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AN IMPROVED VOLTAMMETRIC PROCEDURE FOR THE DETERMINATION OF Zn, Pb, Cd AND Cu IN ATMOSPHERIC AEROSOLS

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An improved anodic stripping voltammetric procedure for the simultaneous determination of Zn(II), Cd(II), Pb(II) and Cu(II), which uses a mixed technique (DP-AC₁-DP) for potential scanning in the stripping step, is developed. A small-volume electrolysis cell (1-mL) is used requiring rather small amounts of aerosol sample. The procedure reaches a low detection limit in the determination of some of the ecotoxic metals which are found at very low concentration range in atmospheric aerosols. Thus, it enables the study of short-term variations in the atmospheric pollution caused by these metal ions. The figures of merit of the method are given, and the minimum values of the concentration ratios of the four metal ions for no interference due to intermetallic effects are determined. The improved ASV method has been applied to check two suburban industrial areas near Barcelona which can be carried out on samples collected over 1-hour and even 1/2-hour periods.

KEY WORDS: Atmospheric aerosols analysis, anodic stripping voltammetry, microanalysis, trace and ultratrace metal analysis.

Anodic stripping voltammetry (ASV) is increasingly used for the simultaneous determination of metal ions at the trace and ultratrace levels, because of its high accuracy, good precision, and very low levels of detection¹⁻⁷. It has found application for the analysis of atmospheric aerosols where the usually very small samples may contain some metal ions at very low concentrations. Thus, among others, Guillain⁸ determined Zn, Cu, Cd, Pb, Sb and Bi in aerosols through pre-electrolysis on a HMDE followed by a differential-pulse potential scan (DP-ASV), and Debbag⁵ studied the determination of Pb and Cu in aerosols by ASV on a thin-layer electrode (TLME).

Several authors^{9,10} reported some important drawbacks in the simultaneous individual determination of certain metal ions in atmospheric aerosols, mainly due to the interactions which are effective on the electrode surface among the deposited metals and which can affect the stripping potentials and/or the shape of the stripping peaks, specially when a TLME is used. Thus, Copeland *et al.*¹¹ described the formation of intermetallic compounds with Cu and Zn, or with Cu and Cd, which are stripped at about the same potential as copper; and Wiss *et al.*⁴ reported also that the magnitude of the effect caused by copper on the peak of zinc is strongly dependent on the concentration ratio of both elements.

Another drawback stems out from the very low concentration range at which some of the ecotoxic metal ions, such as Cu and Cd, are present in atmospheric aerosols.

A very long sampling time is required in order to get measurable amounts of these metals (and thus, it is only possible to obtain average values over these rather long times), or a small-volume electrolysis cell must be used in order to reduce to a minimum the required volume of working solution and avoid excessive dilution of the sample, which would reduce⁵ the sensitivity of the procedure.

In the present work, the instrumental parameters and the experimental conditions are optimized for the ASV procedure for the simultaneous determination of Zn(II), Cd(II), Pb(II) and Cu(II) ions in aerosol samples; the minimum values of the concentration ratios of the four metal ions for no interference due to intermetallic effects are determined, and the application field of the method is defined. On the other hand, a working procedure is developed which uses a 1-mL cell for the electrolytic work and a mixed technique for potential scanning (DP-AC₁-DP) in the stripping step. The procedure shows very low absolute limits of detection, requires rather small amounts of aerosol sample, and allows the measurements of averages over rather short sampling times, enabling the study of short-term variations in the atmospheric pollution caused by the studied metal ions.

EXPERIMENTAL

Reagents and solutions

10^{-3} mol.L⁻¹ stock solutions of metal ions (Cd(II), Zn(II), Cu(II) and Pb(II)), containing a little free nitric acid (pH: 3.9) were prepared from pure metals or from their nitrates (all Merck, reagent grade) and standardized through EDTA titration. 10^{-1} mol.L⁻¹ potassium nitrate (Merck, reagent grade), acidified with nitric acid to pH 3.9, was used as background electrolyte. Water used for preparation of all solutions was ultrapure water obtained from Culligan system ($0.08 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$). Nitrogen gas was purified by successively bubbling through vanadium(II) perchlorate in perchloric acid, sodium hydroxide, water and the background electrolyte solution.

Instruments

Polarograph Metrohm Herisau E 506 Polarecord equipped with a E 505 Polarographic Stand and a three-electrode cell. A Metrohm EA-209/2 HMDE was used as a working electrode; a Metrohm 441/5 Ag/AgCl electrode as a reference; a Pt foil (Metrohm 285) as a counter-electrode.

Spectrophotometer Perkin Elmer 4000 atomic absorption spectrophotometer.

pH-Meter Metrohm Herisau E 350-6 with a combined glass-calomel electrode (Radiometer GK2401B).

An Agla Micrometer Syringe outfit (Bourroughs Ltd.) was used as a burette. All experiments performed at the microscale used a cylindrical, flat-bottomed 1-mL glass cell (Afora V-41628).

ANALYTICAL PROCEDURE

Instrumental working conditions are: pre-electrolysis potential, -1.20 v; scanning range, $+1.5$ v; scanning rate, $15 \text{ mv}\cdot\text{s}^{-1}$; pulse amplitude (for DP-stripping), 40 mv ; AC-potential amplitude (for AC_1 scanning), 20 mv .

Into the micro-cell, a 1-mL volume of the test solution is added, containing $0.1 \text{ mol}\cdot\text{L}^{-1}$ KNO_3 at pH 3.9 and suitable amounts of the metal ions to be determined, in the following ranges: $13.7\text{--}900 \text{ ng Zn(II)}$, $5.25\text{--}990 \text{ ng Cd(II)}$, $6.69\text{--}840 \text{ ng Pb(II)}$ and $7.24\text{--}350 \text{ ng Cu(II)}$. Purified nitrogen gas is bubbled for 5 min through the test solution, a convenient mercury drop is prepared at the HMDE (for instance, a $2.20 \pm 0.05 \text{ mm}^2$ drop corresponding to four micrometer divisions) and the solution is pre-electrolyzed for 5 min at -1.2 v, with stirring. After 1 min rest period, the metal stripping is performed and the stripping peaks are recorded. The potential scan for the stripping is run as follows: it is started at the DP-mode; after the peak for Zn is recorded the mode is turned to the AC_1 -mode for cadmium and lead signals to be registered; then, the DP-mode is restored for the final copper stripping.

Quantitation is performed by the standard addition method, additions being made with the Agla microsyringe. The simultaneous determination of the four metals can be performed in the same aliquot if they are present in amounts within the before mentioned ranges and their concentration ratios are within the tolerance limits (given later in this paper) below which no perturbation appears from intermetallic compounds formation.

Procedure for analysis of atmospheric aerosols

Samples are collected for 1-to-24-h periods in a high-volume sampler on cellulose ester filters ($0.3 \mu\text{m}$ pore diameter, 15-cm diameter) with a circular exposed area of 12.3-cm diameter. A piece of $1/8$ of the filter is cut off for analysis. This piece is treated in a beaker with 6 mL conc. HNO_3 (Merck, 65%, reagent grade) at 165°C over a sand bath until it is fully decomposed, adding small amounts of HNO_3 as required to maintain the volume¹². The resulting gel is filtered and washed through a Whatman 41 filter paper; the filtrate is clear and colourless and a small white residue, or no residue, is left. The filtrate is evaporated to dryness.

The residue is taken into solution with the minimum possible amount of 10% HNO_3 , this is quantitatively transferred to a 10-mL volumetric flask, its pH is adjusted to 3.9 and it is made up to volume by adding the suitable quantity of KNO_3 $0.1 \text{ mol}\cdot\text{L}^{-1}$. This is the test solution for Zn, Cd, Pb and Cu determination according to the procedure above described. A blank is equally run from a non-used filter.

RESULTS AND DISCUSSION

Selection of the stripping mode

For each one of the metal ions under study, taken individually and at several different concentrations, ASV experiments were made with the methodology described under

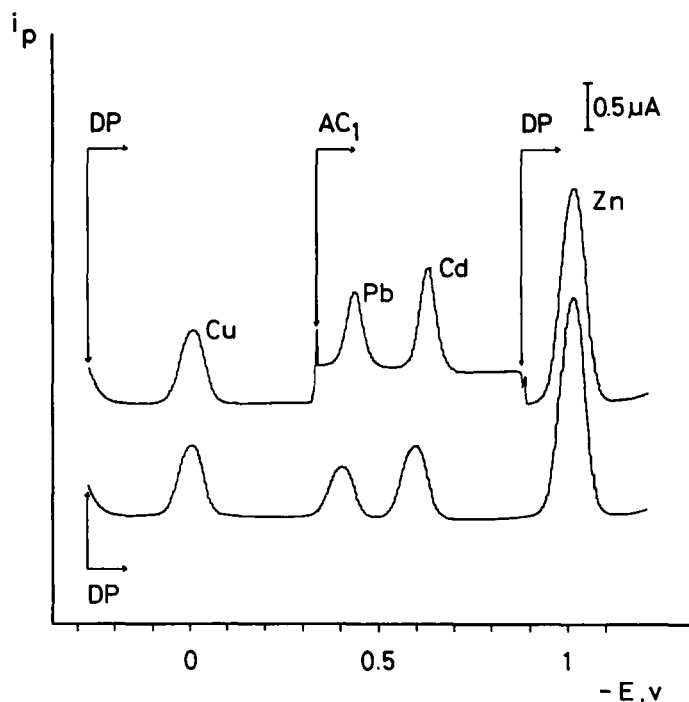


Figure 1 Influence of the AC_1 -stripping mode on voltammogram. $Zn(II)$, $2.54 \cdot 10^{-5}$ M; $Cd(II)$, $1.42 \cdot 10^{-6}$ M; $Pb(II)$, $5.80 \cdot 10^{-7}$ M; $Cu(II)$, $2.92 \cdot 10^{-6}$ M. (Experimental conditions as given in the text; pre-electrolysis time: 3 min).

“Analytical Procedure” using lineal sweep (DC), differential pulse (DP), fundamental alternating current (AC_1) and second harmonic alternating current (AC_2) as potential scanning modes. From the obtained peak intensities and their linearity vs. metal ion concentration, and from the sensitivity shown by each one of the stripping modes (slope of the calibration lines) it results that, the AC_1 mode is the best one for all metal ions except $Zn(II)$. However, this mode yields a not well defined baseline, mainly in the extreme zones of the voltammogram. DP-mode is less sensitive but yields a good baseline in these extreme zones. Thus, a mixed stripping mode will be used: DP-mode for $Zn(II)$ and $Cu(II)$ peaks, and AC_1 -mode for $Cd(II)$ and $Pb(II)$ peaks, which appear in the centre. As it is shown in Figure 1, a better resolution and higher peaks (and, hence, lower limits of detection) are obtained for the $Cd(II)$ and $Pb(II)$ peaks by using this mixed mode instead of the only DP-mode.

Optimization of instrumental parameters

Cell dimensions ASV experiments performed by using 20-mL, 5-mL and 1-mL electrolysis cells (with solutions 10^{-6} mol.L $^{-1}$ of the metal ions) showed that peak height increases with decreasing cell volume, probably because of a better stirring efficiency. An increase in peak height by an average factor of 1.5–1.6 was obtained

on going from one to another of the above said cells. Since a microanalytical procedure for the determination of ultratraces of metal ions is the ultimate goal of this work, a 1-mL cylindrical, flat-bottomed cell was adopted for further studies.

Pre-electrolysis conditions A pre-electrolysis potential of -1.2 v is used. The peak height obtained when DP or AC₁-modes are used for stripping shows a linear relationship to the pre-electrolysis time within the range 1–5 min; thus, a 5-min period has been adopted for routine work. For longer pre-electrolysis times the linearity is lost, according to the effects described by Kemula¹³.

Mercury-drop surface area Increasing peak heights are obtained with increasing drop surface, in agreement with the equations deduced by Lund-Onshus¹⁴ for DP-stripping and Underkofler-Shain¹⁵ for AC-stripping. It is known, however, that the overall efficiency is limited by decreasing solution-to-mercury volume ratios. In the small-volume cell used in this work, a compromise is found with a drop of 2.20 mm² surface, as far as its stability in the stirred solution and its reproducibility are concerned, in accordance with Lund-Onshus findings¹⁴.

Scanning rate According to Frankentahl and Shain¹⁶ peak height increases with the scanning rate. This effect is more pronounced for Zn and Cd than for Pb and Cu. At the higher scanning rates, however, the capacitive current is enhanced more than the faradaic one; at these rates the peak form becomes irregular. As a consequence, an intermediate value of 15 mv.s⁻¹ has been adopted.

Amplitude of the superimposed alternating potential. In a series of ASV experiments performed with the AC₁-stripping mode at different amplitudes (U) of the superimposed alternating potential, the range between 20 and 25 mv showed the optimum results as limit of detection is concerned.

Pulse amplitude Increasing pulse amplitudes U_{DP}, used in DP-scanning mode cause slight increases in peak height but also increased peak widths, resulting in an incomplete peak resolution for Cd and Pb. A value of 40 mv yields fairly well resolved peaks.

Influence of pH The results obtained from solutions with constant metal ion concentration and constant ionic strength, at pH values in the range from 1.45 to 9.90 (adjusted by use of diluted HNO₃ or diluted KOH as required) are shown in Figure 2. At pH above 4.5, the height of all peaks decreases as a result either of hydroxocomplex formation^{17,18} or of adsorption effects on the cell walls and even on the platinum counter electrode¹⁹. Decreased peak heights are observed too in acidic media because of perturbations caused by a high blank current. The intermediate pH range where optimum analytical response is obtained is rather narrow for Cd(II) and Cu(II). The most convenient pH value for the sensitive simultaneous determination of the four metal ions is pH 3.9.

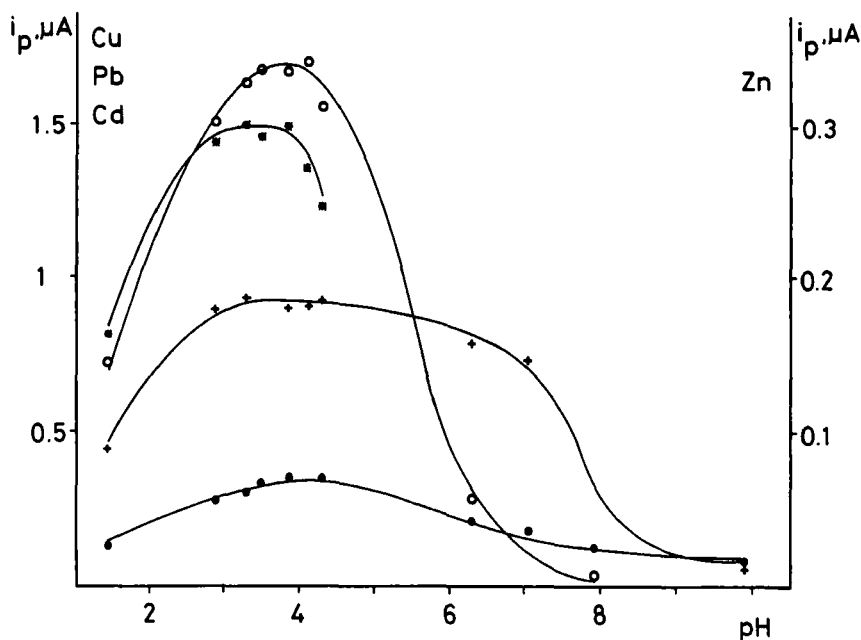


Figure 2 Influence of pH on the intensity of voltammetric peaks. ●) Cd(II), $2.86 \cdot 10^{-7}$ M, peak at -0.612 v; +) Pb(II), $3.38 \cdot 10^{-7}$ M, peak at -0.432 v; *) Zn(II), $1.62 \cdot 10^{-6}$ M, peak at -1.017 v; ○) Cu(II), $3.18 \cdot 10^{-6}$ M, peak at -0.033 v.

FIGURES OF MERIT OF THE RECOMMENDED PROCEDURE

Limits of detection, limits of quantification

The minimum detectable amount of each one of the four metal ions here studied was determined according to the IUPAC recommendations²⁰ from independent replicates of the blank test. The following limits of detection (in $\text{ng}\cdot\text{mL}^{-1}$) are obtained: Zn(II), 13.7; Cd(II), 5.2; Pb(II), 6.7; Cu(II), 7.2. The limits of quantification, in $\text{ng}\cdot\text{mL}^{-1}$ (using a numerical coefficient of 10), are: Zn(II), 47.9; Cd(II), 14.3; Pb(II), 12.9; Cu(II), 12.7.

Concentration ranges

Under the given working conditions, linear responses are obtained within the following concentration ranges (in $\text{ng}\cdot\text{mL}^{-1}$): Zn(II), 13.7–900; Cd(II), 5.2–986; Pb(II), 6.7–834; Cu(II), 7.2–344.

Precision

The precision of the measurements, given by the relative standard deviation (RSD) of the individual results obtained from series of twelve independently-prepared

Table 1 Inter-element effects: $[Y]/[X]$ tolerance ratios.

$X \backslash Y$	Zn	Cd	Pb	Cu
Zn	—	10^4	10^4	10^3
Cd	10^4	—	5.10^3	10^4
Pb	10^4	10^4	—	10^4
Cu	10^4	10^4	10^4	—

$[X] = 10 \text{ ng.mL}^{-1}$

identical solutions, has been determined for each metal ion at two different concentration levels. At the 350 ng.mL^{-1} level, RSD is about 8%; at the 30 ng.mL^{-1} level the value of RSD slightly increases up to 10%.

Inter-element effects: tolerance ratios

According to some authors^{4,11}, the presence of a large excess of one or several of the investigated metal ions can affect the results obtained for some other metal ions when present in very small amounts. The inter-element effects have been studied according to the following: several solutions containing pairs of the metal ions under study, the one to be determined, X, at a constant concentration level of about 10 ng.mL^{-1} , the other one, Y, at successively increasing concentrations, were analyzed according to the recommended procedure. From the minimum concentration of Y which caused difficulties or yielded errors higher than twice the RSD in the determination of the given concentration of X, the limiting tolerance ratio, $[Y]/[X]$, was evaluated. Results are given in Table 1. In all cases, the found tolerance ratios are high enough for no inter-element effect to be apparent in the analysis of common urban atmospheric aerosols, not even in the analysis of cadmium, the element which usually is by far the least abundant of the four studied in this kind of samples.

Interference from other ions

The effect of the presence of several other elements prone to be found in atmospheric aerosols was studied. Results are shown in Table 2, where the maximum concentra-

Table 2 Interference from other ions. Interfering element/metal ion to be determined tolerance ratios.

<i>Ion</i>	Zn	Cd	Pb	Cu
Fe(III)	10^3	10^3	10^3	10^3
Mn(II)	10^3	10^3	10^3	10^3
Cr(IV)	50	50	50	50
Sn(II)	10^3	10^2	1	10
V(V)	10^2	10^3	10^3	10^2
Ni(II)	10^3	10^3	10^3	10^3

tion ratios (interfering element/metal ion to be determined) which do not cause interference are given. Sn(II) is a main interfering ion in Pb(II) and Cu(II) determination.

APPLICATION TO ATMOSPHERIC AEROSOLS

Metal ion concentration in air is highly variable according to the amount of aerosol present and its composition, which depends on the area sampled, the sampling day and the prevailing atmospheric conditions. Some metal ions, like, for instance, cadmium(II), are usually found at very low concentrations, and their quantitative analysis requires to sample air for a much longer time than for the more common metal ions. Procedures with very low limits of quantification for cadmium are needed, in order to be able to shorten the sampling time and to have yet cadmium enough to obtain a significant analytical response. The new ASV procedure here proposed partially fulfills this requirement.

In order to check the new ASV procedure, ten aerosol samples were collected by means of a high-volume sampler, for 24 hours period, in two suburban industrial

Table 3 Characteristics of the ten aerosol samples analyzed, and results obtained from the proposed new ASV method and from the AAS method.

<i>Filter no.</i>	<i>Collected matter (g)</i>	<i>Sampling time (h)</i>	<i>Volume taken (m³)</i>	<i>Total suspended particulate (μg.m⁻³)</i>
1	0.0764	24	576	132.64
2	0.0407	24	576	70.66
3	0.0927	24	576	160.94
4	0.0528	24	576	91.67
5	0.1552	24	544	285.29
6	0.1908	96	960	198.75
7	0.0598	24	576	103.82
8	0.0484	24	576	84.03
9	0.0729	24	576	126.56
10	0.0893	24	576	155.03

<i>Filter no.</i>	<i>Zn(μg.m⁻³)</i>		<i>Cd(ng.m⁻³)</i>		<i>Pb(ng.m⁻³)</i>		<i>Cu(ng.m⁻³)</i>	
	<i>ASV</i>	<i>AAS</i>	<i>ASV</i>	<i>AAS</i>	<i>ASV</i>	<i>AAS</i>	<i>ASV</i>	<i>AAS</i>
1	24.6	25.6	40.0	53.0	792	832	170	176
2	19.9	19.6	30.3	46.0	980	972	219	206
3	23.8	27.7	11.5	14.9	1898	2069	368	376
4	35.6	23.8	24.1	25.1	742	782	164	165
5	13.9	15.8	43.1	50.5	1875	1625	683	686
6	14.0	15.2	17.5	25.9	2092	2120	911	1079
7	7.4	8.2	34.6	35.3	1203	1307	238	238
8	7.2	7.1	5.2	—	479	504	123	116
9	19.7	20.4	5.5	8.1	170	177	151	160
10	27.3	25.5	11.0	13.5	2239	2331	229	217

areas near Barcelona (Molins de Rei, samples nrs. 1–4 and 7–10; Santa Coloma de Gramanet, samples nrs. 5 and 6), and the four elements Zn, Cd, Pb and Cu were analyzed by both a standard atomic absorption spectrometric procedure²¹ and by ASV, as recommended in the present work. For quantification, the standard addition method was used in both procedures. Results are given in Table 3. For each element analyzed in each sample, results obtained from both procedures do not significantly differ (as expressed by the regression lines of AAS results vs. ASV results for each element, which do not significantly differ at the 95% confidence level).

In the case of cadmium, which is usually found in the atmosphere at concentrations near $0.02 \mu\text{g.m}^{-3}$, the ASV procedure here proposed is more convenient than other procedures, particularly when variation of cadmium concentration with time (for instance, hourly variations) is of interest, because the ASV procedure can be carried out on samples collected over 1-hour, and even 1/2-hour, periods.

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