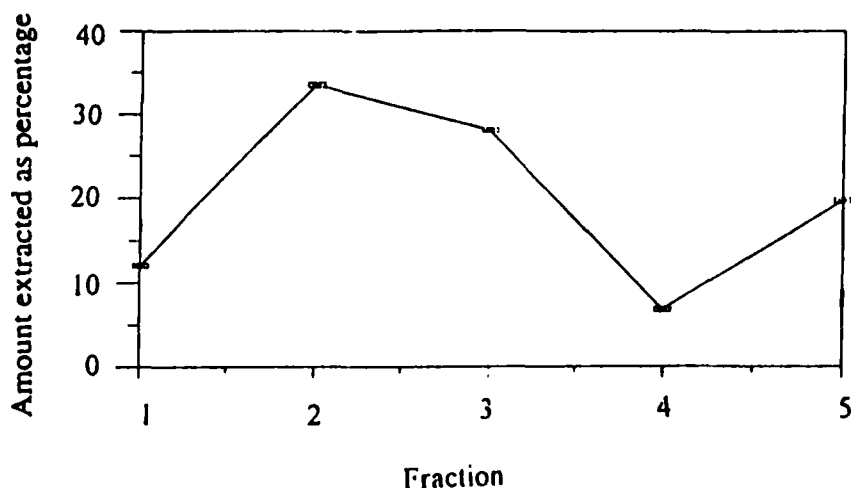


FIGURE 1 Sequential extraction of lead from airborne particulate matter

TABLE IV Comparison of FAAS and WDXRF techniques for the determination of atmospheric lead

<i>Sampling site</i>	<i>No. of samples</i>	<i>Mean + SD FAAS/WDXRF</i>
S1	12	1.09 + 0.14
S2	14	1.16 + 0.3
S3	12	1.10 + 0.19

A comparison between the variation in the concentration of atmospheric lead and that for the other well-known air pollutants was performed in a different sampling station, where the determination of the concentration of PM_{10} , CO, NO, and NO_2 was possible. The sampling period was 12 hours and samples were collected during the days (7 am to 7 pm) and over nights (7 pm to 7 am). The day-time samples contained two traffic rush hours and showed higher concentrations of lead as well as the other air pollutants (Figure 2). However, the similar variation in the concentration of atmospheric lead and the other air pollutants shows that these compounds are releasing into the atmosphere from the same anthropogenic source.

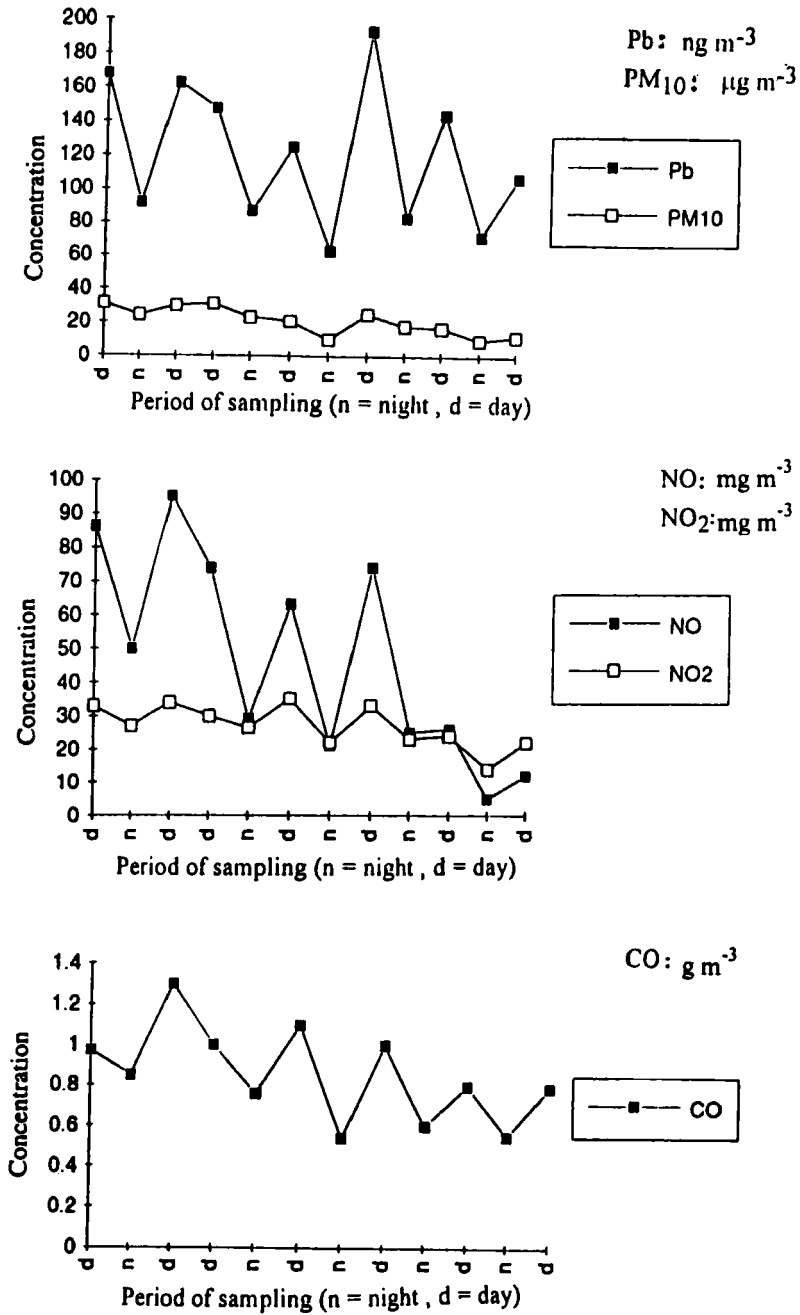


FIGURE 2 Short-term variation in concentrations of lead and some well-known air pollutants

CONCLUSION

From the sequential extraction data, it is apparent that although considerable amount of lead can be introduced into the urban air by exhaust emissions, the introduction of lead via resuspension process is a phenomena that should be noticed especially in the cities like Isfahan which are located in the neighbourhood of desert with a lot of dusts in road-sides. In such an areas a dual role for traffic in introduction of lead into the atmosphere is supposed.

The data generated in this study indicate that WDXRF can be used in place of FAAS for the determination of Pb in airborne particulate matter. Due to the minimal sample preparation and non-destructive nature of the method it could be used in determination of lead in air pollution studies, especially where a huge number of samples must be analysed.

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