

# Comparison of voltammetry and inductively coupled plasma-mass spectrometry for the determination of heavy metals in PM<sub>10</sub> airborne particulate matter

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## Abstract

The potential of the voltammetry method was examined for the determination of heavy metals in ambient air particulate matter (PM<sub>10</sub>) on quartz filter. Cd, Pb, Cu, Zn, As were determined by anodic stripping voltammetry while adsorptive stripping voltammetry was used for the analysis of Ni. The method detection limit of these metals were 9.3, 0.1, 0.8, 0.3, 0.4, 0.1 ng m<sup>-3</sup> for Zn, Cd, Pb, Cu, Ni and As, respectively. In addition, the analysis of a Certified Reference Material NIST 1648, yielded recoveries between 92% and 103%. Consequently, both the detection limit and recovery of the voltammetric method satisfy the requirements of the European Standard for the analyses of heavy metals in PM<sub>10</sub> (EN 14902). A comparison of the inductively coupled plasma-mass spectrometry (ICP-MS) and voltammetry method on the NIST 1648 and PM<sub>10</sub> filters showed the differences between them remained well within the level of uncertainty on the NIST 1648 requested by European Directives for heavy metals (25% for Pb and 40% for As, Cd and Ni, respectively). In addition to its compliance with legislations, the voltammetry method benefits from low investment cost and the potential of complete automation. As such, one may expect voltammetry to provide a reliable alternative to the European laboratories in charge of ambient air monitoring at the time when the European Directives require to measure heavy metals in PM<sub>10</sub> on a regularly basis.

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## 1. Introduction

Heavy metals are of concern as atmospheric pollutants due to their toxic effects (WHO, 1997).

Current European Directives (European Council, 1999, 2004) set limit and target values for heavy metals in ambient air with the aim of minimising their harmful effects on human health. The Directives also established reference methods for the sampling and analysis of heavy metals, e.g., the graphite furnace atomic absorption spectroscopy (GFAAS) and the inductively coupled plasma-mass spectrometry (ICP-MS) methods described in EN

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14902 (European Standard, 2005). Other methods may be used, however, if demonstrated to give results equivalent to the reference ones.

One alternative method for the determination of heavy metals is voltammetry (Zanello, 2003; Henze, 2003). This technique is increasingly being applied for the analysis of heavy metals (in food, soil, medicinal plants, water, etc.) because it can be fully automated, can be used for multi-element analysis, and it requires only relatively low investment costs (e.g., Nedeltcheva et al., 2005; Locatelli and Torsi, 2003; Feeney and Kounaves, 2002; Mamani et al., 2005; Buldini et al., 2001, etc.). Recently, Farghaly and Ghandour (2005) used the voltammetry method for the determination of heavy metals in soil and airborne particulate matter. They report on the analysis of heavy metals in the upper  $\mu\text{g kg}^{-1}$  range for total suspended particulate in air. According to the European Directives, however, only the monitoring of heavy metals in particulate matter smaller than  $10\mu\text{m}$  is required ( $\text{PM}_{10}$ ). This study investigates the potential of the voltammetry method to determine heavy metals in  $\text{PM}_{10}$  according to EN 12341 (European Standard, 1998) in the range of concentration typical for the monitoring in ambient air. More specifically, we evaluate the voltammetry method—under the same sampling and liquid-extraction conditions as the (more costly) ICP-MS reference method—to measure zinc (Zn), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni) and arsenic (As) in ambient particulate matter. The capacity of voltammetry to meet the data quality objective of the Directives (expanded uncertainty less than 25% for Pb and 40% for Cd, As and Ni) and the analytical requirements of EN 14902 (the method detection limits (MDLs), the average recovery rates) is reported.

## 2. Experimental procedure

### 2.1. Sampling and sample digestion

In January 2005,  $\text{PM}_{10}$  was sampled according to EN 12341 (European Standard, 1998) in the vicinity of the city of Krakow (PL). During this campaign,  $\text{PM}_{10}$  containing heavy metals were collected on Quartz filters (Quartz filter QMA 4.7cm—Whatman) using a Low Volume Sampler with a  $\text{PM}_{10}$  head (Derenda LVS version 3.1). The sampling flow rate was  $2.3\text{ m}^3\text{ h}^{-1}$  and the sampling time was 24 h.

The filters were digested in a microwave oven (Milestone ETHOS TC) according to the procedure given in the EN 14902. Each filter was placed in a

Teflon vessel into which 8 ml nitric acid 70% (J.T. Baker Ultrex II) and 2 ml hydrogen peroxide (J.T. Baker Ultrex II) were added before the vessels were sealed. The temperature controlled digestion procedure consisted of (1) 20 min of linearly increasing temperature between ambient and  $220^\circ\text{C}$ , (2) 25 min of constant temperature ( $220^\circ\text{C}$ ) and (3) 20 min of cooling. A portion of the certified reference material, NIST 1648 was placed in one Teflon vessel of the microwave and weighted on the balance. The temperature controlled digestion procedure used for NIST 1648 was analogous to that of the quartz filters. NIST 1648 is intended primarily for use as control material in the evaluation of methods used in the analysis of atmospheric particulate matter. It consists of natural atmospheric particulate matter collected in an urban location.

After the temperature-controlled digestion, the solution in the Teflon vessel was transferred to a 25 ml PFA-volumetric flask (VIT-LAB GmbH), which had previously been cleaned and dried using purified air. When determining the detection limit, recovery and quantification limit (QL) of the voltammetry method, the PFA-volumetric flask had 5 ml of ammonia ( $\text{NH}_3$ ) 25% (Merck Suprapur) added before being filled with MilliQ water (Millipore) to 25 ml. Although this is somewhat different from the Metrohm method (Metrohm, Application Bulletin No 231/2e), the addition of ammonia was needed since the pH of the solution in the PFA-flask is acidic and the determination of Zn is not possible under such pH conditions with the voltammetric method. When aiming to assess the equivalence of the voltammetry and ICP-MS method, on the other hand, the PFA-volumetric flask was first filled up with MilliQ water and then divided into two parts as follows: 10 ml were transferred by pipetting to another flask for ICP-MS analysis whilst the remaining 15 ml had 3 ml of  $\text{NH}_3$  added and were intended for the voltammetry analysis.

### 2.2. Analytical method

Voltammetry is the analytical method based on current-potential measurements in electrochemical cells (Henze, 2003). The analytical signal is the current, which flows through the cell during the reaction of the analyte at the working electrode. Anodic stripping voltammetry (ASV) with the hanging mercury drop electrode (HMDE) can be used to determine all those metals that are soluble in mercury (e.g. Zn, Cd, Pb, Cu). Gold electrode on

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