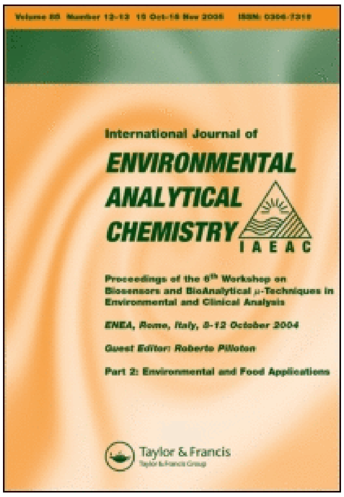

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Determination of Cadmium and Lead in Aerosols in the Zasavje Region in Slovenia Employing Slurry Electrothermal Atomic Absorption Spectrometry

R. Milačič[a]; F. Dolinšek[a]
[a] "Jožef Stefan" Institute, University of Ljubljana, Ljubljana, Jamova 39, Slovenia

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DETERMINATION OF CADMIUM AND LEAD IN AEROSOLS IN THE ZASAVJE REGION IN SLOVENIA EMPLOYING SLURRY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

R. MILAČIČ and F. DOLINŠEK

"Jožef Stefan" Institute, University of Ljubljana, 61000 Ljubljana, Jamova 39, Slovenia

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Investigations of air pollution were carried out in the Zasavje urban industrialized region in Slovenia. Cadmium and lead were measured in respirable (< 2.5 µm) and inhalable (2.5–10 µm) aerosols. Special pumps were equipped with a Nucleopore-Costar polycarbonate membrane filters. Cadmium and lead were measured in those filters by slurry electrothermal atomic absorption spectrometry (ETAAS) on a laboratory-assembled atomic absorption spectrometer with a graphite cup atomizer. A reliability of the employed technique was proved by analysis of the same filters with classical dissolution of aerosol particles in diluted nitric acid and measurement of cadmium and lead by flame atomic absorption spectrometry (FAAS). Good agreement (±5–10%) of the results was obtained between the two techniques for both elements. The study indicated that cadmium and lead in a contaminated area prevailed in the respirable (< 2.5 µm) aerosols. The employed technique was sensitive enough for measurement of cadmium and lead also in non-polluted sites.

KEY WORDS: Air pollution, respirable and inhalable aerosols, cadmium, lead, slurry ETAAS.

INTRODUCTION

Growing environmental concern over the presence of air pollutants has resulted in the development of selective and sensitive measurement techniques for determination of metals[1-8] as well as organic pollutants in aerosols[9-11]. The most commonly used techniques for determination of metals in aerosols being neutron activation analysis[1], X-ray fluorescence[2,3] and flame[4,5] and electrothermal[6-8] atomic absorption spectrometry. The studies of the regional respiratory deposition of inhaled aerosols has shown that deposition efficiency increased with decreasing particle size of aerosols[12,13]. Pollutants bound on these aerosols cause harmful health effects. It is therefore very important to classify the aerosols in various particle size applying appropriate aerosol samplers[2,14]. Separated aerosols are collected on various filters and pollutants measured with an appropriate technique.

Atomic absorption spectrometry is frequently used as an analytical technique for the determination of metals in aerosols[4-8]. In the last decade numerous investigations were carried out on direct determination of metals in solid samples by electrothermal atomic absorption spectrometry[15-21]. This technique was found to be very convenient for direct solid sample analysis by "weighing in"[17,18,21] or by pipetting slurries[15-17,20,21] into a graphite furnace. The technique was verified by applying a comparison analysis to a conventional solution atomization[16–20] or by analysing standard reference materials[20,21]. The main advantage of this technique compared to conventional solution analysis was in the ability to analyse very small quantities of samples and to reduce the possibility of sample contamination.

The aim of our work was to develop a sensitive and reliable analytical procedure for determination of cadmium and lead in respirable and inhalable aerosols. Direct electrothermal atomic absorption analysis was employed by introduction of slurries into a graphite cup atomizer. The technique was verified by applying a comparison analysis with a conventional solution atomization.

EXPERIMENTAL

Instrumentation

Cadmium and lead were measured on a laboratory-assembled atomic absorption spectrometer with a graphite furnace for direct determination of solid samples. The spectrometer was constructed from partly-modified commercial units, laboratory made electronic parts and laboratory-made graphite cup atomizer[21]. The graphite cups used in the present work were of 8 mm o.d., 1 mm wall thickness and 9–12 mm in height.

An atomic absorption spectrometer (Varian AA 5) was used for comparison analysis of cadmium and lead by conventional solution flame atomic absorption spectrometry (FAAS) procedure.

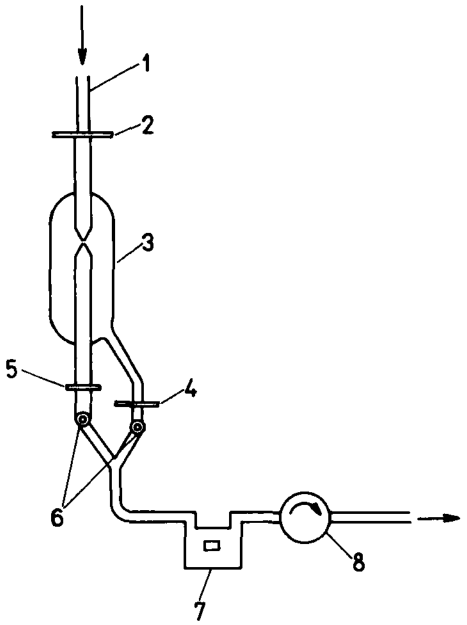

Figure 1 Sampling system for separation and collection of aerosols into particle size < 2.5 μm and 2.5 – 10 μm. 1, plastic tubings for air inlet; 2, plastic net; 3, dichotomous aerosol sampler; 4, membrane filter (d=47 mm) for collection of respirable (< 2.5 μm) aerosols; 5, membrane filter (d=37 mm) for collection of inhalable (2.5 – 10 μm) aerosols; 6, flow rate regulators; 7, flowmeter; and 8, pump.

A system for collection of aerosols is presented in Figure 1. A plastic net (2) was located in the air inlet (1) to retain occasional rubbish. Air samples were pumped with a Gast pump (DAA-Vlll-GD) (8) through a laboratory-assembled glass dichotomous aerosol sampler (3), the construction of which enables to separate aerosols into a particle size < 2.5 µm and 2.5–10 µm[2,14]. The larger aerosol particles (more than 10 µm) were generally not present in the air since they were settled by sedimentation[1]. The separate aerosols were collected on a Nucleopore-Costar polycarbonate membrane filters of pore size 0.4 µm. Respirable (< 2.5 µm) aerosols were collected on filters of 47 mm diameter (4) and inhalable (2.5–10 µm) aerosols on filters of 37 mm diameter (5). Flow rates through the filters were regulated by flow rate regulators (6), so that the volume of pumped air, measured by an Ikom-Rombach flowmeter (7) was about 15 m^3 per day.

A Cole-Palmer (4710 Series) Ultrasonic Homogenizer was used for preparation of sample slurries.

Reagents

Merck suprapur acids and doubly distilled water were used for the preparation of samples and standard solutions. All other chemicals were of analytical reagent grade. Standard stock solutions (1000 µg cm^{-3}) were prepared by dissolving the appropriate salts or metals.

Samples

Respirable (< 2.5 µm) and inhalable (2.5–10 µm) aerosols were collected in polluted sites, in Slovenia, continuously every 10 days. The volume of pumped air was approximately 150 m^3. The sampling system was located in the meteorological stations in Trbovlje, Zagorje and Hrastnik, where automatic measurement of SO_2 pollution, meteorological parameters and suspended particulate matter was carried out. Air was pumped through the plastic tubings placed outside the stations at one meter above the ground. For the control site, a non-polluted area was found in the small Slovenian mountain village of Otlica, located away from the industry and traffic. Aerosols in this area were collected for 30 days (the volume of pumped air was approximately 450 m^3) to enable determination of very low concentrations of cadmium and lead. The concentrations of both elements were expressed in ng m^{-3} to enable the direct comparison between the polluted and non-polluted areas.

Sample preparation and analytical procedures

After collection of aerosols, cadmium and lead were measured in filters employing direct determination by ETAAS. Direct "weighing in" technique was found to be liable to severe matrix effect interferences of polycarbonate membrane filters on atomization of cadmium and lead. A slurry technique, avoiding the ashing of filter, was found to be very convenient for these type of analysis and was applied in the present work. The filter was placed into a narrow glass cylinder (10 cm^3). Then, an appropriate amount of water (2–4 cm^3) was added. Aerosol particles were slurried by ultrasonic agitation (120 W power ultrasonic output) using an ultrasonic device with a 3 mm diameter titanium probe. The ultrasonic application continued 6 times for 30 seconds with 10 seconds interruption for cooling of the titanium probe. The filter, remaining completely white after sonification, was left in the cylinder and the slurry analysed immediately by pipetting 5–10 mm^3 directly into the graphite cup atomizer. Six replicate measurements were made for one determination of cadmium or lead. Aqueous standard solutions were used for calibration.

Analysis of cadmium and lead were carried out under the optimal conditions of measurements[21]. The efficiency of filter washing was controlled by the analysis of a second ultrasonic treatment. When filters became completely white, this treatment gave results below the detection limit. The same feature was observed when the blank filter was treated with the ultrasonic procedure. The blank values for the filters themselves were also below the limit of detection.

For comparison measurements a conventional dissolution procedure of aerosol particles was applied. To a half of a filter, 3 cm^3 of diluted nitric acid (1+2) was added, carefully warmed to approximately 323°K to dissolve the aerosol particles, and evaporated almost to dryness. The residue was filtered and quantitatively transferred into a 5 cm^3 volumetric flask. Cadmium and lead were analysed in these solutions by FAAS.

RESULTS AND DISCUSSION

Comparison between slurry atomization by ETAAS and conventional solution FAAS analysis. The reproducibility of measurements and limits of detection

A slurry atomization technique by ETAAS was previously verified by the analysis of standard reference materials[20,21] as well as by the conventional solution atomization[15–19]. There are no data available in the literature on the analytical procedure for direct determination of aerosols employing slurry atomization. The accuracy of the procedure developed in our laboratory depended mostly on the efficiency of filter washing. Particles of the aerosols should be completely removed from the filter surface. For that purpose the parameters of ultrasonic agitation should be carefully adjusted. The proposed procedure was verified for the analytical use. Filters were cut by halves and each half analysed for cadmium and lead by slurry ETAAS and conventional solution FAAS techniques. The mean ($\bar{x}$) and standard deviation (σ) were calculated from at least six consecutive measurements using either the slurry procedure or the conventional solution technique. The results of these measurements are summarized in Tables 1 and 2. It is evident from Tables 1 and 2 that the reproducibility of measurements is ± 10% for slurry ETAAS and ± 5% for solution FAAS techniques. The results obtained by the slurry ETAAS technique, with the exception of one sample, are closely matched with those by conventional solution FAAS. The agreement between the two techniques for both elements being in general ± 5–10%.

The sensitivity of the slurry ETAAS technique for determination of cadmium and lead was demonstrated by the analysis of aerosols in the non-polluted site, in the Slovenian village Otlica. The results of these measurements are presented in Table 3. It is evident from Table 3 that the technique was sensitive enough for the determination of cadmium and lead in a non-polluted area. The results indicated that both elements prevailed in the coarser aerosol particles (2.5–10 μm), originating mainly from the land surface by the action of the wind. On the contrary, the concentrations of these two elements in the polluted area (Tables 1 and 2) were higher in smaller aerosol particles (< 2.5 μm), originating mainly from combustion sources and other industrial activities. The LOD (3 σ) for the determination of cadmium and lead in aerosols by the slurry ETAAS technique

Table 1 Determination of cadmium in aerosols in the Zasavje region by slurry ETAAS and conventional solution FAAS techniques. Sampling in October 1993.

Site	*Particle size (μm)*	*Slurry ETAAS* $\bar{x} \pm \sigma$ *(ng m⁻³)*	*Solution FAAS* $\bar{x} \pm \sigma$ *(ng m⁻³)*
Trbovlje	< 2.5	0.29 ± 0.03	0.24 ± 0.01
	2.5 – 10	0.22 ± 0.02	0.20 ± 0.01
Zagorje	< 2.5	0.26 ± 0.03	0.23 ± 0.01
	2.5 –10	0.04 ± 0.01	0.06 ± 0.01
Hrastnik	< 2.5	0.20 ± 0.02	0.22 ± 0.01
	2.5 – 10	0.10 ± 0.01	0.08 ± 0.01

Table 2 Determination of lead in aerosols in the Zasavje region by slurry ETAAS and conventional solution FAAS techniques. Sampling in October 1993.

Site	*Particle size (μm)*	*Slurry ETAAS* $\bar{x} \pm \sigma$ *(ng m⁻³)*	*Solution FAAS* $\bar{x} \pm \sigma$ *(ng m⁻³)*
Trbovlje	< 2.5	86 ± 8	80 ± 4
	2.5 – 10	47 ± 5	53 ± 2
Zagorje	< 2.5	31 ± 3	36 ± 2
	2.5 – 10	6 ± 1	5 ± 1
Hrastnik	< 2.5	25 ± 3	29 ± 2
	2.5 – 10	11 ± 1	12 ± 1

Table 3 Determination of cadmium and lead in aerosols in the non-polluted site by slurry ETAAS technique. Sampling in September 1993.

Site	*Particle size (μm)*	*Cadmiun* $\bar{x} \pm \sigma$ *(ng m⁻³)*	*Lead* $\bar{x} \pm \sigma$ *(ng m⁻³)*
Otlica	< 2.5	0.05 ± 0.01	1.8 ± 0.2
	2.5 – 10	0.10 ± 0.01	3.7 ± 0.4

expressed as absolute amount of cadmium and lead in the graphite cup was found to be 0.005 ng and 0.1 ng, respectively. The LOD (3σ) for conventional solution FAAS analysis of aerosols was found to be 5 ng m^{-3} for cadmium and 100 ng cm^{-3} for lead. Depending on the concentration of these two elements in the air, an appropriate volume of sample should be collected in older to ensure enough sample for the analysis. By performing analysis of cadmium and lead in air with slurry ETAAS, this volume should be about 450 m^3 in non-polluted areas.

The advantages of the slurry ETAAS in comparison with the conventional solution FAAS technique for the determination of cadmium and lead in aerosols are: shorter time of analysis, reduced possibility of contamination during the analytical procedure and lower detection limits. Considering all these benefits and the reliability of the results, slurry ETAAS was found to be the technique of choice for the determination of cadmium and lead in aerosols.

Analysis of aerosols in the Zasavje region in the heating season 1992–1993

The developed analytical procedure for determination of cadmium and lead by slurry ETAAS was applied to the study of air pollution in the Zasavje region. Three 10 days measurements within one month (expressed in ng m^{-3}) were summed up and divided by 3 to get the average monthly concentrations. The data for cadmium and lead in respirable (< 2.5 µm) and inhalable (2.5–10 µm) aerosols in the heating season 1992–93 are presented in Figures 2 and 3. It is evident that cadmium and lead prevailed in respirable (< 2.5 µm) aerosols. Data from Tables 1 and 2 indicated similar features. It is also evident that all concentrations for cadmium and lead are higher from those of the non-polluted area (Table 3). The concentrations of cadmium in respirable (< 2.5 µm) aerosols (Figure 2) are 4–12 times higher, while for lead this enhancement is 10–100 times (Figure 3). The highest concentrations for both elements (with the exception of November 1992 in Zagorje) were found in Trbovlje and Hrastnik in the top of the heating season in January and February 1993 due to unfavourable meteorological conditions (frequent thermal inversions). The degree of air pollution with cadmium is similar in all three locations. On the contrary, measurements for lead indicated higher pollution in Zagorje and Trbovlje and essentially lower in Hrastnik where the meteorological station is located out of the center of the city.

CONCLUSIONS

A slurry ETAAS technique was developed for determination of cadmium and lead in respirable (< 2.5 µm) and inhalable (2.5–10 µm) aerosols. The accuracy of the procedure depended mostly on the efficiency of filter washing, so the parameters of ultrasonic agitation should be carefully adjusted. A reliability of the employed technique was verified by conventional solution FAAS analysis. Good agreement (± 5–10%) of the results was obtained between two techniques for cadmium and lead. The technique was successfully applied in investigations of air pollution in the Zasavje urban region in Slovenia as well as in a non-polluted area. The study indicated that cadmium and lead in contaminated areas prevailed in the respirable (< 2.5 µm) aerosols. Compared with the non-polluted area the concentrations of cadmium and lead were 4–12 and 10–100 times higher, respectively.

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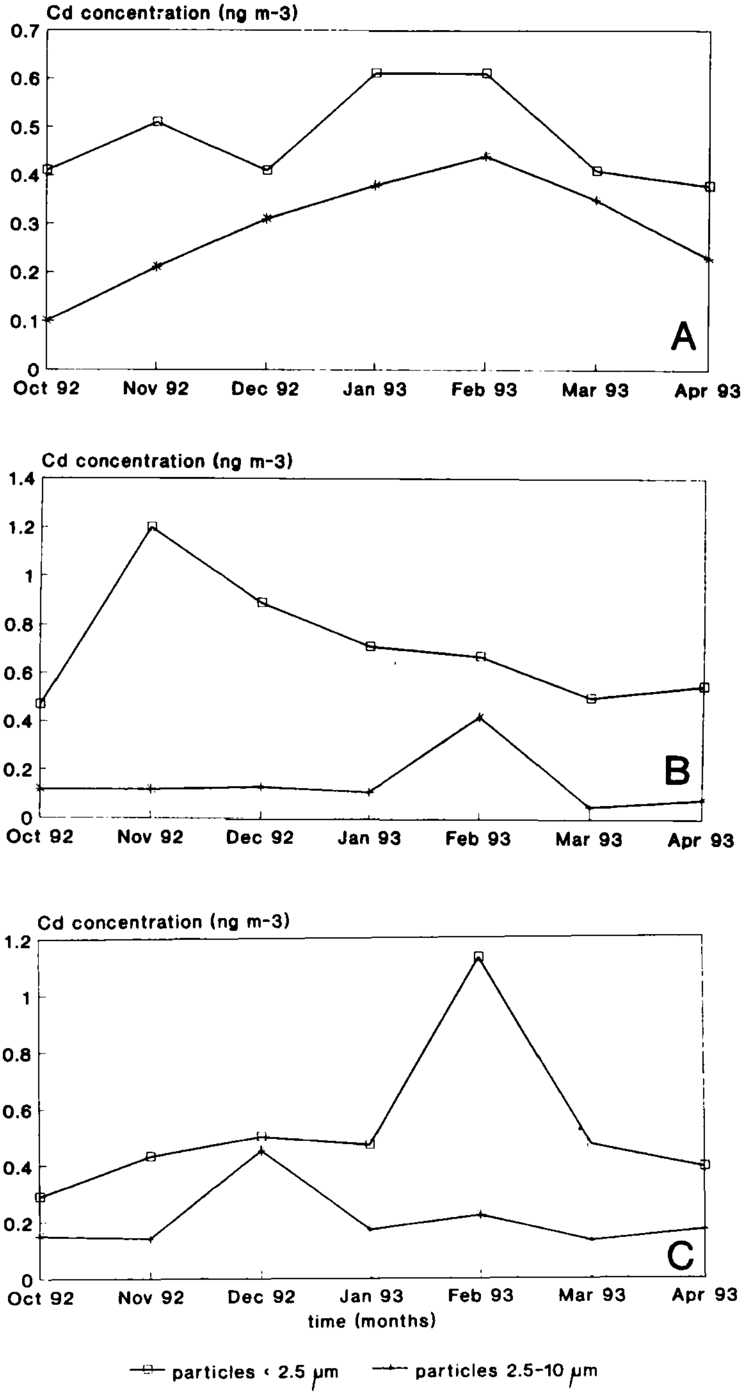

Figure 2 Average monthly concentrations of cadmium in respirable (< 2.5 μm) and inhalable (2.5 – 10 μm) aerosols in Zasavje region by slurry ETAAS in the heating season 1992 – 93: A – Trbovlje; B – Zagorje; and C – Hrastnik.

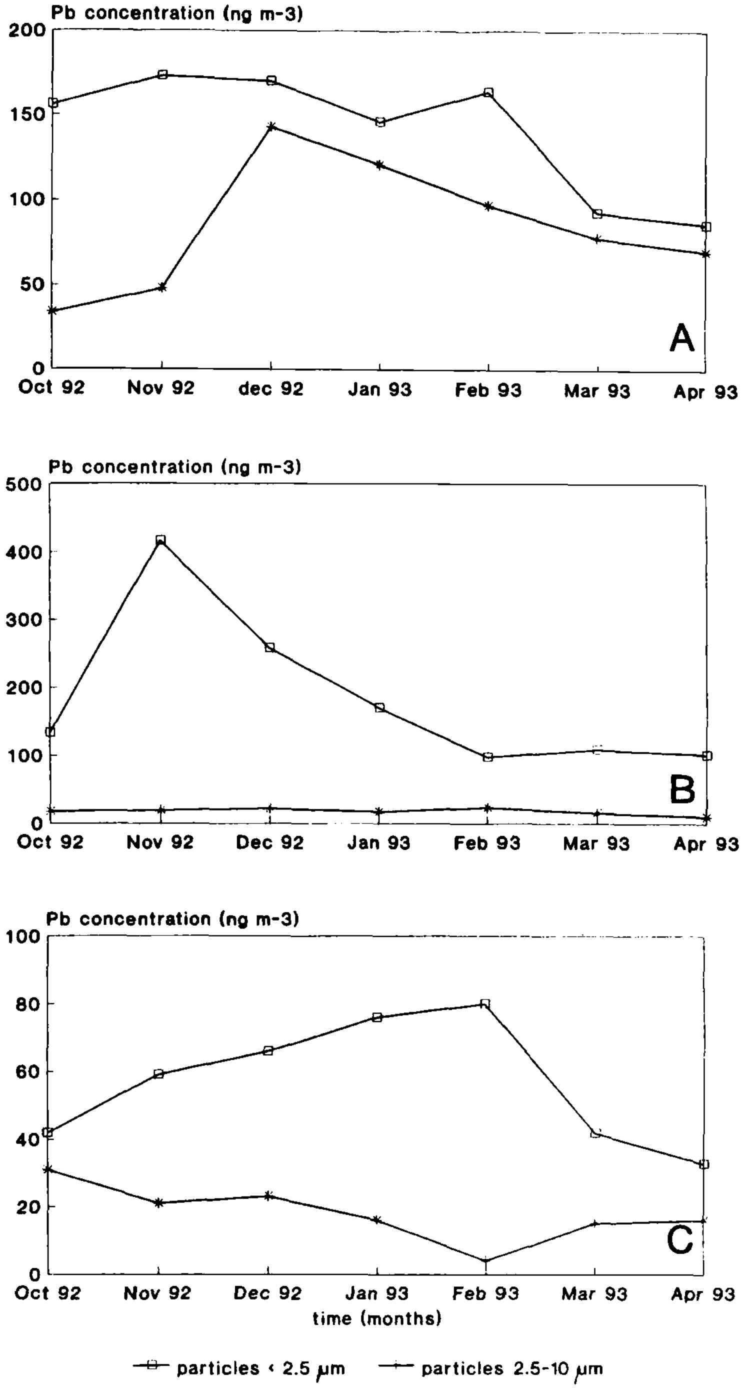

Figure 3 Average monthly concentrations of lead in respirable (< 2.5 μm) and inhalable (2.5 – 10 μm) aerosols in Zasavje region by slurry ETAAS in the heating season 1992–93: A – Trbovlje; B – Zagorje; and C – Hrastnik.

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