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Determination of the total mercury in contaminated soils by direct solid sampling atomic absorption spectrometry using an AMA-254 device and radiochemical neutron activation analysis

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ABSTRACT

High total mercury (T-Hg) contents in soils, up to 25 mg kg^{-1}, were determined by two independent methods: a one-purpose atomic absorption spectrometer AMA-254 (Advanced Mercury Analyser) with direct solid sampling and radiochemical neutron activation analysis (RNAA), using sample masses of 10 mg to 25 mg and about 150 mg, respectively. An excellent agreement between results of both methods was obtained. For quality control (QC) purposes, NIST SRM 2711 Montana Soil and NIST SRM 2711a were analyzed by both methods using the above sample masses. The results obtained compared with the NIST certified values within the uncertainty margins, thus proving the accuracy of the procedures employed. A new mercury value of 1.42 mg kg^{-1} ± 0.12 mg kg^{-1} was determined in NIST SRM 1648a Urban Particulate Matter by RNAA. For achieving accurate results by the AMA-254 spectrometer, optimizing of the analytical procedure was necessary, consisting of analyzing small (10 mg to 25 mg) sample masses. It has been found that the cryogenic grinding used provided sufficiently representative and homogeneous samples. In view of the decomposition procedures employed in AMA-254 and RNAA procedures, it can be inferred that the mercury contained in QC samples was presumably bound in an organic fraction. A test in which HgS was analyzed by RNAA showed that even mercury present in sulfide form would be fully recovered using the procedures employed.

1. Introduction

Mercury exists in the environment in a variety of chemical and physical forms as a result of both natural and man-made releases. The chemical forms involve elemental mercury, inorganic mercury species, and organic mercury species, which exhibit different toxicities for organisms, methylmercury being the most toxic species. Therefore, increased attention has recently been paid to the determination of Hg species in environmental and biological samples [1–3]. Nevertheless, reliable procedures for the determination of T-Hg are still in demand, namely in pollution monitoring, in order to evaluate the efficiency of extraction methods used for speciation analysis, and subsequently in many important decisions. Such procedures usually involve sample digestion as the first step. For soils, various reagents were used, namely concentrated acids, *e.g.*, HNO_3 alone [4,5] or in a mixture with H_2SO_4 [6] or HCl [7–9]. The American Society of Agronomy has proposed the use of a microwave digestion method with a mixture of H_2SO_4 + HNO_3 + HCl [10], while a combination of HNO_3 + HCl was proposed by the U.S. EPA [11]. The International Atomic Energy Agency proposed a method based on oxidative digestion that employs a mixture of concentrated HNO_3 + H_2SO_4 + BrCl [12]. All these reagents and many others, including aqua regia extractions and the use of HF were reviewed in detail by Issaro et al. [13] and were also mentioned in a paper describing the preparation and characterization of a soil reference material from a mercury contaminated site [14]. Following one of the above digestion procedures, the determination of T-Hg in soils and sediments is usually carried out by cold vapor atomic absorption spectrometry (CV AAS) or cold vapor atomic fluorescence spectrometry (CV AFS) measurement [14,15]. Nowadays, procedures for fast, direct solid sampling AAS are available, which are compliant to EPA 7473 and ASTM D6722 methods, using AMA-254 (Leco, USA) or DMA-80 (Milestone, USA) devices. Solid sampling-graphite furnace AAS has also been developed [16], which can also be transformed into a screening method.

We present a simple direct solid sampling atomic absorption spectrometry method using an AMA-254 device for the determination of T-Hg in soils highly contaminated from different pollution sources. This method is fast and much more effective compared with those using a digestion step followed by CV AAS or CV AFS. Excellent accuracy of the T-Hg determination at the level up to 25 mg kg^{-1} using AMA-254 was demonstrated by analysis of several US NIST soil standard

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reference materials (SRMs) and by a comparison with results of RNAA achieved for the same contaminated soil samples and NIST SRMs.

2. Experimental

2.1. Sampling and sample treatment

Samples of contaminated soils from two localities with different pollution sources were analyzed. The first site was an abandoned waste storage ground of a former incineration plant in the suburb of Hradec Králové, Czech Republic, in which agricultural waste, such as fertilizers, preservatives, pesticides, industrial and chemical industry wastes, such as oil, organic solvents, metals, halogens, sulfur, dyes, etc., were incinerated between the years 1993 and 2002. The hazardous waste was stored prior to incineration in a depository without protection and leakage control during the operational period of the incinerator. The Hg content in several soil samples from the former waste depository exceeded the maximum permissible limit of 0.8 mg kg^{-1} [17] and in separate experiments Hg^0 and methyl mercury CH_3Hg^+ were identified as the dominant species there. The second sampling site was selected in the vicinity of a former phenyl mercury chloride-based fungicide production plant next to Příbram, Czech Republic. Although the use of mercury-based fungicides was discontinued at the end of 1980s, the highly elevated Hg contents in soil are still observed close to the plant, reaching up to 10 mg kg^{-1}. Similarly, even four mercury species were detected in this sampling site: Hg^0, inorganic mercury Hg^{2+}, methyl mercury CH_3Hg^+ and phenyl mercury $PhHg^+$ (to be published). Soil pollution with lead, arsenic, cadmium and zinc also occurs in this location due to mining and smelting industry and due to a high content of these elements in the parent rock [18].

The soil samples were collected from the upper layer (0–20 cm), air-dried at laboratory temperature (22–24 °C), sieved through a nylon 2-mm screen and 5-g sample portions were further subjected to cryogenic grinding at liquid nitrogen temperature (77 K) using a SPEX 6770 Freezer Mill (SPEX SamplePrep, USA) to achieve a degree of homogeneity as high as possible. Cryogenic grinding provides not only perfect sample disintegration, but also prevents possible losses of volatile mercury forms by warming up of samples in common planetary ball mill devices. Three samples from each locality were selected for analysis.

Control samples of NIST SRMs were analyzed without any treatment, in the "as received" state. Moisture content was determined on non-analyzed aliquots according to instructions in the respective certificates [19–21] and accounted for.

2.2. Determination of T-Hg with AMA-254

The advanced mercury analyzer AMA-254, originally developed by Altec, Ltd., Czech Republic as an advanced version of Trace Mercury analyzer TMA-254 [22], is a single-purpose atomic absorption spectrometer for determination of mercury traces in various solids and liquids without sample pre-treatment or pre-concentration. A sample is combusted in an oxygen-rich atmosphere (99.5%) and the evolved gasses are then transported *via* an oxygen carrier gas through specific catalytic compounds (to remove interfering impurities, *i.e.*, ash, moisture, halogens, and minerals) to a Au-plated ceramic (an amalgamator), which collects the mercury in vapor. The amalgamator is then heated up to ~700 °C to release mercury to the detection system, which contains the Hg-specific lamp, emitting the light at a wavelength of 253.7 nm. A silicon UV diode detector is used for mercury quantification. The working range is between 0.05 ng and 500 ng.

Samples of contaminated soils and quality control materials with masses of 10 mg to 25 mg were inserted into the AMA-254 spectrometer in a nickel boat, dried at 120 °C for 70 s, combusted in the oxygen atmosphere at 650 °C for 150 s and after 45 s of waiting (the time needed for cleaning of the system) the next sample was introduced. For quantification, a mercury reference standard solution 1000 mg L^{-1} ± 10 mg L^{-1} as Hg^{2+} in dilute nitric acid (Hach Lange, Ltd, Ireland) was used to prepare aqueous calibration solutions (in the range of 0–200 μg L^{-1}) using deionized water with a resistivity of 18.2 MΩ cm^{-1} (Millipore, USA). Each calibration solution contained 1% (v/v) HNO_3, 0.1% (v/v) HCl (Suprapur, Merck, Germany) and mercury-free 0.01% (m/v) $K_2Cr_2O_7$ (Merck, Germany). Of these solutions, 100 μL aliquots were used for calibration. The same volume was used for blank evaluation. All glassware was soaked with 15% (v/v) HNO_3 for 48 h and rinsed several times with deionized water before use.

2.3. Determination of Hg with RNAA

A slightly modified procedure described earlier [23] was used. Briefly, samples of contaminated soils and quality control materials with masses of 100–150 mg were sealed in quartz glass ampoules (Suprasil®310, Heraeus, Germany), which were pre-cleaned by washing in dilute sub-boiled HNO_3 and deionized water (1 + 5). The samples were irradiated in the LVR-15 reactor in Řež at a thermal neutron fluence rate of $3 \cdot 10^{13}$ cm^{-2} s^{-1} for 10 h within the CANAM infrastructure (Ministry of Education, Youth and Sports of the Czech Republic project No. LM2011019). For irradiation, each batch contained 4–5 soil samples, a blank ampoule, an Hg standard for relative standardization, and 2 quality control samples. After 2 to 3 weeks of decay time, the ampoules were cleaned in boiling *aqua regia*, washed with water, cooled in liquid nitrogen and crushed. After addition of 100 μg of inactive Hg carrier, the samples (together with the quartz glass splinters) were decomposed in 5 mL of concentrated HNO_3 in a microwave heated Teflon vessel under elevated pressure in an ERTEC® Magnum II (Poland) device. The quartz glass splinters and a non-decomposed mineral fraction of the samples were separated by filtration over a piece of glass wool in a glass tube, thoroughly washed first with dilute HNO_3 (1 + 5), then by distilled water, and the resulting solution was made to 80 mL with water. Radiochemical separation of ^{203}Hg was carried out by extraction with two portions (10 + 5 mL) of 0.01 mol L^{-1} nickel diethyl dithiocarbamate ($Ni(DDC)_2$) in chloroform from dilute HNO_3 (approximately 1 mol L^{-1}). The separated 15 mL $Ni(DDC)_2$ fractions were counted in 30-mL polyethylene vials for 2 h with an coaxial HPGe detector (relative efficiency 78%, FWHM resolution of 1.8 keV, both for the 1332.5 keV gamma line of ^{60}Co) coupled to a computer controlled Canberra Genie 2000 gamma-spectrometer (Canberra, USA). The 279.2 keV gamma-line of ^{203}Hg was used for Hg quantification by comparison with that of an Hg standard. The Hg standard was prepared by dissolution of metallic mercury in concentrated HNO_3 under reflux. From a stock solution with the mercury concentration of 6.575 mg L^{-1} ± 0.033 mg L^{-1} in dilute HNO_3 (1:10) a 100 μL aliquot was deposited in a quartz ampoule and sealed. After irradiation, the mercury standard was carefully washed out from the ampoule, diluted 1:10 in a volumetric flask and a 250 μL aliquot, which contained 16.44 ng ± 0.13 ng of Hg was made to 15 mL for gamma-spectrometry measurement. The mercury separation yield was 99.4% ± 0.5% (x ± s.d., $N = 3$) as determined in model experiments by spiking non-irradiated soil samples with the ^{203}Hg radiotracer. To three 100 μL aliquots of the mercury stock solution, the same volume of a saturated water solution of thioacetamide was added into the quartz ampoules, which were sealed, and the ampoules were warmed up in a water bath until HgS precipitated.

3. Results and discussion

Results of the T-Hg determination in contaminated soils achieved by two independent methods, AMA-254 and RNAA, are compared in Table 1. Three replicates were analyzed by the former technique, while a single aliquot was assayed by the latter technique and the combined uncertainty was evaluated by taking into account all important uncertainty sources. An excellent agreement of the AMA-254 and