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*Original*

Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion / Illuminati, Silvia; Annibaldi, Anna; Truzzi, Cristina; Libani, Giulia; Mantini, Caterina; Scarponi, Giuseppe. - In: JOURNAL OF ELECTROANALYTICAL CHEMISTRY. - ISSN 1572-6657. - 755:(2015), pp. 182-196. [10.1016/j.jelechem.2015.07.023]

*Availability:*

This version is available at: 11566/234085 since: 2022-06-01T13:55:05Z

*Publisher:*

*Published*

DOI:10.1016/j.jelechem.2015.07.023

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## Accepted Manuscript

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PII: S1572-6657(15)30026-6  
DOI: doi: [10.1016/j.jelechem.2015.07.023](https://doi.org/10.1016/j.jelechem.2015.07.023)  
Reference: JEAC 2192

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 11 March 2015  
Revised date: 17 July 2015  
Accepted date: 18 July 2015

Please cite this article as: Silvia Illuminati, Anna Annibaldi, Cristina Truzzi, Giulia Libani, Caterina Mantini, Giuseppe Scarponi, Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion, *Journal of Electroanalytical Chemistry* (2015), doi: [10.1016/j.jelechem.2015.07.023](https://doi.org/10.1016/j.jelechem.2015.07.023)

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## Determination of water-soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion.

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### Abstract

A two-step microwave (MW) digestion (ramps to 135 °C and to 185 °C) was set up for the subsequent voltammetric determination of the inert fraction of Cd, Pb and Cu in Antarctic aerosol (PM10), after a sequential extraction with water (soluble fraction) and dilute HCl (acid extractable fraction) of the filter samples. A digestion mixture of 5.0 mL HNO<sub>3</sub>, 1.0 mL H<sub>2</sub>O<sub>2</sub>, and 1.0 mL HF was used. The amount of H<sub>2</sub>O<sub>2</sub> was adjusted at a compromise value to avoid interferences from organic substances or from the reagent itself. Hydrogen fluoride was used at the maximum quantity suggested in the literature, since there were no interferences due to excess HF with the voltammetric measurement. Our procedure did not provide for a third digestion step with H<sub>3</sub>BO<sub>3</sub>, as generally required in order to eliminate excess HF when subsequent spectrochemical analyses are to be carried out. Thus the total digestion time was reduced from ~5 h to ~1.5 h. The ultrasensitive technique of square wave anodic stripping voltammetry (SWASV) was used and optimized by maximizing the signal-to-noise ratio (frequency 150 Hz, amplitude 20 mV). The limits of detection (e.g. for atmospheric concentration 0.1-0.3 pg m<sup>-3</sup> for Cd and 1-5 pg m<sup>-3</sup> for Pb and Cu) and the repeatabilities (Cd 21-26%, Pb 16-20%, Cu 11-14% as atmospheric concentration) compared favourably with literature reports. Significant aliquots of metals were present in all the three fractions determined and the inert fraction represented 20-74% for Cd, 10-63% for Pb, and 7-33% for Cu, against total contents of Cd 1-19 pg m<sup>-3</sup>, Pb 17-36 pg m<sup>-3</sup>, Cu 177-429 pg m<sup>-3</sup>. Possibly significant metal fractions could be associated to the crustal origin.

**Keywords:** Square wave anodic stripping voltammetry; Set-up and optimization; Heavy metals; Antarctic aerosol; Chemical fractionation; Microwave digestion

## Highlights

- Speciation of Cd, Pb, Cu in aerosol is obtained by SWASV after sequential extraction
- Microwave digestion is set up and optimized for subsequent SWASV analysis
- SWASV is optimized for trace metal determination of microwave-digested solutions
- Use of microwave digestion and SWASV reduces analysis time of Cd, Pb, Cu in aerosol

ACCEPTED MANUSCRIPT

## 1. Introduction

Traditionally, in Antarctic, and more generally in Polar, research devoted to the reconstruction of present and past changes in the chemical composition of the atmosphere through the analysis of aerosol or ice, only the total content of substances or the simple partition between soluble and insoluble fractions have been considered [1-13]. In particular as regards heavy metals, there is at present no information available in the literature, with the exception of our previous work [14, 15], with reference to their distribution between the soluble and the insoluble fractions in aerosol, snow and ice. This is possibly due to difficulties in the treatment and analysis of samples under uncontaminated conditions and with sufficient sensitivity [16, 17]. However the global climatic and environmental changes which occurred in past glacial/interglacial cycles were always accompanied by substantial variations in the content of the atmospheric aerosol and, at the same time, in the distribution between soluble and insoluble phases in the Antarctic ice [9, 10]. Although the solubility depends on the chemical nature of particles and on the operative dissolution conditions [18, 19], the soluble/insoluble discrimination of impurities present in the aerosol and deposited on the polar ice caps is an important tool for identifying the sources of chemical substances and detecting the changes that have taken place due to the climatic changes of the past.

In our previous work [14, 15] we established the basis for a three-aliquot chemical fractionation of Cd, Pb and Cu in Antarctic aerosol with the aim of gaining further information to be used for better discrimination between sources and to obtain more reliable relationships between air and snow. A simple sequential extraction procedure was taken into account and adapted from atmospheric literature [20, 21], in which extraction with water (water-soluble fraction, or simply soluble fraction) is followed by extraction with diluted hydrochloric acid (dilute-HCl-extractable fraction, or acid extractable, or simply extractable fraction) and then by the total dissolution of the residual material (inert fraction). At that time only the first two fractions were determined and a set of samples collected during the austral summer in the vicinity of the Mario Zucchelli Italian Station were analysed, applying square wave anodic stripping voltammetry (SWASV) and using a rotating thin mercury film electrode (TMFE).

In this work, after the previous experience in chemical fractionation of trace metals by sequential extraction [14, 15], we set up a microwave (MW) digestion procedure for the determination of the inert fraction of metals (as the third fraction of the programme) in aerosol samples, and the procedure was optimized for the subsequent voltammetric measurements by SWASV. At the same time we took the opportunity to revise the procedure of the first two stages, passing from the UV-treatment to the MW-digestion of extracted solutions for the sample preparation (mineralization) for voltammetry. Indeed, several reports are available on MW digestion set-up for subsequent spectrochemical analysis, especially by inductively coupled plasma mass spectrometry (ICP-MS) (see e.g. [22-36]), also dealing with large amounts of filter material [24, 25, 30, 35], but also by atomic absorption spectrometry (AAS) (e.g. [34, 37, 38]) or by inductively coupled plasma-optical emission spectrometry (ICP-OES) (see e.g. [32, 34, 38, 39]). However, no analogous information is available for voltammetric analysis.

Complete microwave dissolution and mineralization is generally obtained when mixtures of mineral acids are added to sample aliquots placed in closed MW vessels, and temperature and pressure are raised by microwave heating [40]. As regards the digestion solution, mixtures of concentrated  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and HF have generally been used. Nitric acid is generally the first choice; it is used as a strong oxidizing agent for organic matter (such as the cellulose filter paper in our application) which increases its oxidizing capacity at elevated temperatures. It breaks down the complex hydrocarbons into water and carbon dioxide and forms water-soluble salts with most elements.  $\text{HNO}_3$  also has minimum matrix effect for ICP-MS since H, N and O already exist in the plasma. The acids HCl and  $\text{H}_2\text{SO}_4$  are generally avoided as they introduce additional interference elements, Cl and S, into the ICP-MS system [41]. Hydrogen peroxide is generally added in smaller quantities to ensure the complete oxidation and mineralization of organic matter. In our case most of the organic matter is due to the filter paper (more than 99% of the mass). Since silica and silicates are among the major components of aerosol

samples (e.g. the NIST 1648a air particulate reference material [42] contains about 27% silica), HF is often added as one of the few chemicals that can dissolve these substances [24, 25, 43, 44]. HF is a weak non-oxidizing acid with a strong complexing capacity in aqueous solutions; moreover it increases the solubility and stability of those metals which form sparingly soluble products. However, residual HF in the digestate is corrosive to the nebulizer, the spray chamber and the plasma torch of ICP-MS systems; it causes spectral and non-spectral interferences and impairs the detection limits of several elements [25]. To mitigate these problems, minimal amounts of HF are used in these circumstances; nevertheless, after the normal digestion steps, in order to remove the residual HF from the solution,  $\text{H}_3\text{BO}_3$  is generally added, followed by a further digestion stage [25]. For atmospheric aerosols with a heavy matrix of cellulose due to the material of the filter used, a three-step MW digestion procedure for subsequent ICP-MS analysis was set up by Yang et al. [25]. A mixture of 5-mL concentrated  $\text{HNO}_3$ , 4-mL 30-32%  $\text{H}_2\text{O}_2$  and 0.5-mL concentrated HF was used in two temperature ramps, followed by a third step, after the addition of a 5-mL 5% boric acid solution.

In the present work the procedure of Yang et al. [25] has been modified for the application of the voltammetric measurements of Cd, Pb and Cu by SWASV. In this case no problems arise from residual HF (either from corrosion or interferences) [45, 46], while there are some problems with regard to possible  $\text{H}_2\text{O}_2$  excess [47]. Thus, changes have been made both to the suggested quantities of  $\text{H}_2\text{O}_2$  and HF to be added and to the MW ramps used, eliminating the digestion stage with  $\text{H}_3\text{BO}_3$ , hence reducing the number of digestion steps and total treatment time. The set up and optimization processes for sample digestion and voltammetric analysis are the main focuses of the present work and full discussion of the whole dataset produced from sample analyses from an environmental point of view will be deferred to a subsequent paper.

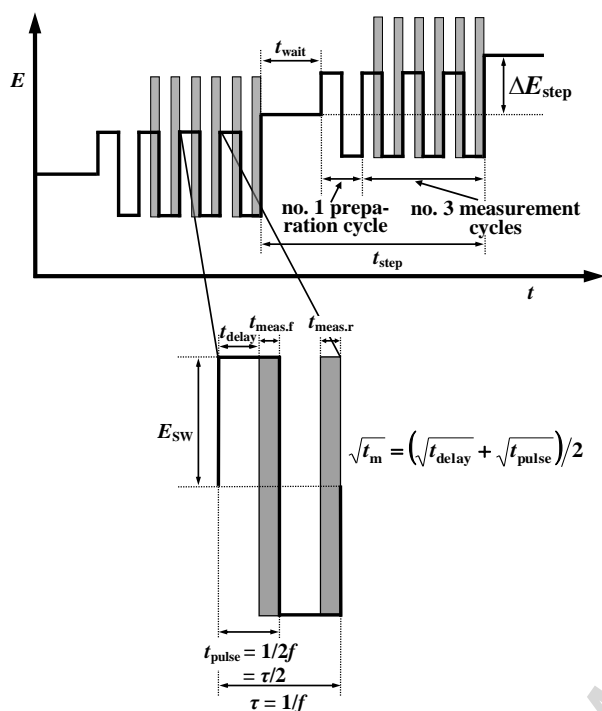
## 2. Material and methods

### 2.1. Laboratories, apparatus and general procedures

Most of the experimental part has already been described in a previous paper [14] to which the reader is referred for full details. The following is a brief summary.

Clean room laboratories with areas in Class 5 (ISO 14644-1) (formerly Class 100, US Fed. Std. 209e) were available both in Antarctica [48] and in Italy [49]. To collect PM10-aerosol samples a teflon-coated, high-volume sampler (model TE-6070V-BL, from Tisch, Village of Cleves, OH, USA) calibrated on site, and precleaned 8×10 inch (20.3×25.4 cm) cellulose filters (Whatman 41, Cat. No. 1441-866, thickness 220  $\mu\text{m}$ , ashes  $\leq 0.007\%$ , pore size 20-25  $\mu\text{m}$ , basis weight 85  $\text{g m}^{-2}$ ), were used. Computerized microbalances with readabilities 0.01 mg were from Mettler Toledo (Greifensee, Switzerland), models AT261 in Antarctica and XS205 in Italy, both tested in the field and in the laboratory against certified reference “weights” (OIML class E1). Pre-cleaned low-density polyethylene (LDPE) bottles (from Kartell, Italy) were used for both the storage of filters and subsequent treatments carried out in Italy before voltammetric analysis.

A microwave (MW) accelerated reaction system MARS 5 (magnetron frequency 2450 MHz) from CEM (Matthews, NC, USA) was used. The power output is switchable to 300 W  $\pm 15\%$ , 600 W  $\pm 15\%$ , 1200 W  $\pm 15\%$ , and any intermediate value can be obtained through a selection of a percentage of the full scale power. A 14-position alternating turntable is available inside a fluoropolymer-coated microwave cavity. General guidelines from the manufacturer suggest switching to 300 W, 600 W, 1200 W (and 100% maximum power) when one operates with 1-2, 3-5, 6 or more vessels, respectively. MW vessels were 100-ml HP-500 plus in Teflon PFA (perfluoroalkoxy copolymer) from CEM (maximum pressure 350 psig, pounds per square inch gauge, maximum temperature 210 °C). To control temperature and pressure an HP-500 plus control vessel was always used, filled with the same matrix as that present in the sample vessel. The system makes it possible to operate in four modalities: standard control, power/time control, ramp to temperature, ramp to pressure.



**Fig. 1.** Potential-time waveform, and current sampling scheme (dashed area) used in square-wave voltammetry. Symbol meanings:  $\Delta E_{\text{step}}$  = step height (2-12 mV);  $t_{\text{step}}$  = step time (0.05-9.9 s);  $t_{\text{wait}}$  = waiting time, i.e. time elapsing between the beginning of the potential step and the start of the SW potential modulation;  $E_{\text{sw}}$  = SW amplitude (1-50 mV);  $t_{\text{meas}}$  = current sampling time, equal in forward ( $t_{\text{meas.f}}$ ) and reverse ( $t_{\text{meas.r}}$ ) pulses (0.1-32 ms);  $f$  = frequency (10-250 Hz);  $t_{\text{pulse}}$  = pulse time =  $1/(2f)$ ;  $\tau$  = period;  $t_m$  see text.

The voltammetric instrumentation consisted of a Metrohm (Herisau, Switzerland) 746 VA Trace Analyser and a 747 VA Stand, equipped with a Teflon PFA cell and a three-electrode system, which includes an epoxy-impregnated graphite (Ultra Trace Graphite Ref. No. 6.1204.180) rotating disk working electrode (to be used, after Hg deposition, as a rotating TMFE), an Ag/AgCl, KCl 3 mol L<sup>-1</sup> reference electrode (to which all potentials are referred throughout) and a glassy carbon rod counter electrode. The instrument allows anodic stripping voltammetric procedures to be performed automatically and the typical potential waveform and the current sampling capability required in square wave (SW) mode (see Fig. 1 and [45]) to be used. In this mode a number of SW alternating potential cycles (preparation and measurement cycles) are superimposed on a stepwise potential scan at the end of each step. The current sampling window is located at the end of each pulse (forward and reverse) always under the condition that the delay time within each pulse before the beginning of the current sampling ( $t_{\text{delay}}$ ) is >1 ms. As in other commercial instrumentation, the current is sampled and integrated over the period  $t_{\text{meas}}$  and the charge obtained is divided by  $t_{\text{meas}}$  to obtain the final averaged current. This current corresponds [50] to the measurement at the time point  $t_m$ , where  $\sqrt{t_m} = (\sqrt{t_{\text{delay}}} + \sqrt{t_{\text{pulse}}})/2$ . The instrumental parameters which can be set independently refer to: the square wave amplitude ( $E_{\text{sw}}$ ) and frequency ( $f$ ), the step height ( $\Delta E_{\text{step}}$ ) and time ( $t_{\text{step}}$ ), the number of SW cycles superimposed in each step, and the current measurement time interval ( $t_{\text{meas}}$ ), which is equal in forward and reverse pulses. The other parameters that can be set by adjusting those previously mentioned are: the time elapsing between the beginning of the potential step and the start of the SW potential modulation, or the waiting time ( $t_{\text{wait}}$ ), which depends on  $t_{\text{step}}$ ,  $f$  and on the number of SW cycles superimposed in each potential step; the delay time within each pulse before the beginning of the current sampling ( $t_{\text{delay}}$ ), which depends on  $f$  and  $t_{\text{meas}}$ ; and the pulse time, equal in forward and reverse pulses ( $t_{\text{pulse}}$ ), which depends on  $f$ .

All acids in contact with samples were of ultrapure grade (UpA from Romil, Cambridge, UK), with impurities that, after dilution, were well below the detection limits. Impurities (in ppt) were as follows; HCl, assay 32-35%: Cd <0.1, Pb <1, Cu <3; HNO<sub>3</sub>, assay 67-69%: Cd <1, Pb <1, Cu <3; HF, assay 47-51%: Cd <0.1, Pb <1, Cu <10. Acids used for the initial stages of material cleaning were of reagent grade. Other reagents include H<sub>2</sub>O<sub>2</sub> (ultrapure Romil, assay 30-32%;

impurities (in ppt): Cd <1, Pb <1, Cu <1, again below detection limits when diluted for analysis), Al<sub>2</sub>O<sub>3</sub> (superpure BDH, Poole, England), KCl (ultrapure, *trace select* Sigma-Aldrich, St. Louis, MO, USA), hexadistilled Hg (superpure Merck). Ultrapure water was of Milli-Q grade from Millipore (Bedford, MA, USA). Atomic absorption standards (Cd (II), Pb (II), Cu (II), 1000±2 mg L<sup>-1</sup>) were from Carlo Erba (Milan, Italy). Research-grade nitrogen (purity ≥99.999%) was from Sol (Monza, Italy). The air particulate Certified Reference Materials NIST SRM 1648 [51] and 1648a [42] were obtained from the National Institute for Standards and Technology (Gaithersburg, MD, USA).

Description of the extensive decontamination procedures generally used in our laboratory for LDPE bottles and all other plastic material has already been reported elsewhere [14, 49]. Briefly, a careful and prolonged acid washing procedure was applied to bottles, with repeated treatments using, in sequence, detergent solution, 1+10 diluted analytical grade HNO<sub>3</sub>, 1+10 diluted superpure HCl and final storage in 1+1000 diluted ultrapure HCl until use. A similar procedure was used for PFA microwave vessels except that the final washing was carried out with HNO<sub>3</sub>/HF solution (5 to 100 and 1 to 100 diluted, respectively). For both kinds of containers the cleaning continued until values comparable to voltammetric instrumental blanks were reached. For the microwave vessels, after the above decontamination procedure, they were repeatedly treated with digestion solutions (see below) and subjected to MW digestions for 1-h cycles until low, stable and reproducible blanks were obtained.

Cellulose filters were specifically prepared at the University of Venice (Italy) for use by four groups working on the Antarctic project for trace element determinations. The filters were washed and decontaminated carefully with diluted HCl (Merck, Suprapure-grade), rinsed with Milli-Q water, dried under ISO Class 5 laminar flow cabinets and stored in acid-cleaned plastic bags until use in Antarctica [30].

## 2.2. Samples

Eight samples of PM10-atmospheric aerosol were collected during the 2000-2001 austral summer (from about mid-November 2000 to mid-February 2001) at the Faraglione Camp (74° 42' 58" S – 164° 06' 54" E), about 3 km south of the “Mario Zucchelli” Italian Station (MZS), formerly Terra Nova Bay Station (see Fig. S1). Details of the site and of sampling conditions have been reported elsewhere [14]. Long exposure times of between about 7 and 14 days were used to comply with the requirements of trace elements determination. The aerosol mass determinations were carried out gravimetrically, by differential filter weighing [48, 52], in the clean chemistry laboratory available at the station under controlled temperature (±0.5 °C) and relative humidity (±1%) [48]. One quarter of each filter was reserved for our work and put into the decontaminated LDPE bottles and stored frozen (–20 °C) until analysis. Blank filters (“field blanks” and “blanks as received”) were also collected in the field.

## 2.3. Sample treatments

MW assisted digestion was carried out principally to ensure total dissolution and mineralization of the residual material of the sequential extraction procedure previously set up [14], i.e. the inert fraction, together with the filter in which it is contained in order to obtain the inert fraction itself. However, MW digestion was also applied to digest the water- and the acid-extracts, in this case only as a preparatory step for the voltammetric measurements, instead of using UV-treatment as in the past [14].

Of the part of each filter remaining from the previous work [14] (1/8 of the original), half of this, i.e. 1/16 of the original, or a lower aliquot (i.e. 1/32), was subjected to sequential extraction with 100 ml of ultrapure water for two days (water-soluble fraction), followed by 100 ml of 0.022 M ultrapure HCl (2+1000 diluted), pH ~2, for a further two days (acid-extractable fraction). These two extracts were then subjected to a MW mineralization procedure set up for the

subsequent voltammetric analysis. The filters containing the residue from these extractions were then totally solubilized and mineralized using a microwave digestion procedure (a blank filter aliquot and the same digestion solution were used inside the control vessel) designed to obtain the third fraction of the general planned method, i.e. the inert fraction, again with the aim of setting the proper conditions for voltammetry.

Basically, an  $\text{HNO}_3/\text{HF}$  mixture was used for digestion of the inert fraction together with the filter itself, while dilute  $\text{HCl}$  solutions were used for digestions of both the water-soluble and acid-extractable fractions. However, in each case  $\text{H}_2\text{O}_2$  was also added before digestion, to obtain a complete mineralization of soluble organic material, which interferes in the voltammetric measurements. Thus, for this work, an appropriate amount of  $\text{H}_2\text{O}_2$  was also added to the extraction solutions (water-soluble and acid-extractable fractions) before MW digestion, while in the previous work [14] this result was obtained through UV-irradiation of extracts. In both cases the amount of  $\text{H}_2\text{O}_2$  and the MW digestion conditions were optimized to avoid interference either from organic substances ( $\text{H}_2\text{O}_2$  too low) or from residual  $\text{H}_2\text{O}_2$  in the digestate (too much  $\text{H}_2\text{O}_2$  with residual content not destroyed). In both these latter situations, disturbing large waves were observed in the baseline of voltammograms.

In general (details below), in the case of MW digestions devoted to the determination of the inert fraction, the filter aliquot containing the residue from the previous extractions was placed inside a microwave vessel and ultrapure  $\text{HNO}_3$ , ultrapure  $\text{H}_2\text{O}_2$  and ultrapure  $\text{HF}$  were added. For digestions of water-soluble and acid-extractable fractions, an aliquot of solutions was put in a MW vessel and ultrapure  $\text{H}_2\text{O}_2$  was added (in case of the water-soluble fraction ultrapure  $\text{HCl}$  was also added to obtain the same acid matrix of the acid-extractable fraction). In all cases digestions were carried out using the “ramp to temperature” mode, with pressure limit constraints, in two steps. Two-vessel digestions were always carried out with the same matrices in the sample vessel and in the control vessel. When digestions of sample filters were carried out, a 1/16-aliquot of a blank filter was inserted in the control vessel. In accordance with the manufacturer’s instructions for digestions with 1-2 vessels inside the oven, a 300-W power was always used. After digestion, the solutions were diluted to 100 mL using ultrapure water and in this form subjected to voltammetric analysis. Tests were also carried out using blank filters (see below).

To test the measurement additivity of the three-aliquot fractionation with respect to the total content obtained by a direct digestion procedure of a whole sample, an aliquot of filter sample no. 8 was subjected directly to microwave digestion using the same procedure described here, to obtain total metal contents. The results were then compared with the total content computed from the sum of the soluble, extractable and inert fractions.

To be consistent with the previous paper [14], and in any cases in which concentrations of extraction solutions are reported, results will be referred to 1/8 of the filters, except when differently stated.

### 2.3.1. MW digestion for inert fraction

After preliminary tests concerning the optimal amount of  $\text{H}_2\text{O}_2$  and the time of the digestion ramps (see Section 3), the procedure was set up as follows. The filter aliquot containing the residue of the previous extraction procedure was put into a microwave vessel along with 5.0 mL of ultrapure  $\text{HNO}_3$ , 1.0 mL of ultrapure  $\text{H}_2\text{O}_2$  and 1.0 mL of ultrapure  $\text{HF}$ . The vessel was capped, fastened on the track and placed in the MW oven together with the control vessel, containing the same digestion mixture. In accordance with the manufacturer’s instructions for digestion of 1-2 vessels, a 300-W power with 100% maximum was set in all cases. Then the digestion procedure followed in two steps, two ramps-to-temperature steps (a number of ramp/hold times were tested) as below. In the first step a lower temperature to be reached and a low increasing rate were selected to digest the filter, and in the second step a higher temperature (and correspondingly high power) with similar temperature increase rate were used to complete the digestion with the full oxidation of organic matter.

Step 1. The temperature was gradually ramped to 135 °C in 12 or 36 min, with pressure limit at 200 psig, followed by a 2-, 4-, or 20-min hold time.

Step 2. The temperature was gradually ramped to 185 °C in 6 or 18 min (pressure limit at 250 psig), followed by a 4-, 8-, or 16-min hold time. The vessels were left to cool naturally to room temperature, then they were vented, opened and the solution was diluted to 100 mL.

Different volumes of H<sub>2</sub>O<sub>2</sub> from 0.5 to 2.0 mL were tested together with different digestion times, from 30 min to 90 min and the effect on completeness of dissolution and on possible voltammetric interferences was observed. The increase in total digestion time was tested since improved recoveries have been reported by increasing the digestion time [33]. The amount of HF was always set at the maximum reported in the literature, i.e. 1.0 mL (see e.g. [24, 37]), since this acid generally increases metal recoveries and does not create problems with voltammetry [45, 46].

### 2.3.2. MW digestion for soluble or extractable fractions

MW digestions of water-soluble and acid-extractable fractions were carried out in the same HCl-matrix [41]. Ten mL of the solutions were put in the MW vessels and 20 µL of ultrapure H<sub>2</sub>O<sub>2</sub> were added; in the case of the soluble fraction 20 µL of ultrapure HCl were also added to obtain the same acid matrix as the extractable fraction. Again two ramps to temperature were applied, as for the inert fraction, except that in the first one temperature was increased less gradually to the higher value of 160 °C in 30 min and in the second one, after a 1-min hold time, the temperature was raised very slowly to a final lower value of 170 °C in 30 min, followed by a 1-min hold time. In both cases two vessels (sample and control vessels) were introduced into the oven, then a 300-W power with 100% maximum power was applied, and a 300-psig maximum pressure was set. At the end, vessels were left cool naturally to room temperature, vented, opened and the solutions transferred directly to the voltammetric cell for analysis, without further dilution.

### 2.4. Voltammetric analysis. General procedures and optimization

Detailed descriptions of the electrochemical pre-treatment of the graphite electrode [45, 47], the TMFE preparation and the overall procedure used for SWASV measurements in background subtraction mode [14] have already been reported. Here we limit the discussion to the set up and application of the technique for use with MW digested solutions.

As usual the mercury film deposition was carried out at a potential of -1000 mV in a solution of  $6 \times 10^{-5}$  mol L<sup>-1</sup> Hg(NO<sub>3</sub>)<sub>2</sub>. After the TMFE preparation, base voltammograms were plotted in order to evaluate the (good) performance of the electrode and to determine the electrostability range in the different solutions of this work.

For the voltammetric measurements different strategies were applied according to the concentrations detected. In particular separate analyses of metals were sometimes carried out, with Cd and Pb determined simultaneously in one analysis, and Cu alone in another, while in other cases Cd was determined separately from Pb and Cu, measured together, and finally, in a few others, all three metals were determined separately. Accordingly, after pouring a 10-mL outgassed solution into the voltammetric vessel, metal depositions were carried out at different potentials ( $E_d$ ), while the deposition times ( $t_d$ ) varied, due to the metal(s) involved and the concentrations detected, from 15 s to 45 min. To select the optimal deposition potentials for each specific analysis, pseudopolarographic experiments were carried out by varying the deposition potentials and recording the respective peak currents with all other parameters fixed. These experiments were carried out on sample no. 7 with the final solutions spiked for Cd to obtain a concentration of 140 ng L<sup>-1</sup>, so that the set of analyses could be carried out using low  $t_d$  values and finished in one-two working days.

The anodic scan subsequent to the deposition step (the stripping step), almost always started from the deposition potential, with a few exceptions for Cu determination in soluble and extractable fractions (see Section 3.2.3.). The final potential was set to +50 mV for HCl/H<sub>2</sub>O<sub>2</sub> digested solutions (soluble and extractable fractions) and +70 or +80 mV for HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HF-digestates (inert fraction). Concerning the potential scan (see Fig. 1 for potential-time waveform and current sampling scheme) the main square wave instrumental parameters, i.e. the SW amplitude ( $E_{sw}$ ) and the SW frequency

(*f*) were optimized to obtain the pair of values with the best signal-to-noise (*S/N*) ratio. The following values were tested:  $E_{sw}$  10, 15, 20, 25, 30 mV; *f* 50, 100, 150, 200 Hz. For the initial set-up of the voltammetric measurements (i.e. before the optimization)  $E_{sw}$  and *f* were set at the instrumental default values of 25 mV and 100 Hz, respectively. For the step parameters and the current sampling location in the pulses, the settings were fixed as follows. The step height ( $\Delta E_{step}$ ) was set (according to our previous experiences [45, 47, 49]) at 8 mV. The number of SW cycles superimposed on each potential step, as suggested in the literature to obtain a better *S/N* ratio [53], was set at 4: one for conditioning (preparation cycle) and three for measurement (measurement cycles), then the average value of the last three measurements was plotted against applied potential to record the voltammograms. The step time ( $t_{step}$ ) and the current sampling time ( $t_{meas}$ ) were adjusted, according to the frequency, to obtain constant (or approximately constant) values for (i) the time elapsing between the beginning of the potential step and the start of the SW potential modulation ( $t_{wait}$ ) and (ii) the delay time, within each pulse, between the beginning of the pulse and the beginning of the current sampling ( $t_{delay}$ ), respectively. In particular,  $t_{step}$  was adjusted to obtain approximately the same waiting time of ~60 ms in each case. Thus it was set at 150 ms for *f*=50 Hz, and at 100 ms when *f*-values from 100 Hz to 200 Hz were used (note that the instrument's resolution for  $t_{step}$  is 50 ms and that finer settings are not allowed). As regards the parameter  $t_{meas}$ , it was adjusted to have a delay time of 1.5 ms in each case. Thus it was set as follows ( $t_{meas}$  in ms, *f* in Hz): 8.5, 50; 3.5, 100; 1.8, 150; 1.0, 200. All optimization experiments were carried out on sample no. 7 with the final solutions spiked for Cd to obtain a concentration of 140 ng L<sup>-1</sup> so that low deposition times could be used and one set of measurements completed within one working day. The results of the optimization tests will be interpreted according to the theoretical predictions obtained for SWASV of reversible systems when a TMFE is used [50, 54].

The background voltammograms to be subtracted from the analytical voltammograms were obtained immediately before sample analysis by applying an equilibration potential ( $E_{equil}$ ) equal to the deposition potential with electrode rotation on, for an equilibration time ( $t_{equil}$ ) of 0.5 s in all cases except when Cd was involved ( $t_{equil}$ =1 s). A SW anodic scan followed with parameters as in the specific sample analysis. Quantification was achieved using the multiple standard addition method.

### 2.5. Quality control

During the work, repeated measurements of the laboratory blank were carried out with the electrochemical cell in optimal conditions (after the normal cleaning procedures). Blank measurements concerned: (1) the instrumental blank, obtained from measurements made on blank electrolytes (~0.022 mol L<sup>-1</sup> HCl; solution containing ~0.76 mol L<sup>-1</sup> HNO<sub>3</sub> and ~0.28 mol L<sup>-1</sup> HF); (2) the blank from LDPE bottles used for extractions, measured on HCl solutions stored inside them for two days; (3) the blank from MW vessels used for digestion, measured on either HCl or HNO<sub>3</sub>/HF solutions stored inside them for two days; (4) the blank from MW vessels after digestion with HCl solution or (5) after digestion with HNO<sub>3</sub>/HF solution.

The evaluation of the filter blanks is much more important than the laboratory blanks. In fact, due to the much greater mass of the filter with respect to the collected aerosol (a factor of ~400 is typical), the contribution of the cellulose material of the filters is expected to be significant even if analytes are present in it as trace impurities. For the present work the field blank filter no. 1 (see [14]) was selected since it is representative of the average blank obtained from previous measurements on soluble and extractable fractions [14]. It was used and treated in exactly the same way as sample filters to obtain the blanks after extraction with water and MW digestion (water-soluble filter blank), extraction with HCl and MW digestion (acid-extractable filter blank), and MW digestion of the residue (inert filter blank).

In our laboratory, the accuracy of the voltammetric procedures for trace metal determinations in environmental samples is routinely tested using certified reference materials, see e.g. [14, 45, 47, 55-57]. As regards aerosol

measurements, the NIST 1648 [51] and 1648a [42] urban particulate reference materials were used (~2 mg). In the first case, the entire fractionation procedure was applied directly to the reference sample. In the second about 2 mg were combined with 1/16 of a blank filter and subjected directly to the total dissolution/mineralization by the optimized microwave digestion. The quantitativity of the sequential extraction and MW digestion procedure was tested against a direct digestion of a sample filter (sample no. 8) in order to verify that the total computed concentrations are in agreement with the direct measurements of total contents.

### 3. Results and discussion

#### 3.1. Set up of MW digestion of filter samples

Several tests were carried out for the MW digestion of filter samples, changing the amount of H<sub>2</sub>O<sub>2</sub> from 0.5 mL to 2.0 mL in the sequence 0.5 - 1.0 - 1.5 - 2.0 mL, and total digestion time as 30 - 60 - 90 min.

As regards the optimal amount of H<sub>2</sub>O<sub>2</sub> it was noted that using the lowest tested quantity, i.e. 0.5 mL, disturbing waves from dissolved organic substances, evidently not completely mineralized, were observed in the voltammograms, whichever digestion time was used, interfering with metal determinations. Conversely, as we increased the H<sub>2</sub>O<sub>2</sub> amount above 1.0 mL, the voltammograms showed a very big wave due to residual H<sub>2</sub>O<sub>2</sub>, which caused the analysis to stop because of “current overload”. The optimal amount of H<sub>2</sub>O<sub>2</sub> was therefore set at 1.0 mL in all the subsequent experiments.

The results of experiments carried out with different total digestion times showed that with a 30-min digestion (first ramp 12 min with a 4-min hold, second ramp 6 min with an 8-min hold) some residue was always present whichever amount of H<sub>2</sub>O<sub>2</sub> was used. Conversely complete filter dissolution and sample digestion was achieved using either a 60-min (first ramp 36 min with a 2-min hold, second ramp 18 min with a 4-min hold) or a 90-min (first ramp 36 min with a 20-min hold, second ramp 18 min with a 16-min hold) total digestion time. These results, together with the fact that some difficulty was observed in determining the correct baseline in both the Cd and Cu measurements (see Fig. 2), led to the 60-min total digestion time being selected in all the subsequent experiments.

As a consequence, all the measurements carried out below refer to the use of a digestion mixture of 5.0 - 1.0 - 1.0 mL of HNO<sub>3</sub> - H<sub>2</sub>O<sub>2</sub> - HF, respectively, and applying the following schedule for ramp/hold times: 36 min for the first ramp with a 2-min hold time and 18 min for the second ramp with a 4-min hold time.

Figure 3 reports the temporal profiles of temperature, pressure and power during digestions with solutions of water-extracts (curves a) and acid-extracts (curves b) and of inert residue (curves c) for sample filter no. 7 together with comparison with curves referred to a blank filter (curves d, e, and f, respectively).

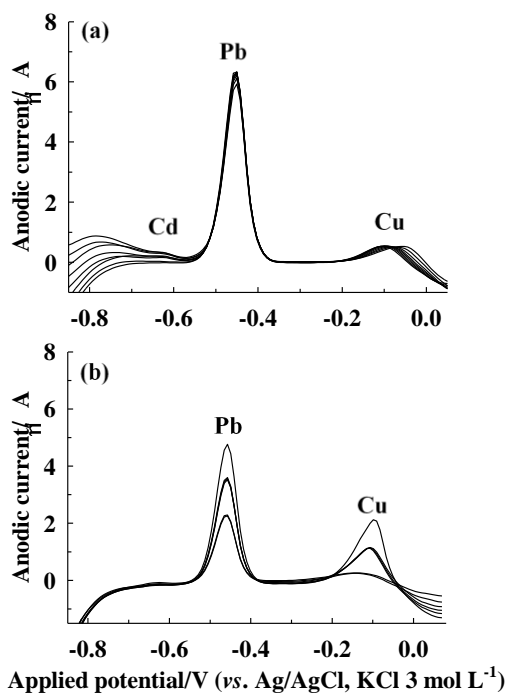


Fig. 2. Voltammograms obtained for the inert fraction after a 90-min digestion time, showing problems with both Cd and Cu peak measurements. Analyses for determination of (a) Cd, (b) Pb and Cu.

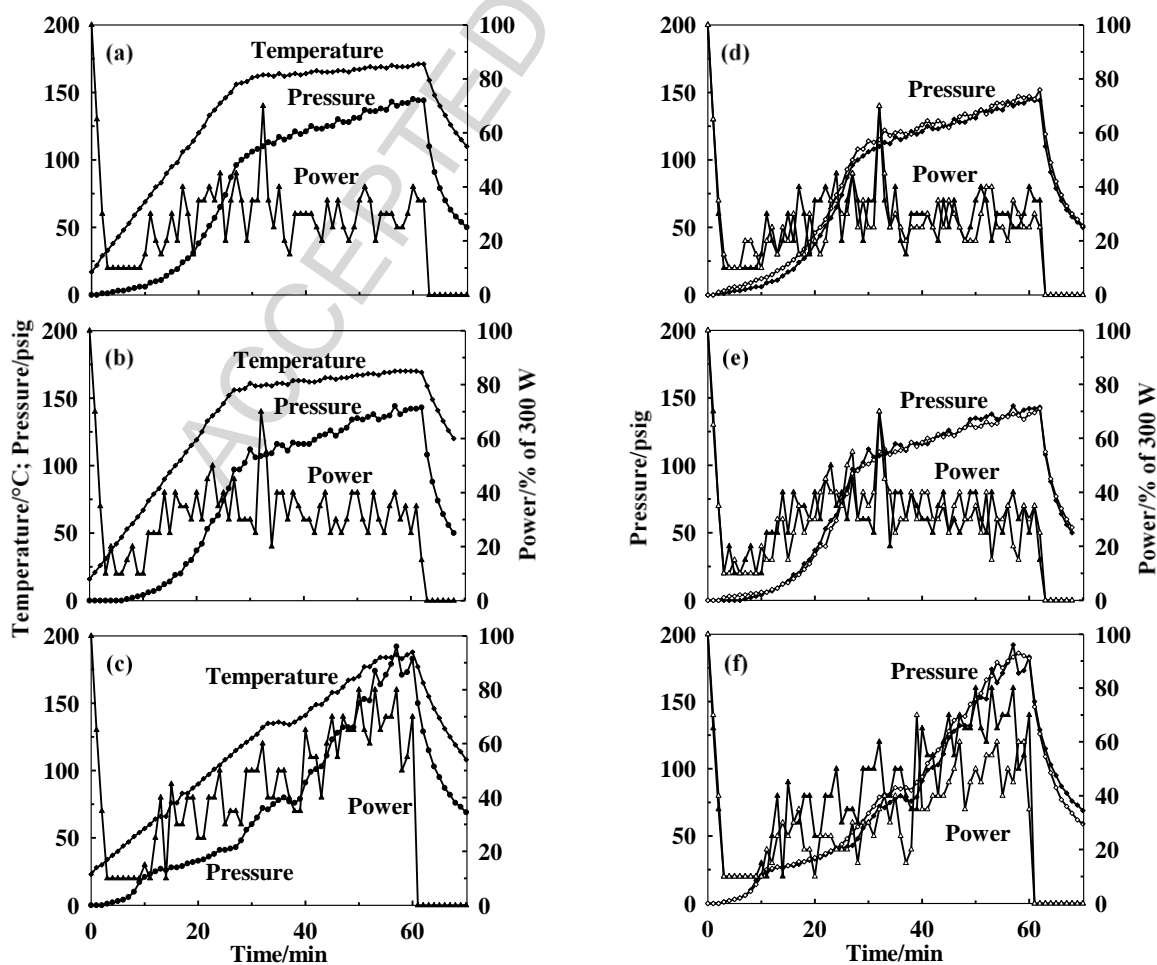
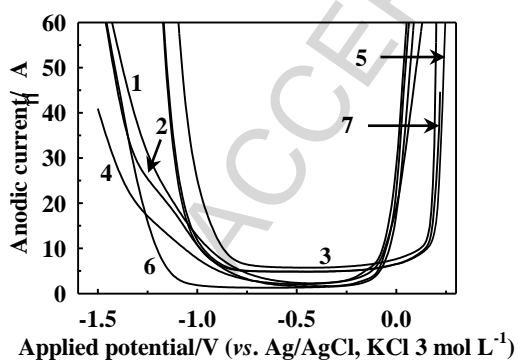


Fig. 3. Temperature, pressure and power temporal profiles during the two-stage digestions of (a) water-soluble fraction in HCl/H<sub>2</sub>O<sub>2</sub> mixture, (b) acid-extractable fraction after H<sub>2</sub>O<sub>2</sub> addition, and (c) inert fraction in HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HF mixture. In (d), (e), (f) comparison of sample data (solid symbols) with blank solutions (open symbols). Mode “ramps to temperature”; two vessels in the oven and a 300-W power in each digestion. Sample no. 7.

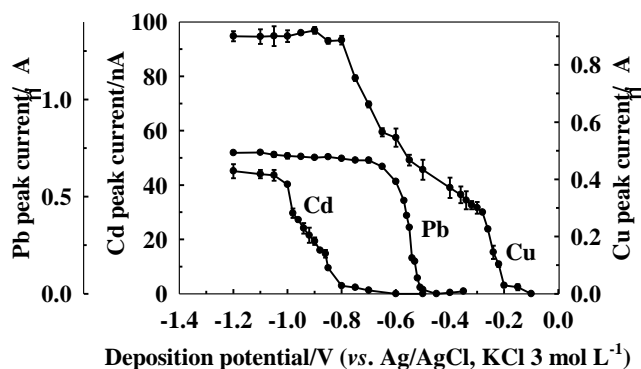
Firstly it can be seen that practically identical profiles are observed for the digestions of water-soluble and acid-extractable fraction, with very small differences between sample filter and blank filter treatments. After the increase in power occurring between the 10- and 20-min digestion times, followed by a rapid increase in pressure between 20 min and 30 min (while temperature rises from 60 °C to 160 °C), power stabilizes at 30-40% of the maximum allowed (set at 300 W) until the end of the digestions, with pressure and temperature increasing gradually between 100 psig and 140 psig, and 160 °C to 185 °C, respectively, in about 30 min.

Concerning the digestions of filters (sample and blank) for determination of the inert fraction, a somewhat lower increasing rate in pressure is observed at the beginning, compared to water- and acid-extractable solutions, as a consequence of the more gradually increasing rate of temperature and of the contextual filter disintegration, although quite similar power is applied in this part of digestion compared to that used for extractable solutions. Two increasing waves in pressure are observed at around 10-min and 30-min digestion time, respectively; afterwards pressure increases to a maximum of about 180 psig at the end of the digestion, while power also increases continuously up to about 60-80%. Comparing sample filter digestion with blank filter digestion it can be seen that higher power is systematically required for the sample filter (about 50% more between 15 min and 40 min, and ~40% more from ~40 min to the end of digestion), although the pressure obtained is generally about 10 psig lower than for the blank filter. Both these observations can be ascribed to the presence of the aerosol particulate matter and its digestion in the sample filter.

From a comparison with other procedures reported in the literature for the preparation of filter samples for subsequent spectrometric analyses (see e.g. [24, 25, 30]) it can be stressed that avoidance of the third step with  $\text{H}_3\text{BO}_3$  makes it possible to reduce overall digestion time considerably from ~5 h [25] (including cycles of chilling in a freezer at -20 °C, not required here) to ~1.5 h. Conversely, it has been reported [33] that increasing digestion time to 60 min (using a digestion solution of  $\text{HNO}_3$  alone) increases the recoveries substantially, though they nevertheless remain quite low (around 80%) in the absence of HF. Note that our recoveries obtained using a 60-min digestion time and an  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HF}$  digestion solution, are quite satisfactory (see Section 3.3).



**Fig. 4.** Base SWASV voltammograms showing the electrostability ranges for digested solutions of (1) soluble fraction, (2) HCl extractable fraction, (3) inert fraction. Comparison with electrolyte blank digested solutions of (4) HCl- $\text{H}_2\text{O}_2$ , (5)  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$ -HF, and blank not digested solutions of (6) HCl and (7)  $\text{HNO}_3$ -HF. See text for acid concentrations. Experiments carried out on sample no. 7.



**Fig. 5.** Pseudopolarograms for Cd, Pb and Cu in a digestate of the inert fraction obtained from sample no. 7 spiked with Cd to obtain a final concentration of 140  $\text{ng L}^{-1}$ .

### 3.2. Voltammetric set-up and optimization

#### 3.2.1. Electro-stability ranges of digestate solutions

The electro-stability ranges of digestates for the inert fraction ( $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HF}$  digestion) and the water- and acid-extractable fractions (HCl/ $\text{H}_2\text{O}_2$  digestion procedures) are reported in Fig. 4, together with those of the related blank solutions. They were all obtained by SW scans in the positive direction from the cathodic to the anodic limit.

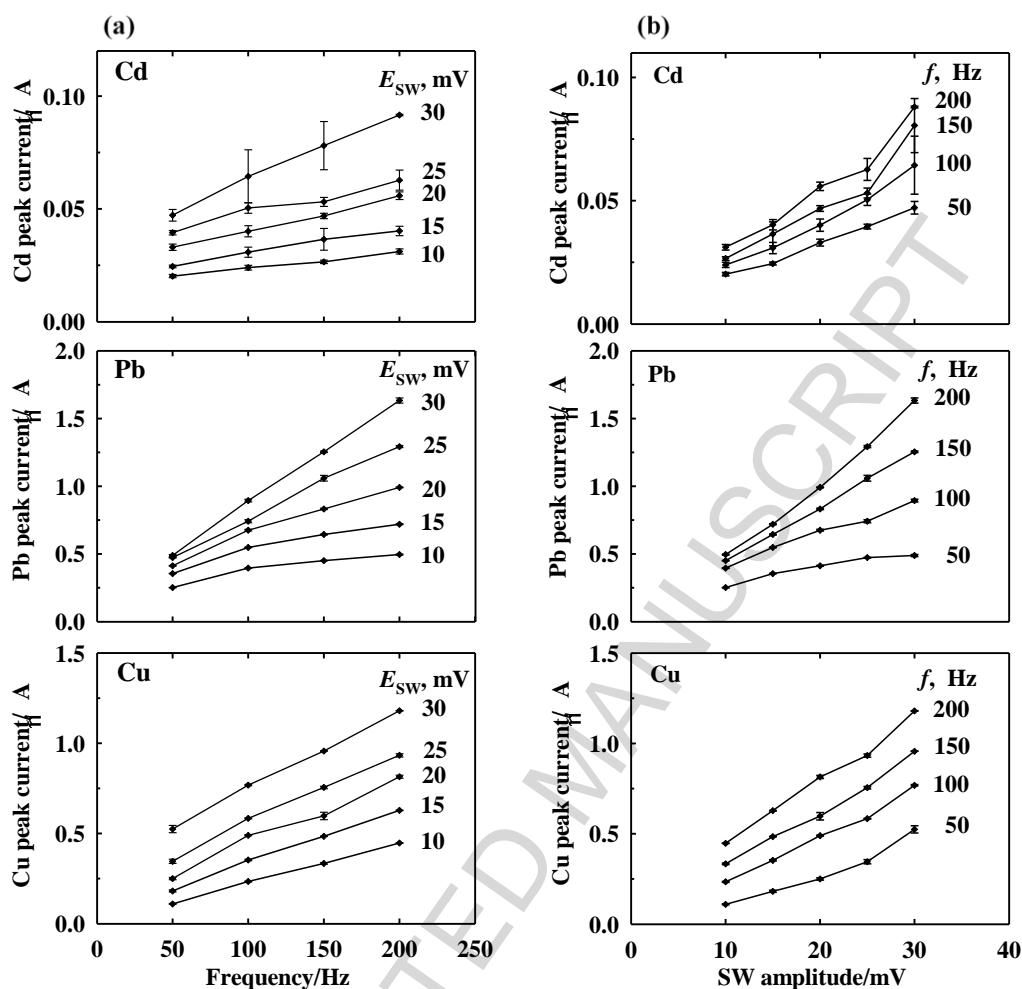
As regards the inert fraction, it can be seen that the useable potential interval for metal determinations in the  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HF}$  digestate (Fig. 4, curve 5) ranges, for electrolyte blank solutions, from  $-1.16$  V to  $+0.25$  V vs. Ag/AgCl  $\text{KCl } 3 \text{ mol L}^{-1}$ , while for the digested solution of sample no. 7 (curve 3), it extends between  $-1.08$  V and  $+0.20$  V. Thus the electrostability range is about  $1.30/1.40$  V. Note that in the presence of the sample filter a  $100$ -mV positive shift occurs in the cathodic limit and a  $50$ -mV negative shift is observed in the anodic limit of the interval with respect to the blank solutions, thus leading to a  $150$ -mV narrowing of the useful range. It can be observed that the electrostability range practically coincides with previous results obtained by us with  $\text{HNO}_3$  and HF solutions [45].

For the  $\text{HCl}/\text{H}_2\text{O}_2$  digestates, all the intervals appear to have shifted in the negative direction (about  $200$  mV) with respect to those of the  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HF}$  solutions; limits are observed at  $-1.40/-1.50$  V and  $+0.05/+0.10$  V for the cathode and anode, respectively. As a consequence, even if the total amplitude of the electrostability range is not significantly changed (around to  $1.5$  V), the anodic limit is lowered while the cathodic limit is extended. Note that even if no practical differences are observed between blank and sample solutions concerning the cathodic and anodic limits, a discrete wave can be seen close to the cathodic limit (between  $-1.0$  V and  $-1.3$  V) in all the curves referred to solutions with  $\text{H}_2\text{O}_2$  added to HCl (curves 1, 2, 4). This wave is not present in the HCl blank solution (Fig. 4, curve 6) or in other solutions containing  $\text{H}_2\text{O}_2$  but in combination with  $\text{HNO}_3$  (curves 3, 5, 7).

### 3.2.2. SWASV set-up and optimization for inert fraction

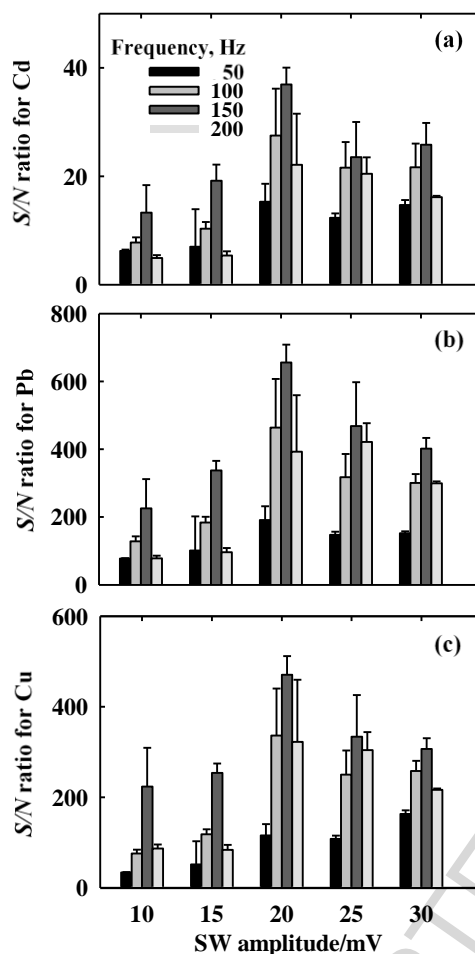
The results of pseudopolarographic experiments carried out in digestates of the inert fraction (see Fig. 5) show quite well-defined waves. However in all cases the semilogarithmic plots obtained by plotting  $\log [i_p / (i_{pL} - i_p)]$  vs.  $E_p$  (with  $i_{pL}$  = peak current under limiting conditions) showed linear trends in the part close to the half-wave potential but with slopes well below the theoretical values predicted by theory for a simple, reversible electronic transfer mechanism at the electrode (data not shown here to save space). The half-wave potentials, obtained by semilogarithmic plots, are  $-0.92$  V for Cd,  $-0.56$  V for Pb and  $-0.52$  V for Cu, while the corresponding plateaus are reached for about Cd  $-1.05$  V, Pb  $-0.70$  V and Cu  $-0.80$  V.

Regarding the voltammetric set-up for the inert fraction, due to the generally much lower concentration of Cd with respect to those of Pb and Cu, separate analyses were carried out for Cd, on the one hand, and Pb and Cu together on the other, using different instrumental settings for the deposition step and the potential scan step. The deposition potentials ( $E_d$ ), selected from the pseudopolarographic experiments, were  $-1100$  mV and  $-900$  mV for determinations of Cd alone and Pb/Cu together, respectively, while the deposition time ( $t_d$ ), according to the concentrations detected, was  $30$ - $45$  min for Cd determinations and  $1$ - $5$  min for Pb/Cu determinations. The subsequent anodic scan always started from the deposition potential ending at  $+70/+80$  mV in each case. Sometimes, due to higher Cd values than usual, a different strategy was used, in which Cd and Pb were determined simultaneously ( $E_d=-1100$  mV,  $t_d=10$ - $30$  min, scan from  $-1100$  mV to  $+70$  mV) and Cu separately ( $E_d=-900$  mV,  $t_d=3$ - $5$  min, scan from  $-900$  mV to  $+70$  mV).



**Fig. 6.** Dependence of metal peak currents on (a) the frequency at different SW amplitudes and (b) the amplitude at different frequencies, for a digestate of the inert fraction. Error bars:  $\pm$ SD from 3-4 measurements. Experiments on sample no. 7 spiked with Cd to a final concentration of  $140 \text{ ng L}^{-1}$ .

Results of the optimization tests are reported in terms of the changes of peak current, peak potential and  $S/N$  ratio with SW frequency and SW amplitude. The peak current increases with frequency at constant amplitude (Fig. 6a) but not exactly linearly as predicted by theory [50, 54] for a simple, reversible electronic transfer mechanism at the electrode. Furthermore, we noted that no better linearity is obtained if, as suggested by Penczek 1986 [50], we plot  $i_p$  against  $1/t_m$ , (not reported here to save space). Moreover  $i_p$  also increases with SW amplitude at constant frequency (Fig. 6b), again close to linearity (at least in the range considered). However, since noise too increases rapidly with both frequency and amplitude there is a limit to the increase of  $i_p$  (and then improving sensitivity) with increasing  $f$  and/or  $E_{sw}$ . In fact the  $S/N$  ratio (Fig. 7), after increasing with both  $E_{sw}$  and  $f$ , reaches a maximum at  $E_{sw}=20 \text{ mV}$  and  $f=150 \text{ Hz}$  for all three metals. The existence of practical limits to increasing sensitivity by increasing SW amplitude has been theoretically predicted [50, 54] and experimentally verified [45, 47, 58-61]. From these results it is important to observe that the  $S/N$  ratio is of the order of several hundreds for Pb and Cu, and a few tens for Cd. Note again that different optimal  $E_{sw}$  and  $f$  have previously been obtained by us in HF solution [45],  $E_{sw}=25 \text{ mV}$ ,  $f=100 \text{ Hz}$ ) and in UV digested wine samples [47],  $E_{sw}=20 \text{ mV}$ ,  $f=100 \text{ Hz}$ .

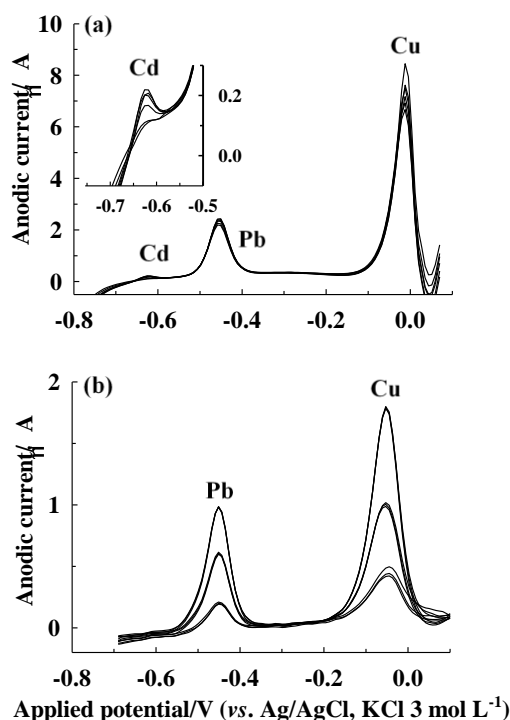


**Fig. 7.** Signal-to-noise ratios vs. SW amplitude at different frequencies for (a) Cd, (b) Pb and (c) Cu for a digestate of the inert fraction. Experimental conditions as in Fig. 6.

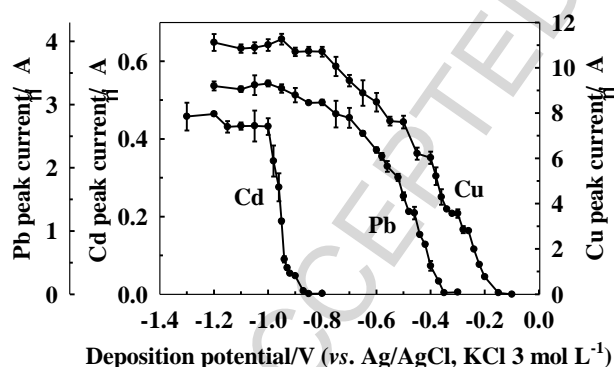
According to theory, the peak potentials also change with both frequency and amplitude, i.e. tens of mV in the positive or negative directions, respectively, in the ranges explored, with slight curvature (Fig. S2, see *Supplementary material* for data and full discussion). Moreover, as predicted by theory [50, 54] and experimentally verified in the literature [45, 47, 61, 62], an approximately linear behavior is obtained for the plot of  $E_p$  vs.  $\log A$  (where  $A$  is a dimensionless parameter related to  $f$ , see *Supplementary material*) (Fig. S3). However, from an analytical point of view, no practical influence in peak resolution is obtained if frequency and/or amplitude are changed.

These results were therefore no longer considered as regards optimization and the pair of values of  $E_{sw}=20$  mV and  $f=150$  Hz was adopted as the optimal parameters and set for all subsequent measurements.

Typical voltammograms obtained in sample n. 7 using the optimized parameters are reported in Fig. 8. The peak potentials, determined from the pseudopolarographic experiments ( $n \sim 30$ ), were: Cd  $-623 \pm 7$  mV, Pb  $-451 \pm 11$  mV, Cu  $-47 \pm 4$  mV (vs. Ag/AgCl, KCl 3 mol L<sup>-1</sup>).



**Fig. 8.** Typical voltammograms obtained with a digested solution of the inert fraction and after each of two standard additions. (a) Determination of Cd ( $t_d$  45 min), (b) determination of Pb and Cu together ( $t_d$  5 min). Sample no. 7.

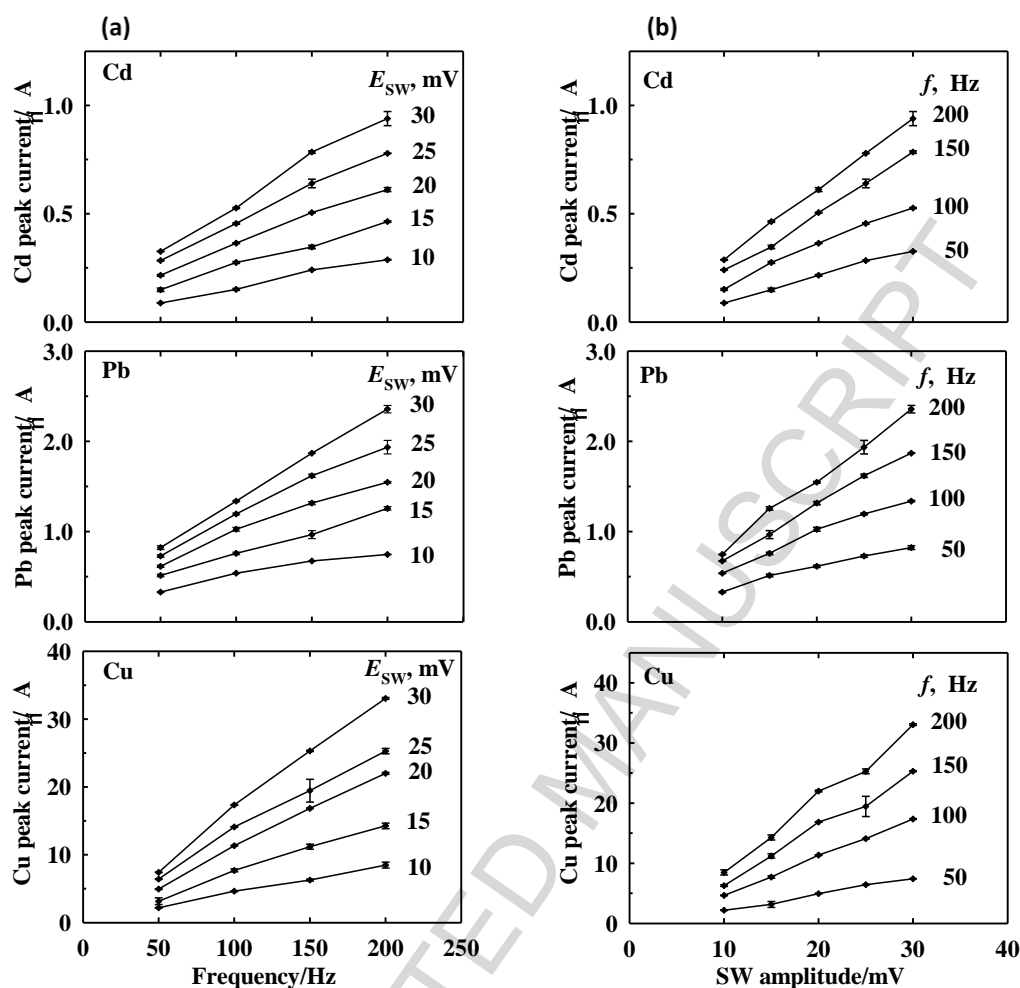


**Fig. 9.** Pseudopolarograms for Cd, Pb and Cu in a digestate of the soluble fraction obtained from sample no. 7, spiked with Cd to obtain a final concentration of  $140 \text{ ng L}^{-1}$ .

### 3.2.3. SWASV set-up and optimization for soluble/extractable fractions

For the soluble and the extractable fractions, given the almost identical final matrices, experiments were carried out with the soluble fraction and results were assumed to be valid also for the acid extractable fraction.

The pseudopolarographic curves reported in Fig. 9 show halfwave potentials at about  $-0.96 \text{ V}$  for Cd,  $-0.52 \text{ V}$  for Pb and  $-0.40 \text{ V}$  for Cu, while the corresponding plateaus are reached at about Cd  $-1.00 \text{ V}$ , Pb  $-0.95 \text{ V}$  and Cu  $-0.85 \text{ V}$ . In accordance with these results the deposition potential for determination of Cd or Cd and Pb simultaneously (the latter more frequent in the case of the soluble fraction than the extractable fraction) was selected at  $-1100 \text{ mV}$  and scan from  $-1100 \text{ mV}$  to  $+50 \text{ mV}$ . Determinations of Pb or Pb/Cu together were carried out with  $E_d = -1000 \text{ mV}$  and scan from  $-1000 \text{ mV}$  to  $+50 \text{ mV}$ . In a few cases, where Cu concentration was particularly high, determination of Cu alone was carried out with  $E_d = -1000 \text{ mV}$ , very short deposition times and with the scan starting from  $-500 \text{ mV}$  to avoid high amalgam concentration and distortion of the anodic Cu peak (see e.g. Fig. 8a) due to oversaturation, as observed in the past [47]. Deposition times were 5-45 min when Cd alone or Cd/Pb were determined, 15 s to 5 min when Pb alone or Pb/Cu were measured, 23-60 s for Cu determinations alone.



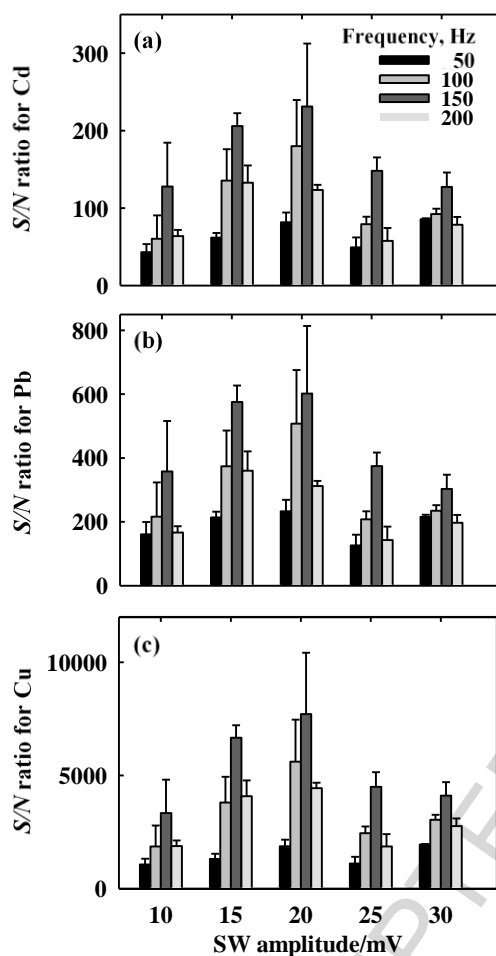
**Fig. 10.** Dependence of metal peak currents on (a) the frequency at different SW amplitudes and (b) the amplitude at different frequencies, for digestates of the soluble fraction. Error bars:  $\pm$ SD from 3-4 measurements. Experiments on sample no. 7 spiked with Cd to a final concentration of  $140 \text{ ng L}^{-1}$ .

Concerning the experiment carried out for the optimization of SW frequency and amplitude, it can be observed that results, reported in Figures 10, 11, S4, S5, are qualitatively quite similar to those obtained for the inert fraction (compare with Figures 6, 7, S2, S3). Thus only a brief summary is reported here. For all three metals we again note that the peak current tends to increase linearly with both frequency and SW amplitude (Fig. 10) with increasing rates of the same proportions observed for the inert fraction (compare with Fig. 6) and that no better linearity is obtained by plotting  $i_p$  vs.  $1/t_m$  (not shown here). However, from an analytical point of view, if we observe the  $S/N$  ratio in Fig. 11, no advantage in terms of sensitivity is obtained on increasing  $E_{SW}$  above 20 mV and  $f$  above 150 Hz. Thus also for the soluble and the extractable fractions the optimal values of  $E_{SW}$  and  $f$  are 20 mV and 150 Hz, respectively, and these values were used in subsequent experiments.

Changes in peak potential with frequency and amplitude are modest in this case too, and they are in general agreement with theory (see *Supplementary material* for data and full discussion). In short, changes in  $E_p$  vs.  $f$  at constant  $E_{SW}$  (Fig. S4a) are  $<10$  mV for the full range of  $f$  and for all  $E_{SW}$  values (i.e. generally lower than those for the inert fraction). Conversely changes in  $E_p$  vs.  $E_{SW}$  at constant  $f$  (Fig. S4b) are higher for Pb ( $\sim 23$  mV over the full range of  $f$ ) and lower for Cd and Cu (both  $\sim 11$ - $14$  mV) (i.e. higher and lower, respectively, than those of the inert fraction). In this case too, linear trends are observed for the curves of  $E_p$  vs.  $\log A$  (see Fig. S5).

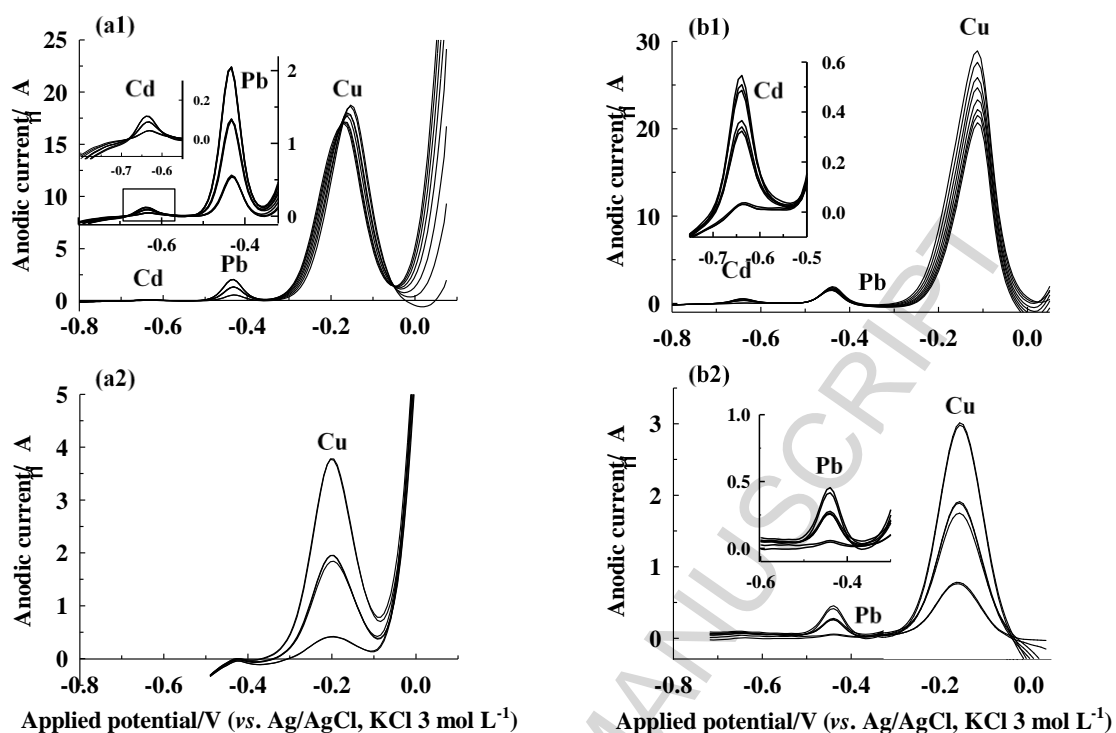
Again in the present situation no significant change in peak resolution is observed with changes in frequency and/or amplitude. Thus the peak potential variation is not considered as a further parameter to be optimized in the voltammetric set

up besides the  $S/N$  ratio. Thus the pair of values  $E_{SW}=20$  mV and  $f=150$  Hz is also considered optimal for the determination of the soluble and extractable fractions.



**Fig. 11.** Signal-to-noise ratios vs. SW amplitude at different frequencies for (a) Cd, (b) Pb and (c) Cu for digestates of the soluble fraction. Experimental conditions as in Fig. 10.

Typical voltammograms are reported in Fig. 12. The peak potentials obtained from pseudopolarographic experiments or from the analyses of samples ( $n \sim 30$  in each case) were practically coincident or not very different between soluble and extractable fractions, with: Cd  $-631 \pm 8$  mV, Pb  $-436 \pm 5$  mV, Cu  $-199 \pm 6$  mV for the soluble fraction; and Cd  $-636 \pm 5$  mV, Pb  $-435 \pm 5$  mV, Cu  $-142 \pm 4$  mV for the extractable fraction.



**Fig. 12.** Typical voltammograms obtained for the determination of (a) the soluble fraction, (a1) Cd and Pb simultaneously ( $t_d$  10 min), (a2) Cu alone ( $t_d$  15 s) (sample no. 6); and (b) the extractable fraction, (b1) Cd alone ( $t_d$  30 min), (b2) Pb and Cu simultaneously ( $t_d$  30 s) (sample no. 8).

### 3.3. Blanks, detection limits and accuracy

A summary of the results of measurements carried out to evaluate blanks in all the analytical steps (instrumental blank, digestion blank, filter blank) is reported in Table 1. No data is given for container blanks (LDPE bottles and MW vessels) since as always they were cleaned until measured blank values were the same as the instrumental blank: they were used only on this condition. As regards the instrumental blank, it can be noted that, for the HCl solution, as in the past [14, 45, 56], no signals are observed for Cd and Cu (values below detection limits of the technique, i.e.  $\sim 0.5$  ng L<sup>-1</sup>), while for Pb minimal amounts are detected, around a few ng L<sup>-1</sup>. Instead for the HNO<sub>3</sub>/HF solution definite signals, albeit low, are observed for all three metals, Cd  $3.0 \pm 0.2$  ng L<sup>-1</sup>, Pb  $16.6 \pm 0.4$  ng L<sup>-1</sup>, Cu  $28 \pm 1$  ng L<sup>-1</sup>. With reference to the digestion blanks, when we consider HCl solutions no increments are observed for Cd and Pb with respect to the instrumental blank, while a minor signal appears for Cu ( $7.8 \pm 1.2$  ng L<sup>-1</sup>). When we pass to the HNO<sub>3</sub>/HF mixture, digestion blanks of  $3.1 \pm 0.2$  ng L<sup>-1</sup> Cd,  $17.5 \pm 0.9$  ng L<sup>-1</sup> Pb and  $29 \pm 1$  ng L<sup>-1</sup> Cu are detected, which are substantially undifferentiated with respect to the instrumental blanks.

Much more important is the blank due to the filter, where we observe values of up to tens of ng L<sup>-1</sup> for Cd, up to 1-2 hundreds ng L<sup>-1</sup> for Pb, and in the order of 4-5 hundreds ng L<sup>-1</sup> for Cu. Such high blank concentrations are not surprising, since similar values were obtained by us for the soluble and extractable fractions [14] and by others when the total MW digestions of sample filters were considered [24, 25, 30]. As a consequence relatively high blank values needed to be subtracted from the measured concentrations. Note that in the literature blank values of up to 20% of the measured contents are reported [39] for the NIST SRM 1648, a matrix with much higher metal contents than ours. For the remote samples considered in this work, the blank contribution to the content in the solutions of the three fractions represents 35-65% for Cd, 28-53% for Pb, 12-22% for Cu, as interquartile range. Acceptable results, in terms of both accuracy and repeatability, are nevertheless obtained for the sample concentrations detected, since the repeatabilities of the blanks to be subtracted are

generally below 10%, as relative standard deviation, with the sole exceptions of the inert fraction of Cd and Pb, where they are about 25% and 19%, respectively.

Table 1 also reports the detection limits (defined as three times the standard deviation of the overall blank) referred to: the final sample solution concentration in  $\text{ng L}^{-1}$ , the mass fraction in the aerosol in  $\mu\text{g g}^{-1}$ , and the atmospheric concentration in  $\text{pg m}^{-3}$ . It can be seen that LODs of measured concentrations in solution are different for different metals and fractions. Though quite similar values are observed for Cd ( $3\text{-}5 \text{ ng L}^{-1}$ ), the results obtained for Pb and Cu range from  $\sim 10$  to  $\sim 70 \text{ ng L}^{-1}$  and are differentiated for each fraction. With reference to aerosol mass fractions and atmospheric concentrations, LODs are around  $0.1\text{-}0.3 \mu\text{g g}^{-1}$  and  $\text{pg m}^{-3}$  for Cd,  $1\text{-}5 \mu\text{g g}^{-1}$  and  $\text{pg m}^{-3}$  for Pb and Cu. It can be noted that generally higher or much higher results are reported in the literature for similar conditions using ICP-MS:  $2\text{-}14 \text{ pg m}^{-3}$  Cd,  $6.4\text{-}10 \text{ pg m}^{-3}$  Pb,  $20 \text{ pg m}^{-3}$  Cu [30, 35];  $15 \text{ pg m}^{-3}$  Cd,  $150 \text{ pg m}^{-3}$  Pb and  $930 \text{ pg m}^{-3}$  Cu [25]. LOD values for solution concentrations, which are more similar to ours, are reported in the case of analyses referred to a much smaller amount of filter paper ( $\sim 13 \text{ cm}^2$  instead of  $\sim 60 \text{ cm}^2$  surface area):  $30 \text{ ng L}^{-1}$  Cd,  $27 \text{ ng L}^{-1}$  Pb,  $56 \text{ ng L}^{-1}$  Cu [24].

The accuracy of the optimized digestion-voltammetric overall procedure for trace metal determinations in aerosol samples was tested by analysing the NIST 1648 and 1648a urban particulate reference materials for metal fractionation and for direct digestion of samples, respectively (Table 2). In both cases results show that the computed or the measured total contents of all three metals agree well with the certified values. If we look at the results of NIST 1648 we note that for Cd and Cu the distributions show substantial aliquots ( $\geq 24\%$ ) in all three fractions, with the highest values for the inert in the case of Cd (51%) and the extractable in the case of Cu (42%). Conversely, for Pb the metal is almost totally present in the extractable fraction (92%) in agreement with its main source in urban particulate, i.e. leaded gasoline. Moreover we observe that the water-soluble fraction of NIST SRM 1648 is in good agreement with literature data [39] especially when Pb is considered.

As regards the additivity test, the results (reported in Table 3) show that the total contents obtained by summing the water-soluble plus acid extractable plus inert fractions of metals are in good agreement with those obtained by direct digestion of the sample as it is. This agreement suggests that the sequential extraction of sample filters and the digestion of the residue were done quantitatively, and subsequent analyses performed accurately.

#### 3.4. Metal fractionation from selected samples. Repeatability

The analytical results obtained from the chemical fractionation in three selected samples (nos. 5, 7 and 8) are reported in Table 4 for solution concentrations after blank subtraction and metal content in the aerosol, expressed as both mass fractions in the aerosol and atmospheric concentrations.

As regards analytical data with respect to the limits of detection, we observe that for the inert fraction, sample values are on average 2.3-53 times the LOD for Cd, 3.3-21 times for Pb, 29-263 times for Cu. Again, similar results are observed for the soluble fraction (1.4-6.3 times for Cd, 3.6-10 times for Pb, 26-70 times for Cu) and the extractable fraction (1.5-10 times for Cd, 1.4-4.3 times for Pb, 72-160 times for Cu). It is to be stressed that, given the very high sensitivity of the technique, in all the cases the ultra trace metal determinations were carried out directly on digestate solutions without any preliminary enrichment procedure.

**Table 1** Instrumental blanks, digestion blanks and filter blanks detected for cadmium, lead and copper, and limits of detection (LOD), calculated as three times the blank standard deviation, for digested solutions and also expressed as mass fraction and atmospheric concentration in aerosol; number of replicates 3-5; reference to 1/8 of filter and dilution to 100 mL; blanks from LDPE containers with HCl solution and MW vessels with HNO<sub>3</sub>/HF solution substantially equal to or lower than the instrumental blank(s)

Blank parameter/LOD	Metal		
	Cd	Pb	Cu
Blanks, Concentration ( $\pm$ SD) <sup>a</sup> , ng L <sup>-1</sup>			
Instrumental blank			
HCl solution	<0.5	2.4 $\pm$ 1.8	<0.5
HNO <sub>3</sub> /HF solution	3.0 $\pm$ 0.2	16.6 $\pm$ 0.4	28 $\pm$ 1
Digestion blank <sup>b</sup>			
MW vessel, HCl	same as instrumental blank		7.8 $\pm$ 1.2
MW vessel, HNO <sub>3</sub> /HF	3.1 $\pm$ 0.2	17.5 $\pm$ 0.9	29 $\pm$ 1
Filter blank			
soluble fraction	17.2 $\pm$ 1.2	109 $\pm$ 11	412 $\pm$ 20
extractable fraction	20.2 $\pm$ 1.6	244 $\pm$ 24	480 $\pm$ 8
inert fraction	1.6 $\pm$ 1.2	10.8 $\pm$ 5.2	452 $\pm$ 4
Blank to be subtracted			
soluble fraction	17.2 $\pm$ 1.2	111 $\pm$ 11	420 $\pm$ 20
extractable fraction	20.2 $\pm$ 1.6	246 $\pm$ 24	488 $\pm$ 8
inert fraction	4.7 $\pm$ 1.2	28.3 $\pm$ 5.3	481 $\pm$ 4
Limits of detection			
LOD <sup>c</sup> , ng L <sup>-1</sup>			
soluble fraction	3.6	27	60
extractable fraction	4.8	69	24
inert fraction	3.6	16	12
LOD <sup>d</sup> , $\mu$ g g <sup>-1</sup>			
soluble fraction	0.24	1.8	4.1
extractable fraction	0.33	4.7	1.6
inert fraction	0.24	1.1	0.81
LOD <sup>e</sup> , pg/m <sup>3</sup>			
soluble fraction	0.17	1.3	2.9
extractable fraction	0.23	3.3	1.1
inert fraction	0.17	0.76	0.57

(<sup>a</sup>) Uncertainties as  $\pm$  standard deviation from 3-4 repetitions

(<sup>b</sup>) Includes instrumental blank

(<sup>c</sup>) LOD for sample metal concentration in digestion solutions.

(<sup>d</sup>) LOD for particulate metal concentration calculated using the average aerosol mass of 11.8 mg.

(<sup>e</sup>) LOD for atmospheric metal concentration calculated using the average air volume of 16798 m<sup>3</sup>.

**Table 2** Accuracy test of NIST SRM 1648 and 1648a urban particulate matter

Metal fraction	Metal mass fraction		
	[% of total computed]		
	Cd, mg kg <sup>-1</sup>	Pb, %	Cu, mg kg <sup>-1</sup>
NIST 1648 urban particulate			
Soluble <sup>a</sup>	19 $\pm$ 1	0.015 $\pm$ 0.0001	134 $\pm$ 2
	[24%]	[2.5%]	[24%]
Extractable <sup>a</sup>	20 $\pm$ 2	0.564 $\pm$ 0.012	238 $\pm$ 21
	[25%]	[92%]	[42%]
Inert <sup>a</sup>	41 $\pm$ 1	0.033 $\pm$ 0.003	198 $\pm$ 6
	[51%]	[5.4%]	[35%]
Total computed <sup>a</sup>	80 $\pm$ 2	0.612 $\pm$ 0.012	570 $\pm$ 22
Total certified <sup>b</sup>	75 $\pm$ 7	0.655 $\pm$ 0.008	609 $\pm$ 27
Recovery % (SD, %)	107 (10)	93 (2)	94 (6)
NIST 1648a urban particulate			
Total measured <sup>a</sup>	79 $\pm$ 7	0.678 $\pm$ 0.032	619 $\pm$ 37
Total certified <sup>c</sup>	73.7 $\pm$ 2.3	0.655 $\pm$ 0.033	610 $\pm$ 70
Recovery % (SD, %)	107 (10)	104 (7)	101 (13)

(a) Average  $\pm$  standard deviation from 3-4 measurements

(b) Certified values  $\pm$  95% tolerance interval [51]

(c) Certified values  $\pm$  expanded uncertainty [42]

**Table 3** Additivity test carried out on sample no. 8. Comparison between results of sequential extractions and direct total digestion. Reference to 1/8 of filter and solution diluted to 100 mL. Data after blank subtraction

Fraction	Metal concentration <sup>a</sup>		
	Cd, ng L <sup>-1</sup>	Pb, ng L <sup>-1</sup>	Cu, µg L <sup>-1</sup>
Water-soluble	5.2±1.6	97±4	4.19±0.06
HCl-extractable	7.4±2.6	101±21	2.37±0.14
Inert	8.4±1.8	340±10	3.16±0.07
Total computed	21±4	538±24	9.72±0.17
Total measured	17±4	570±30	9.34±0.14
Recovery % (SD, %)	124 (36)	94 (7)	104 (2.4)

(a) Average ± standard deviation from 3-4 repetitions

First of all it is useful to observe that the new results obtained here for the soluble and extractable fractions applying the new MW digestion (Table 4) are consistent with those previously obtained by the UV digestion procedure [14]. This allows us to state the good comparability of the two methods, while observing that the MW procedure is easier and less time-consuming than the UV procedure.

As regards the inert fraction, we note, for the first time in the Antarctic context, that it lies in the order of Cd 0.5-10 µg g<sup>-1</sup> or 0.3-14 pg m<sup>-3</sup>, Pb 3-23 µg g<sup>-1</sup> or 4-15 pg m<sup>-3</sup>, Cu 20-200 µg g<sup>-1</sup> or 12-140 pg m<sup>-3</sup>. Moreover it can be seen that the metal portion present in the inert fraction, in the temporal period considered, is generally higher for Cd (between 20% and 74%) and Pb (10-63%), and lower, but still quite high, for Cu (7-33%), showing a considerable/high contribution of the metal contents deriving from crustal origin. Note that generally in anthropized areas metals are distributed for the most part in the water-soluble and/or the acid-extractable fractions, especially for Pb [21, 31, 39] (see also in the present work results for the NIST SRM 1648 in Tab. 2), which suggested that anthropogenic contribution may exist mainly in these fractions [21]. In our remote area the portions present as water-soluble and acid-extractable fractions are generally lower than in anthropized areas.

Although a complete analysis of data, in term of sources and seasonal variation, will be reported in a subsequent paper dealing with all the collected samples, we can note from the results reported here that the total metal contents in the aerosol, expressed as mass fraction or atmospheric concentration, varied from Cd 1.4-15 µg g<sup>-1</sup> or 0.94-19 pg m<sup>-3</sup>, to Pb 29-36 µg g<sup>-1</sup> or 17-36 pg m<sup>-3</sup>, to Cu 300-664 µg g<sup>-1</sup> or 177-436 pg m<sup>-3</sup>.

The average measurement repeatability, expressed as pooled relative standard deviation when we consider the net concentrations of the extraction/digestion solutions, obtained after blank subtraction, show the highest values for Cd (22%, 13% and 12% for the soluble, extractable and inert fractions, respectively), lower for Pb (10%, 14%, 5%, respectively), and the lowest for Cu (2%, 4% and 3%, respectively). The values undergo small increments when we pass to data on mass fraction (Cd 24%, 16%, 15%; Pb 11%, 17%, 11%; Cu 9%, 8%, 13%), and atmospheric concentrations (Cd 26%, 21%, 24%; Pb 16%, 20%, 16%; Cu 11%, 12%, 14%) due to the contributions from aerosol mass or volume uncertainties. In conclusion, even in the presence of quite high blank contributions, generally good repeatabilities are finally obtained for Pb and Cu, while a less good but still acceptable value, (considering the very low concentration) is observed for Cd.

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**Table 4** Analytical results of metal chemical fractionation in the selected samples (nos. 5, 7 and 8) in terms of solution concentration from sequential extraction/digestion (after blank subtraction, reference to 1/8 of filter and dilution to 100 mL), mass fraction in the aerosol and atmospheric concentration (taking account of the collected aerosol mass and air volume, respectively, as reported in [14])

Metal fraction and total computed	Solution concentration, ng L <sup>-1</sup> [% of total computed]			Pooled relative SD	Mass fraction in aerosol, µg g <sup>-1</sup> [% of total computed]			Pooled relative SD	Atmospheric concentration, pg m <sup>-3</sup> [% of total computed]			Pooled relative SD
	Sample 5	Sample 7	Sample 8		Sample 5	Sample 7	Sample 8		Sample 5	Sample 7	Sample 8	
Cd												
soluble	18±4 <sup>a</sup> [7%]	23±4 [55%]	5.2±1.6 [25%]	22%	1.0±0.2	1.4±0.3	0.36±0.12	24%	1.3±0.3	0.79±0.17	0.23±0.07	26%
extractable	49±4 [19%]	11±2 [26%]	7.4±2.6 [35%]	13%	2.8±0.3	0.64±0.10	0.51±0.19	16%	3.5±0.5	0.38±0.07	0.33±0.12	21%
inert	192±14 [74%]	8.5±1.5 [20%]	8.4±1.8 [40%]	12%	11±1	0.51±0.09	0.57±0.13	15%	14±2	0.30±0.06	0.38±0.24	24%
total computed	259±15	42±5	21±4		15±1	2.6±0.4	1.4±0.3		19±2	1.5±0.2	0.94±0.28	
Pb												
soluble	153±27 [30%]	281±16 [58%]	97±4 [18%]	10%	8.6±1.6	17±1	6.6±0.7	11%	11±2	10±1	4.4±0.5	16%
extractable	299±24 [59%]	96±25 [20%]	101±21 [19%]	14%	17±2	5.7±1.5	6.9±1.6	17%	21±3	3.4±0.9	4.5±1.0	20%
inert	53±7 [10%]	111±6 [23%]	340±10 [63%]	5%	3.0±0.4	6.6±0.4	23±2	11%	3.8±0.6	3.9±0.4	15±2	16%
total computed	505±37	488±30	538±24		29±3	29±2	36±7		36±4	17±1	24±2	
Cu												
soluble	1570±30 <sup>b</sup> [26%]	2950±50 [59%]	4190±60 [43%]	2%	88±5	176±6	286±27	9%	112±11	104±11	188±19	11%
extractable	3840±50 [64%]	1730±100 [34%]	2370±140 [24%]	4%	216±11	103±7	162±18	8%	274±28	61±7	106±12	12%
inert	610±10 [10%]	350±10 [7%]	3160±70 [33%]	3%	34±2	21±1	216±21	13%	43±4	12±1	142±15	14%
total computed	6020±60	5030±110	9720±170		338±12	300±9	664±39		429±30	177±13	436±26	

<sup>(a)</sup> Uncertainties as ± SD from 3- 4 repetitions

<sup>(b)</sup> The last figure (i.e. the last zero), which is not significant, is left in to maintain the order of magnitude and the comparability with results of Cd and Pb

#### 4. Conclusions

In accordance with the main aim of the work, it has been demonstrated that a complete MW digestion of the filter sample remaining after the extraction procedure with water and with diluted HCl, to obtain the inert metal fractions, can be obtained using a digestion mixture of 5.0 mL HNO<sub>3</sub>, 1.0 mL H<sub>2</sub>O<sub>2</sub> and 1.0 mL HF in a two-step “ramps to temperature” mode.

The overall treatment was optimized for the subsequent determination by SWASV of Cd, Pb and Cu. Nitric acid, generally suggested in the literature as the first choice since it is a strong oxidizing agent, especially at elevated temperature, was used at the recommended amount of 5.0 mL. The amount of H<sub>2</sub>O<sub>2</sub> was set at an intermediate, compromise value of 1.0 mL to avoid interference either from organic substances, when too low a quantity of H<sub>2</sub>O<sub>2</sub> is used, or from residual undestroyed reagent, when too much H<sub>2</sub>O<sub>2</sub> is added. Hydrogen fluoride was added at the maximum quantity reported in the literature, i.e. 1.0 mL, and at the same time no other digestion step with H<sub>3</sub>BO<sub>3</sub> was required since the presence of excess HF does not create problems with voltammetry. The overall procedure allows the digestion time to be reduced from literature values of up to ~5 h [25] to about 1.5 h.

The work has also obtained MW digestion of the soluble and the extractable fractions in a reduced time of ~1.5 h, well below the time required in the past (~12 h) using a UV treatment [14].

It has been shown that the digested solutions obtained from a chemical fractionation based on a sequential extraction procedure (water-soluble, acid-extractable, inert fractions) can be analysed for Cd, Pb, and Cu by the ultrasensitive voltammetric technique of SWASV without any preliminary enrichment of samples. The optimal pair of values for SW frequency and amplitude, obtained maximizing the signal to noise ratios, has been found, for all the three fractions and for all three metals, to be  $f=150$  Hz and  $E_{sw}=20$  mV.

The limits of detection referred to the aerosol mass fractions and to the atmospheric concentrations were around 0.1-0.3  $\mu\text{g g}^{-1}$  and  $\text{pg m}^{-3}$  for Cd, and about 1-5  $\mu\text{g g}^{-1}$  and  $\text{pg m}^{-3}$  for Pb and Cu. These values are significantly lower than literature results [24, 25]. Measurement repeatabilities, expressed as pooled relative standard deviations for solution concentrations, showed the highest values for Cd (22%, 13% and 12% for soluble, extractable and inert fractions, respectively), while lower values were obtained both for Pb (10%, 14% and 5%, respectively) and Cu (2%, 4% and 3%, respectively). Slight increases were obtained, of course, when we passed to data expressed as mass fraction and atmospheric concentration, due to uncertainties introduced by measurements of aerosol mass and air volume, respectively.

The optimized procedures allowed us to obtain the first preliminary estimates of the distribution of the studied metals in the Antarctic aerosol between the three fractions, defined as water-soluble, dilute-acid-extractable and, above all, inert fraction. Results show that significant aliquots of metals are present in all three fractions. In particular the inert fraction represents 20-74% for Cd, 10-63% for Pb, 7-33% for Cu, possibly highlighting that significant aliquots of the metal contents derive from crustal origin, in this respect completing information given in the past [14], where the inert fraction of metals was not available.

Analyses of all the samples collected in Antarctica are now in progress and the complete series of results will be reported in a future work, together with an interpretation of results in terms of summer evolution of metal contents and their fractionation, and of possible contributions from natural and anthropogenic sources.

#### Conflict of interest

The authors declare no conflict of interest.

## Acknowledgements

Financial support from the Italian *Programma Nazionale di Ricerche in Antartide* under the projects on “Chemical Contamination”, “Study of sources and transfer processes of the Antarctic aerosol” and “Air-snow exchanges and relationships for trace elements and organic compounds of climatic interest” is gratefully acknowledged. Many thanks are due to the technical personnel of ENEA (*Ente Nazionale Energia e Ambiente*) at Terra Nova Bay and to the scientists of the Antarctic expedition for the sampling activities on site.

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## Highlights

- Speciation of Cd, Pb, Cu in aerosol is obtained by SWASV after sequential extraction
- Microwave digestion is set up and optimized for subsequent SWASV analysis
- SWASV is optimized for trace metal determination of microwave-digested solutions
- Use of microwave digestion and SWASV reduces analysis time of Cd, Pb, Cu in aerosol

ACCEPTED MANUSCRIPT