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Analytical Note

The direct determination of HgS by thermal desorption coupled with atomic absorption spectrometry

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ABSTRACT

This research was aimed at the direct determination of HgS in environmental samples by means of thermal desorption coupled with atomic absorption spectrometry. Operating parameters of the apparatus used for thermal desorption (including a prototype desorption unit) are described in this work, as well as the procedure for measuring mercury release curves together with an evaluation of the analytical signal including two methods of peak integration. The results of thermal desorption were compared with HgS contents obtained by sequential extraction. The limits of quantification of the proposed method for the selective determination of the black and red forms of HgS were 4 μg kg^{-1} and 5 μg kg^{-1}, respectively. The limit of quantification of red HgS in soils was 35 μg kg^{-1}. The developed analytical procedure was applied to soil and sediment samples from historical mining areas.

1. Introduction

Mercury production from red HgS represents a major anthropogenic impact on the natural Hg cycle in the environment. Elemental Hg released during ore processing and Hg forms contained in tailings constitute a considerable environmental burden. Areas of Hg mineral deposits [1] are also significant sources of environmental contamination. Mercury speciation in tailings depends on the initial speciation of Hg in the ore, the method of ore processing, and the physico-chemical parameters of the material. The main Hg forms in these localities are red HgS, black HgS, and metallic Hg [2]. The release of colloidal HgS and ongoing speciation changes allow the subsequent transport of the mercury.

Red HgS is the most important Hg mineral, which is often found in the form of veins or scatters in rocks in areas with hot springs. Mercury can be transported in hydrothermal fluids as the elemental form in aqueous solution or as gaseous Hg [3]. The geochemical mechanism of Hg mineral precipitation is the hydrothermal reworking of marine black shales, which leads to three types of Hg deposits [4]. The hot-spring type of Hg deposit is the most common and often geologically young [1]. Hydrothermal HgS crystallizes between 195 °C and 160 °C, a typical temperature range for the formation of Hg ore is from 200 °C to 100 °C [5]. Red HgS inverts to black HgS at 345 ± 2 °C (in a pure HgS system), but impurities (e.g., Fe and Zn) and also non-stoichiometry decrease the inversion temperature [4]. In addition, small particles of secondary Hg minerals are formed during ore processing. Black HgS is a relevant secondary mineral, which is formed in the course of the calcination process from the ore of silica-carbonate type of Hg deposit [1].

Accurate determination of HgS and nonsulfidic Hg forms in tailings enables the environmental risks of contaminated materials to be evaluated. Sequential extraction [6] is the most frequently used method for the determination of various Hg forms. An alternative method for the study of Hg speciation in solid samples is thermal desorption [7]. This method is based on the thermal release of individual Hg forms according to their thermal stability. The thermal behavior of Hg forms depends also on the intensity of their binding to the matrix. Instrumentation for this method, the preparation of calibration materials, the characteristic intervals for desorption temperatures, and the evaluation of mercury release curves have been described in the literature [8]. The method is particularly suitable for the identification of metallic Hg, matrix-bound Hg, and HgS [7]. Matrix-bound Hg is composed of bivalent and elemental Hg, mobile and semi-mobile Hg forms [7,8,9]. Matrix-bound Hg is formed by Hg readsorption during cooling of tailings. Metallic Hg can penetrate into the rocks at elevated temperature and adsorb within inner-sphere sorption sites [8].

The direct determination of HgS in solid samples stands in focus in this work. The thermal behavior of HgS was described in many papers [7,9,10]. Generally, the thermal desorption coupled with atomic absorption spectrometry (TD-AAS) is often realized by in-house fabricated devices coupled with common atomic absorption spectrometers [7] or by commercial pyrolyzer coupled with single-purpose mercury analyzer [11]. This paper describes in details a prototype of the desorption unit

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used in previous works [9,12]. The previous publications are primarily concerned with the thermal stability of mercury compounds without any detailed description of the equipment.

The aim of this research was to develop an analytical procedure for the direct determination of red HgS in tailings, soils, and sediments. Specifically, the focus was on (i) developing a procedure to determine HgS by means of thermal desorption, (ii) the processing of mercury release curves, and (iii) the application of the suggested procedure on environmental samples.

2. Materials and methods

2.1. Locations and samples

Two deposits of red HgS in the Czech Republic were studied in this research. The first historical mine was Jedová hora (Poison Mountain) near Neřežín (N49°47′34″, E13°53′15″). The locality of Jedová hora forms part of the unmetamorphosed Ordovician sedimentary and volcanosedimentary sequences of the Barrandian Basin [5]. Mercury was mined here as a byproduct of iron ore mining from the 18th century until 1870 [2,13]. Hydrothermal vein mineralization was formed in this deposit. The presence of black HgS was not proven. The ore was processed directly in the mine grounds by melting in cylindrical retorts with the subsequent condensation of mercury into water [13].

The second locality was a negligible deposit near Bezdružice (N49°53′47″, E12°59′15″). The mineralization associated with metamorphosed shales of the Neoproterozoic, Cambrian–Ordovician and Silurian ages [5] also occurs as red HgS. The primary association of mercury with gold is uncertain due to its scattered occurrence in old heaps and in a nearby stream. The ore was mined in shallow pits and floated in situ in the 17th and 18th centuries [14].

Seven samples of soil (JH1–JH7) were collected in the vicinity of the former mining pit at Jedová hora. Each sample was collected as a soil profile (0–25 cm) after the removal of fresh organic material from the surface. Red HgS from Jedová hora obtained directly from the rock was also studied in this work. Two sediments from the stream (TS68 and TS83) and two soil samples (TP80 and TVP402) were taken in the vicinity of Bezdružice.

2.2. Reference materials and reagents

The following standard and certified reference materials were used: $Hg(NO_3)_2$ in 2 mol L^{-1} HNO_3 for AAS (1000 mg L^{-1} ± 4 mg L^{-1} Hg^{2+}, Fluka, Germany); CRM 020 Trace Metals—Sandy Loam 2 (RTC, USA) with a total mercury content of 1.12 ± 0.03 mg kg^{-1}; and CRM CC 580 Estuarine Sediment (No. 0160, IRMM, Belgium) with a total mercury content of 132 ± 3 mg kg^{-1}.

HCl (A.C.S. reagent, Hg < 0.0000005%, Sigma-Aldrich, Germany), KOH (p.a., ≥86%, Hg < 0.00001%, Fluka, Germany), HNO_3 (p.a., 65%, Hg < 0.0000005%, Sigma-Aldrich, Germany), $Na_2S \cdot nH_2O$ (32–38%, Sigma-Aldrich, Germany), and $K_2Cr_2O_7$ (A.C.S. reagent, Hg < 0.000001%, Merck, Germany) were used in the preparation of extraction or calibration solutions. The synthetic red form of HgS was obtained from Sigma-Aldrich (p.a., 99%). Black HgS was prepared by precipitation as follows: a solution of 0.1 mol L^{-1} $HgCl_2$ (A.C.S. reagent, 99.5%, Sigma-Aldrich, Germany) was added to an unsaturated Na_2S solution at laboratory temperature; precipitated HgS was repeatedly decanted and dried afterwards to a constant weight at laboratory temperature.

2.3. Preparation of samples and calibration materials

The samples from Jedová hora and Bezdružice were dried to a constant weight at laboratory temperature. Each sample was sieved and the proportion with particle sizes of below 2 mm was used for analysis. This proportion was pulverized in the mill (Pulverisette 7, Fritsch, Germany) to a particle size of below 63 μm. The processed samples were stored in polyethylene vials at 4 °C.

Sample dilution with sea sand (Penta, Czech Republic) was performed in an agate mortar for the samples with high mercury content (JH1 and JH5). The sand was previously heated at 1000 °C for 2 h. The dilution of CRM CC 580 by sand was performed at a ratio of 100 mg of certified material to 900 mg of sand. The sample of red HgS from Jedová hora was also ground in a mortar with sand. Calibration samples containing black or red HgS in sand were prepared with Hg concentrations ranging from 6 ng g^{-1} up to 1.2 μg g^{-1}.

Calibration solutions for the AMA-254 analyzer were prepared from CRM $Hg(NO_3)_2$ for AAS at concentrations of 1 μg L^{-1}, 10 μg L^{-1}, 100 μg L^{-1}, and 1000 μg L^{-1}. Solutions were stabilized using HNO_3 and $K_2Cr_2O_7$.

2.4. Instrumentation

The determination of total mercury content in all samples (including solid calibration materials and solutions) was performed using an AMA-254 analyzer (Altec, Czech Republic). This single-purpose, single-beam atomic absorption spectrometer enables the direct dosing of liquid and solid samples. The source of radiation is an Hg lamp with a wavelength of 253.65 nm. Two operating ranges of the analyzer are provided by means of two cuvettes with different lengths in the optical path.

Thermal desorption was performed using a Perkin Elmer 3030 atomic absorption spectrometer (USA) with deuterium background correction. An electrodeless discharge lamp (Perkin Elmer, USA) operating at a wavelength of 253.7 nm was used as the source (power 5 W). The spectral bandwidth was 0.7 nm. A quartz tube (of length 18.5 cm) in the optical path of the spectrometer was heated to 800 °C in an AEHT-01 heating block (RMI, Czech Republic). The output signal of the spectrometer was digitized using a converter to enable the processing of the analog signal. In-house fabricated TK15e unit is designed to allow controlled heating of a gas from laboratory temperature up to 480 °C. The instrument includes a control unit enabling the digital setting of parameters for gas heating and a heater. The scheme of the heater of TK15e unit and the quartz tube in the optical path is presented in Fig. 1. The heating of the gas is regulated by a temperature sensor fixed in the end part of the heater, into which a sample is inserted. The gas supplied to the heater is used both for sample heating (most of the flow) and as an analyte carrier. The separation of these two flows is enabled by a system of two concentric glass tubes—the inner tube contains a fritted capsule with the sample; gas flowing between the inner and outer tubes is used for heating. The flow of carrier gas is regulated by a commercial flowmeter placed on the output from quartz tube. The three main advantages of high flow of warming gas are (a) thermal stability of the system including regular heating of the sample particles, (b) minimum delay in the power control of the heating unit in relation to actual temperature of the sensor, and (c) prevention of the condensation of pyrolysis products (from materials with a high content of organic carbon).

2.5. Analytical procedure

The AMA-254 analyzer was calibrated in the range 0.05–200 ng Hg by means of calibration solutions. Calibration by liquid standards is more convenient than using solid standards [15]. The determination of total Hg content in solid samples was performed under the following conditions: 20 s drying time, 150 s decomposition, and 45 s delay. Six replicated analyses were performed for each sample.

Thermal desorption was carried out according to the following procedure. The inlet flow of argon was 10 L min^{-1}; the flux of the carrier gas was 500 mL min^{-1} or 100 mL min^{-1}, and the remainder of the flow was used as a warming gas in the heater. The heating rate was 30 °C min^{-1}; mercury release curves were observed in the temperature range 50–450 °C. Thus, the duration of each analysis was approximately