ON-LINE PRE-CONCENTRATION AND SIMULTANEOUS STRIPPING VOLTAMMETRY ANALYSIS OF AIRBORNE ZINC, LEAD AND CADMIUM TRACES

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ABSTRACT

A Venturi-scrubber pre-concentration device used in conjunction with square wave anodic stripping voltammetry (SW-ASV) has been developed for simultaneous determination of heavy metals in contaminated airborne matter. The method was tested using various zinc, lead and cadmium mixtures. These were performed using contamination controlled air intakes. Successful analytical interpretation of the experimental results was achieved. Methods detection limits range from 1 ng/m^3 for Cd(II) to 3 ng/m^3 for Zn(II). The method was also applied to determination of lead and zinc in local ambient air (resulting in lead and zinc concentrations of about 10 ng/m^3). The data was validated with conventional filter sampling analysis. The method offers in-situ capabilities of pre-concentration routines, and avoids most of procedural complexities, which are commonly found in similar applications.

INTRODUCTION

Heavy metals are recognized as important elements from the perspective of human and environmental health because of their high toxicity even at very low concentrations /1,2/. Many of them originate in industry and get released into the atmosphere. The characteristic of ambient air is therefore necessary to discover the extent of such metal contamination and to control the dangerous dumping. In addition, knowledge of heavy metal concentrations and distribution in ambient air provides valuable information on the pollution source.

Traditionally, the methods for characterizing heavy metal traces in contaminated air involve using of filter-based sampling and pre-concentration followed by atomic absorption spectrometry (AAS) analysis /1-3/. Because of the low concentrations involved, undesirable sample losses are expected during sampling and filter extraction steps. Furthermore, metal-content measurements have to be performed quickly upon sampling, because of a possible change in species distribution during storage and transport of the samples.

Electroanalysis is a very powerful tool for studying metallic traces /4/. Among these techniques the anodic stripping voltammetry (ASV) is the most useful one owing to its user-friendly operational routine as well as great selectivity and sensitivity to a number of environmentally important metals /5,6/. The major advantage of ASV over AAS is its ability to monitor simultaneously even extremely low levels of hazardous metallic traces (without chemical-separation stages) /6/. Although most of the ASV measurements are carried out onto environmentally relevant aqueous samples, there are several ASV-based approaches, which utilize filter sampling facilities for detecting ambient traces of heavy metals /7-11/.

Here we report measuring trace amounts of airborne zinc, lead and cadmium simultaneously at low detection limit. Similar to our recent studies /12/ Venturi-scrubber based aerosol sampling was employed in conjunction with square wave anodic stripping voltammetry (SW ASV). The method was applied to samples collected from local ambient air. The major objective of the method is the development of an on-line analytical procedure, which requires no filter sampling or any sample preparation steps.

EXPERIMENTAL

Venturi Apparatus:

The sampling and pre-concentration facility used was described in our previous report /12/. Briefly speaking, we replaced the conventional (filter-based) sampling with a Venturi scrubber based device. The sample accumulation occurs in the sampling container, containing the collecting liquid (0.1 M HNO_3) enriched by the contaminant ions. This way, the filter extraction step is excluded.

Electroanalytical measurements:

The square wave anodic stripping voltammetric experiments were performed using PARC model 309 Automatic Voltammetric Electrode, coupled to a model 384B Polarographic Analyzer (EG&G, Parc). The reference and auxiliary electrodes were Ag/AgCl saturated KCl, and platinum wire placed in a mercury pool, respectively. Deposition and rest times for each experiment were 60 s and 5 s respectively.

The SW AS voltammograms were recorded from an initial potential of –1.25 V to –0.3 V at a scan rate of 200 mV/s. Backgrounds checks were made using 25 ml of supporting electrolyte (0.1 M HNO_3) before measuring each sample. The cell and the electrodes were rinsed with purified water between the measurements.

Reagents and solution preparation:

The target lead-, cadmium- and zinc- containing materials were prepared from analytical grade chlorides (Merck-reagents). The particle size of the salts used was 20-50 μm. Atomic absorption (AA) standard solutions of lead, cadmium and zinc (1000 mg/ml each) and nitric acid (Ultrapure reagent) were obtained from Merck. All solutions were prepared with purified water (Seralpur UP 50 system, Seral).

ANALYTICAL SCHEME

Sampling and pre-concentration procedure:

Figure 1 shows the experimental arrangement used for sampling, pre-concentration and analysis of lead, cadmium and zinc in air samples. This setup includes both the proposed technique and the parallel standard validation method. The analytical procedure of this system involves three stages:

(1) A flow of contaminated air was drawn through the glass fiber filter (Staplex), joined on Staplex Hi-Volume Sampler (*3* in Figure 1) inlet. The flow rate was measured by flow meter *2*. Then the sampled metal containing contaminants were extracted from the filter by 0.1M HNO_3 solution.

(2) The lead, cadmium and zinc contaminated air intakes were forced via a 30 mm hole in the filter tightly attached to the sampler's *2* inlet towards the

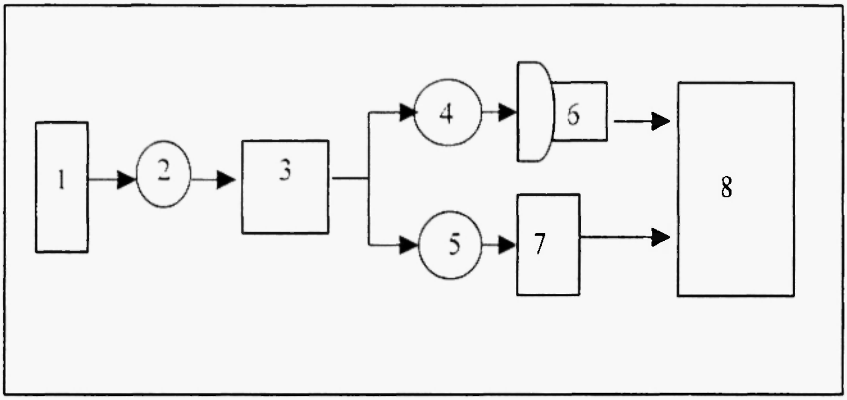

Fig. 1: Schematic diagram of the sampling and pre-concentration system equipped with electroanalytical detector. 1- Contaminant mixture, 3 – Staplex Hi-Volume sampler, 2, 4, 5 – flow meters, 6 – filter holder with glassy fiber filter, 7 – Venturi-based sampler, 8 – polarographic analyzer

pre-concentration set-up. The sampling/pre-concentration system contains two sub-systems: glassy fiber filter sampler, depicted in Figure 1 by *6* and Venturi-scrubber-based apparatus (*7* in Figure 1). The gas flow rate at the inlet of sampling device *6* was equal to that of *7*. The flow rates were measured using flow meters *4* and *5*, respectively to *6* and *7*. The filter was treated with 0.1 M HNO_3 to extract the metal ions.

(3) The lead, cadmium and zinc ions containing solutions obtained by extraction of filters in previous experiment stages and the collection solution from the Venturi-device were analyzed using SW ASV measurements.

Samples quantification and calibration:

Calibration graphs were prepared by plotting the concentration of each metal ion (μg l^{-1}) against the peak height (nA). The covered concentration range of Pb(II) and Cd(II) was 0.1 - 50 μg l^{-1} and of Zn(II) was 0.5 - 50 μg l^{-1}.

RESULTS AND DISCUSSION

Analysis of lead, cadmium and zinc containing particulates:

Direct analysis of airborne heavy metals in a mixture would allow rapid *in situ* analysis of contaminated air and screens to find the valuable information for their source of origin.

For demonstrating the principle, experiments were performed using fixed (by weight) mixtures of lead, cadmium and zinc chlorides. Blowing mixtures of the metal chlorides produced the contaminated air inflows. The air samples were treated as described in the analytical scheme.

Figure 2 presents typical AS SW voltammograms for the sample containing lead, cadmium and zinc obtained in various steps of the experiment. The stripping peak potentials were –0.472 V, -0.670 V, and -1.102 V for, respectively, lead, cadmium and zinc.

Figure 2A shows voltammograms corresponding to stage (1): sampling of particles at the air blower input. Figure 2B and 2C present voltammograms obtained by extraction of filter *6* (see in Figure 1) before and after pre-concentration on the filter, respectively.

Figure 2D shows voltammograms measured in collection solution from the Venturi sampling device. It can be seen that the pre-concentration results in Figures 2C and 2D agree very well with the initial sample measurement, depicted in Figure 2A. The initial mixture contained one part of Cd, one part of Pb and two parts of Zn.

Figure 3 presents the averaged result of four measurements for pre-concentrated metals in the same mixture. It is evident that the data are not distorted by the pre-concentration procedure.

The sampling data for various metals mixtures are presented in Table 1. Note, that the composition of the mixtures (by weight) were chosen to produce contaminant inflows at fixed mass flow rates according to the metals' content in correspondent metal chloride. It can be concluded that the pre-concentrated samples keep this composition proportional to the metal distribution in the initial inflow.

Detection limits

In respect of these, the pre-concentration times in Venturi-sampling and stripping analysis facilities as well as the air flow-rates are strongly device-

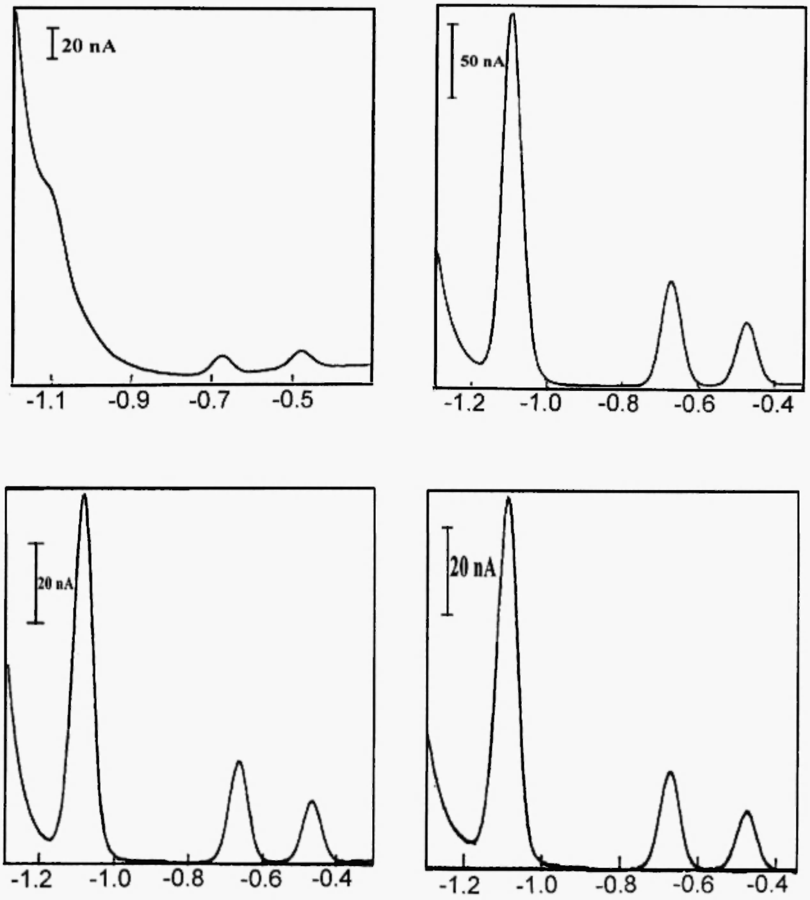

Fig. 2: **A** – SW AS voltammograms for Zn, Cd and Pb in sample collected in step (1). The collection time is 60 min. **B** - SW AS voltammograms for Zn, Cd and Pb in sample collected in step (2). The collection time is 5 min. **C** – SW AS voltammograms for Zn, Cd and Pb in sample collected on glassy fiber filter in step (2). The collection time is 60 min. **D** – SW AS voltammograms for Zn, Cd and Pb in sample collected using Venturi-device in step (2). The collection time is 60 min. AS SWV conditions: Deposition time 2 min at –1.25 V vs. Ag/AgCl. Potential scan rate 200 mV/sec.

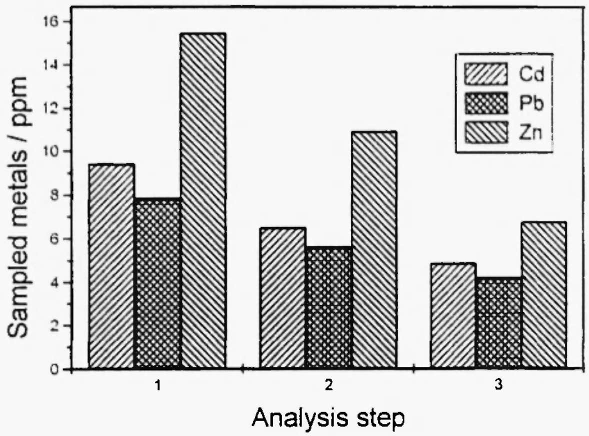

Fig. 3: Cadmium, lead and zinc concentrations (ppm) determined in air sample containing Cd, Pb and Zn in relation 1:1:2 (by weight of the metal), respectively.

Table 1

Lead, cadmium and zinc concentrations collected during 60 min from various mixtures

Composition of the mixture by weight of the metal chloride			Amount of metal sampled by filter in step (1) ppm			Amount of metal sampled by filter in step (2) ppm			Amount of metal sampled using Venturi-device in step (2) ppm		
Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn	Pb	Cd	Zn
1:	1.2 :	1.5	8.1	8.2	7.7	6.5	6.1	5.55	4.7	5.1	3.2
1 :	1.2 :	3	7.5	7.8	15.1	6.2	6.2	11.3	4.4	4.4	8.6
1 :	2.4 :	1.5	8.6	16.9	7.9	6.8	12.2	2.9	5.1	9.1	3.1
2 :	1.2 :	1.5	17.2	7.9	7.6	14.2	5.97	5.2	8.5	4.9	3.4
2 :	2.4 :	1.5	15.6	17.1	8.2	13.7	11.2	5.4	8.2	9.8	3.8
2 :	1.2 :	3	14.7	6.9	17.4	12.1	4.2	10.8	8.8	2.5	9.1
1 :	2.4 :	3	7.2	16.1	15.4	6.5	12.3	10.1	5.2	10.2	8.7

specific. Hence the absolute detection limits of the method for these elements turn out to be difficult for rigorous analytical modeling.

However, the detection limit can be calculated from the defined time (and rate) of sampling and electrolysis. The detection limits of anodic stripping analysis with 1 min pre-electrolysis were 0.2, 0.1 and 0.3 $\mu g/l^{-1}$ for Pb(II), Cd(II) and Zn(II), respectively. Thus, for a 60 min sampling time at flow rate of 0.04 m^3/min, the limit of detection was calculated to be 2, 1, 3 ng/m^3 for Pb(II), Cd(II) and Zn(II), respectively. It is evident that, by choosing appropriate pre-concentration/pre-electrolysis times as well as by establishing desirable air influxes, by far lower limits of detection could be obtained.

Analysis of real sample

Figure 4 shows the ASV tracing for laboratory air sample at 360 min sampling. The electrode response indicates the presence of 5.9 $\mu g/l^{-1}$ of lead and 6.0 $\mu g/ l^{-1}$ of zinc. Cadmium is below the detection limit. Thus for the lead- and zinc- contaminated air inflows the corresponding metal contents

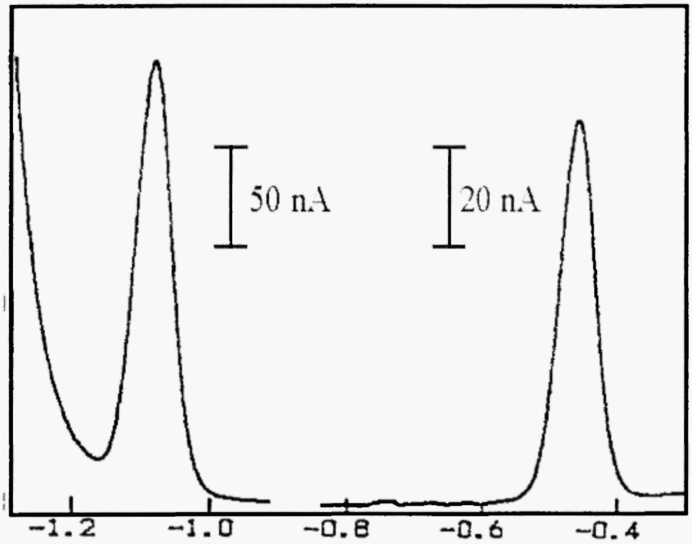

Fig. 4: SW AS voltammograms for Zn and Pb in a sample collected from the laboratory air. The collection time is 6 hr. AS SWV conditions: Deposition time 2 min at −1.25 V vs. Ag/AgCl. Potential scan rate 200 mV/sec.

were 0.012 μg/m^3 for Pb and 0.015 μg/m^3 for Zn. The sample was also analyzed using the conventional filter sampling. The determined concentrations were 0.017 μg/m^3 for Pb and 0.018 μg/m^3 for Zn. At this stage, it can be concluded that, for particulate metallic contaminants, our approach appears less efficient than the filter-sampling ones. However, we plan to improve sampling efficiency and, hence, the sensitivity of the method.

CONCLUSIONS

The application of Venturi-scrubber pre-concentration followed by SW ASV (square wave anodic stripping voltammetry) analysis, with a HMDE (handing mercury drop electrode), to simultaneous determination of cadmium, lead and zinc in airborne particulate matter is discussed.

Practical quantification limits of 0.01μg/m^3 have been demonstrated; improved sampling efficiency would result in higher sensitivity of the method to ambient metallic traces.

Coupling electrochemical instrumentation with *on-line* collection and pre-concentration has several advantages as it decreases the risk of contamination, eliminates collection and storage of samples, and provides information on ambient metal contaminants distribution in real time.

REFERENCES

1. E. Berman, *Toxic Metals and Their Analysis*, Heyden and Son:London, 1980.
2. N.I. Ward, *Trace elements*, in: *Environmental Analytical Chemistry*, ed. by F.W. Fifield, P.J Haines, Academic and Professional: London, 1995.
3. C. Vandecasteele, C.B. Block, *Modern Methods for Trace Element Determination*, Wiley: Chichester, 1993.
4. K. Asbley, *Electroanalysis*, 6, 805 (1994).
5. Kh. Brainina and E. Neyman, *Electroanalytical Stripping Methods*, in: *Chemical Analysis*, ed. by J. D. Winefordner, Wiliy: New York, 1993, V. 126.
6. J. Wang, *Stripping Analysis*, VCH Publishers: Deerfield Beach, FL, 1984.

7. G. Golovos, G.S. Wilson and J. Moyers, *Anal. Chim. Acta*, **64**, 457 (1973).
8. G. Golovos, G.S. Wilson and J. Moyers, *Int. J. Environ. Anal. Chem.*, **3(3)**, 239, (1974).
9. R.N. Khandekar, R.G. Dhaneshwar, M.M. Palrecha and L.R. Zarapkar, *Fresenius' Z. Anal. Chem.*, **307(5)**, 365, (1981).
10. J. Hertz, I. Schmidt and L. Thoeni, *Int. J. Environ. Anal. Chem.*, **17**(1), 1, (1984).
11. E. Casassas, A.M. Perez-Vendrell, and L. Puignou, *Int. J. Environ. Anal. Chem.*, 45(1), 55, (1991).
12. I. Belostotsky, V.V. Gridin, I. Schechter, and Ch.N. Yarnitzky, Reviews in Anal. Chem., 18(5), 243, (1999).