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Developing the method for analytical determination of cadmium, arsenic and nickel in ambient air

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ABSTRACT

This paper presents the development of a method to determine heavy metals as arsenic (As), cadmium (Cd) and nickel (Ni) in PM 10 suspended particulate matters, according to the European standards EN 12341:2014 and EN 14902:2005 concerning measuring methods for heavy metals in air. PM 10 suspended particulate matter samples are retained on the filter and this step is followed by mineralization and atomic absorption spectrometry analysis (AAS) to determine the concentration of As, Cd and Ni. The method developed for the following aplicability areas for cadmium: 0.1 - 50 ng/m^3, arsenic: 0.5 - 350 ng/m^3 and nickel: 2 - 100 ng/m^3 can be used to determine the heavy metal concentrations of As, Cd and Ni in air samples.

Key words: *heavy metals, air pollution, PM$_{10}$, standard method, toxic effects*

1. INTRODUCTION

Annually, millions of toxic pollutant tons are released into air, both from natural sources, but especially from anthropogenic ones [1,2]. Thus, heavy metals can be inhaled directly from air or may contribute to soil pollution by fallout. Plants assimilate the dissolved metals from the contaminated soil [3], on one hand, and on the other hand, groundwater pollution occurs by infiltration, from which, the further pollutant transfer to the surface and drinking waters occurs [4,5]. Heavy metals contaminated plants represent the food for animals and people [6].

Starting with the literature on heavy metal pollution level, it is very useful to know the concentration of heavy metals in urban atmospheric powders to precisely determine the pollution level and possible measures that can be taken to mitigate pollution effects or to rehabilitate the affected areas.

Suspended particulate matters (PM) is one of the most important atmospheric pollutants in the European countries [7], and present the most frequently exceeded of normative [8]. The PM is the generic term used for a mix of aerosol particles (solid and liquid) with different sizes and chemical composition. PM10 refers to particles with less than 10 µm aerodynamic diameter, exposure to PM polluted air may affect health, both on short and long term [9,10], because of the broad range of different toxic substances that it contains [9].

Arsenic (As), cadmium (Cd) and nickel (Ni) are included in the group of metals causing effects on human health and natural ecosystem [11,12,13,14,15,16,17]. It is estimated that several million people are exposed to arsenic chronically throughout the world. Arsenic concentrations in air range from 1 to 3 ng/m^3 in remote locations (away from human releases), and from 20 to 100 ng/m^3 in cities [18]. Contamination with high levels of arsenic is of concern because arsenic can cause a number of human health effects [18,19]. Several epidemiological studies have reported a strong association between arsenic exposure and increased risks of both carcinogenic and systemic health effects and affects virtually all organ systems including the cardiovascular, dermatologic, nervous, hepatobilliary, renal, gastro-intestinal, and respiratory systems [18]. Cadmium is a toxic element for people that can cause kidney and bone damage and is carcinogenic by inhalation [20]. The form of nickel emitted to the atmosphere varies according to the type of source. Nickel species associated with combustion, incineration, and metals smelting and refining are often salts, including nickel oxides, nickel sulfate, nickel silicate, nickel sulfide, and nickel chloride [21]. Some nickel compounds are carcinogenic, increasing the risk of lung cancer. The most common harmful effect on human health is the allergic reaction, with about 10-20% of the population being sensitive to nickel. In high concentration, nickel and its compounds can cause acute and chronic toxic effects on aquatic life [11].

Breathing in air polluted with drifting dust harms human health, therefore predicting the concentration of air pollutants is very important [22]. Factors associated with the possible health effects of exposure to arsenic, cadmium and nickel have been investigated for many years in occupational environments, one of the measures designed to reduce the harmful effects on human health and natural ecosystems is that of developing methods of monitoring and assessing the level of their concentrations in air.

This study has developed a method to determine cadmium, arsenic and nickel content of powders in ambient air according to EN 12341:2014 Ambient air. Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of suspended particulate matter [23]. Reference method and field test procedure to demonstrate reference equivalence of measurement methods [23] and EN 14902:2005 Ambient air quality - Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter [24]. The areas of method applicability, in terms of concentration, are the following: cadmium: 0,1 – 50 ng/m^3; arsenic: 0,5 – 350 ng/m^3; nickel: 2 – 100 ng/m^3.

2. EXPERIMENTAL SECTION

The equipment used for determining the heavy metals is as follows: PM10 sequential or single-filter samplers; Microwave mineralisation oven, model BERGHOF MWS-3, programmable, designed for continuous operation at high digestion pressures (> 100 bar), temperatures above 230 ° C and microwave power of 1,450 W; Varian SpectrAA 240 atomic absorption spectrometer, fully automated with double real beam, equipped with: automatic turret for 4 lamps, monochromator with holographic network, full reflexive optical system, large band photomultiplier detector (185 ÷ 900 nm), GTA 120 graphite furnace (with heating speed of max. 2000^{o}C/min and precision of temperature control of 1^{o}C), single-element hollow cathode lamps for Cd, As and Ni, deuterium lamp for background correction, etc. The spectrometer has the wavelength range (185 - 900 nm) automatically selectable from the software and the measurable absorbance range from 0.001 to 3. The following reagents are used for determination: ultrapure water; concentrated nitric acid (HNO_3), ρ ~ 1,42 kg/L, mass fraction ~ 70%; hydrogen peroxide (H_2O_2), mass fraction ~ 30%; single or multi-element stock standard solution, having a certified concentration; argon cylinder having a concentration of ≥ 99.99%; certified reference material (MRC) with representative sample matrix for PM10 particulate matter in ambient air.

Sampling. In order to take samples, the sampler is installed in the field according to the manufacturer's instructions, an unexposed filter is loaded into the sampler, the sampler is programmed and turned on. At the end of the sampling period (24 hours), the exposed filter is extracted and stored for being transported to the analysis laboratory. Specific data for each sample are registered (including timeout, flow rate, the sampled air volume, weather conditions during sampling, etc.).

3. RESULTS SECTION

Sample analysis by graphite furnace atomic absorption spectrometry. The exposed filter is placed in the mineralisation tank that was previously washed with nitric acid and hydrogen peroxide and rinsed thoroughly with ultrapure water; the mineralization mixture is added (8 mL of nitric acid and 2 mL of hydrogen peroxide) taking care that the filter is completely immersed; the sample is mineralised at about 220^{o}C; the mineralised sample is transferred to a 50 mL volumetric flask and it is filled to the mark with ultrapure water; a blank sample is mineralised in parallel with the sample for the laboratory reagents used for analysis, as well as the blank field filter.

The wavelengths recommended for determining the analytes are as follows: 228.8 nm for cadmium; 193.7 nm for arsenic; 232.0 nm for nickel.

Calibration. The concentration range for preparing the calibration solutions is selected, taking into account the maximum concentration of each existing analyte in the air, the volume of the absorbed air sample and the volume of sample solutions to be analyzed. Typically, the calibration ranges used are 0 - 2 μg/L for cadmium and 0 - 20 μg/L for arsenic and nickel.

A blank calibration solution and 5 calibration solutions are prepared from the multi-element stock standard solution or from the working standard solution covering the range of previously selected concentrations (0.25/0.5/1.0/1.5/2.0 μg/L for cadmium and 1.0/5.0/10.0/15.0/20.0 μg/L for arsenic and nickel).

The calibration solutions are measured in increasing concentration order and calibration curves are plotted for cadmium, arsenic and nickel using the software incorporated in the atomic absorption spectrometer. If the value obtained for the calibration function is less than 0.995 then the calibration is repeated.

Measuring the sample solutions. At least three successive measurements of blank reagent solution, blank filter solution, blank field solution and the sample solutions shall be made. Concentrations of cadmium, arsenic and nickel are determined by using the appropriate calibration curves.

If the measured concentration is less than 3 times the method detection limit, the relative standard deviation of the three successive measurements shall be less than 10%. Otherwise, the analysis is repeated and if the problem persists, the spectrometer settings will be checked.

If the measured concentration is higher than the upper limit of the calibration range, the sample solution is dilluted appropriately and measurements are repeated taking care that the dilution factor is included in the final concentration calculation.

Determining method detection limit. Method detection limit is estimated under the analytical working conditions for each metal of interest proceeding as follows:

- ten blank filter solutions are prepared using the same type of filter as the one used to collect the sample;
- blank filter solutions are measured and method detection limit is calculated for each metal of interest and this are compared with legislative requirements. The method detection limit must be 10% of the target values set for Cd, As and Ni, respectively 5 ng/m3 for cadmium, 6 ng/m3 for arsenic and 20 ng/m^3 for nickel [25].

Calculating the results. The analyte mass *a* (m_a) on the filter is calculated in ng, using the following relation [24]:

$$m_a = \beta_a \cdot v_s \cdot F \cdot \frac{A_{tot}}{A_{part}} \qquad (1)$$

Where: m_a analyte *a* mass, expressed in ng;

β_a analyte *a* mass concentration in the sample solution, expressed in ng/mL;

v_a sample solution volume, expressed in mL;

F sample dilution factor;

A_{tot} area of the exposed filter, expressed in cm^2;

A_{part} area of the mineralised segment of the exposed filter, expressed in cm^2.

In case of completely mineralised filters, relation *(1)* becomes [24]:

$$m_a = \beta_a \cdot v_s \cdot F \qquad (2)$$

Similarly, analyte *a* mass is calculated in blank field filters (m_{Fa}) and in blank laboratory filters (m_{La}).

Calculating the mean of blank laboratory filter. The mean of blank laboratory filter ($\overline{m_{La}}$) [24] for analyte *a* is calculated as the average value of all blank laboratory filters ($m_{La,j}$) of the filter group used:

$$\overline{m_{La}} = \frac{\sum_{j=1}^{n} m_{La,j}}{n} \qquad (3)$$

Where: $\overline{m_{La}}$ average value of blank laboratory filter of analyte *a*, in ng;

$m_{La,j}$ analyte *a* mass in the blank laboratory filter *j*, expressed in ng;

n numarul de filtre martor de laborator.

Calculating the analyte concentration (Cd, As si Ni) in air. Concentration C_a of analyte *a* is calculated in the sampled air, expressed in ng/m^3, by means of equation *(4)* [24]:

$$C_a = \frac{m_a - \overline{m_{La}}}{V} \qquad (4)$$

Where: C_a mass concentration of analyte *a* in the sampled air, expressed in ng/m^3;

V sampled air volume, expressed in m^3.

Calculating method detection limit. Standard deviation of blank laboratory filters is calculated using relation *(5)* [24]:

$$S_{LBa} = \sqrt{\frac{\sum_{j=1}^{n} \left(\overline{m_{La}} - m_{La,j}\right)^2}{n-1}} \qquad (5)$$

Where: S_{LBa} standard deviation of blank laboratory filters of analyte *a*, in ng/filter;

n number of blank laboratory filters.

Method detection limit is further calculated for analyte *a*, using relation *(6)*[24]:

$$DL_{Ma} = t_{f=n-1} \cdot S_{LBa} \qquad (6)$$

Where: DL_{Ma} method detection limit for analyte *a*, expressed in ng/filter

$t_{f=n-1}$ Student factor for n measurements and a trust level of 95 %.

Calculating method detection limit, as Cd, As and Ni concentrations in air. Method detection limit is calculated as Cd, As and Ni concentrations in air for a sample volume taken over 24 hours using the relation *(7)*[24]:

$$DL_{MCa} = \frac{DL_{Ma}}{V} \qquad (7)$$

Where: DL_{MCa} method detection limit for analyte *a*, expressed in ng/m^3;

V air sample volume, expressed in m^3.

Estimating method uncertainty. The uncertainty of the analytical step is determined using a MRC (certified reference material) that should be broken and analyzed at least 14 times using the method described above. If the average concentration of the obtained results is within the measuring uncertainty range listed in the MRC certificate, that means the error detected in the analytical step is an insignificant systematic error and it will not be considered. In this case, both the mean deviation from the certified value ($\bar{e}$) and the relative mean deviation from the certified value ($\bar{e}_{rel}$) are equal to zero.

If the average concentration of the obtained results is not within the measuring uncertainty range listed in the MRC certificate, then the absolute and relative mean deviations from the certified value are calculated with relations *(8)* and *(9)* [24]:

$$\bar{e} = \frac{\sum_{i=1}^{n} \left(c_i - c_{MRC}\right)}{n} \qquad (8)$$

$$\bar{e}_{rel} = \frac{\bar{e} \cdot 100}{c_{MRC}} \qquad (9)$$

Where: $\bar{e}$ absolute mean deviation from the certified value;

$\bar{e}_{rel}$ relative mean deviation from the certified value;

c_i analysis *i* result of MRC;

c_{MRC} certified value for the analized analyte;

n number of MRC analyses.

4. CONCLUSIONS

(Times New Roman 10) Improving monitoring and assessing air quality will lead to pollution decrease and maintaining a sustainable environment, harmful effects on human health and natural ecosystems will be minimized, respectively. Developing a method for evaluation of metals as arsenic, cadmium and nickel in PM10 suspended particulate matter performed in this paper is a useful tool for developing possible methods for their control in order to improve population health.

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