



Determination of total mercury in bauxite and bauxite residue by flow injection cold vapour atomic absorption spectrometry



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ABSTRACT

A simple method for precise and accurate determination of total mercury in bauxite and bauxite residue was developed by using the flow injection mercury system. Samples of the solid materials were first microwave digested in acidic and oxidising conditions to convert all mercury to an aqueous ionic form. Following filtration and dilution, ionic mercury was reduced to elemental mercury with acidic SnCl₂ to produce a cold mercury vapour. The mercury absorbance calibration graph was linear up to 20 µg·kg⁻¹ with R² > 0.999. The detection limits were determined to be 23 ng·kg⁻¹ and 17 ng·kg⁻¹ for bauxite and bauxite residue respectively. The relative standard deviation for 1 µg·L⁻¹ mercury standard solution (n = 27) was 1.5%. In the absence of a certified bauxite reference material, accuracy of the method was tested with the closest available zinc concentrate reference material. Spiking known amounts of mercury in bauxite and bauxite residue samples was also tested; 95–111% recovery was obtained for both samples. The method developed in this paper is recommended for measuring total mercury in bauxite and bauxite residue.

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1. Introduction

Mercury has long been recognised as a neurotoxic element [1]. It is ranked third in the “priority list of hazardous substances” by the United States Comprehensive Environmental Response, Compensation, and Liability Act [2]. The United Nations also finalised the legal document “Minamata Convention of Mercury” with the aim to reduce mercury emission; 140 countries are signatories to this convention [3]. Recognising the growing international concern over mercury emissions, the International Council on Metals and Mining (ICMM) adopted a Mercury Risk Management Position Statement to position its members in a leadership role on the issue [4]. Rio Tinto Alcan and Queensland Alumina Limited began collaboration with the University of Queensland in 2011 to develop an improved understanding of mercury in their operations.

Mercury can be found both naturally as well as introduced into the environment by anthropogenic activities [5]. Reliable monitoring of mercury release and distribution is challenging due to issues with both sampling and measurement. Many instrumental analytical methods can be employed to determine the trace level of mercury in various samples. The most commonly cited techniques are: atomic

absorption spectrometry [6–11], atomic fluorescence spectrometry [12–15], inductively coupled plasma mass spectrometry (ICP-MS) [16–19], inductively coupled plasma atomic emission spectrometry (ICP-AES) [20], electroanalysis [21,22], and neutron activation analysis [23,24].

Cold vapour atomic absorption spectrometry (CV-AAS) is a widely used method because of its high sensitivity and selectivity for mercury. This method involves generation of elemental mercury from an acidified solution with a reducing agent (e.g. SnCl₂, NaBH₄) or by other means such as photoreduction, electrochemical (EC) vapour generation, and ultrasound promoted cold vapour generation [25].

The CV-AAS technique requires that the elemental and organic forms of mercury be oxidised into ionic mercury in the feed solution [8]. The conversion of complex solids into an aqueous form is accomplished by heating the samples with concentrated acids. Wet digestion is used most commonly as mercury is lost to the vapour phase during dry ashing. Oxidants are also employed during wet digestion with the most common acids and oxidising agents being HCl, HNO₃, H₂SO₄, HClO₄, KMnO₄, K₂Cr₂O₇ and H₂O₂. Elemental mercury, methyl mercury, dimethyl mercury are potential volatile components of the mercury species in a sample. Due to these volatile components, along with the tendency of mercury to adsorb on vessel walls and the requirement for complete digestion of the mercury, care must be taken in the selection of respective digesting agents and overall procedure. The choice of digestion acid depends upon the type of sample and the form of mercury present in the sample. For example, samples

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containing organic mercury need strong oxidising agents such as aqua regia and bromine monochloride solution. Samples high in silica may require hydrofluoric acid for complete solid dissolution. Perchloric acid also has strong oxidising power but can be dangerous for the sample high in organic content and it requires heating >200 °C to achieve its maximum oxidising power [26].

The sample preparation step in mercury determination is a challenging part of the process, as it consumes time and can result in loss of analyte due to its volatile nature. Pressure microwave digestion is a good alternative to ambient pressure digestion [27]. The advantages of pressure digestion are a fast digestion time, greater accuracy, less consumption of reagents, reduced sample size and less contamination [28–31].

Bauxite ore is a sedimentary rock that arises due to weathering of volcanic rocks [32]. The minerals are generally well oxidised with aluminium, iron and silicon being the major components. Metallurgical grade alumina is produced from bauxite ore using the Bayer process which involves digestion of bauxite with hot sodium hydroxide under high pressure at temperatures in the range of 130 °C to 280 °C depending on the feed material. Bayer process residue (bauxite residue) is the fraction of the bauxite ore that remains undigested. The mercury content of bauxite ore can vary significantly with values of 20–100, 500–700 and 1200–2000 $\mu\text{g}\cdot\text{kg}^{-1}$ being reported [33]. The mercury varies with the geographical origin of bauxite ore [34] and, within a single deposit, mercury content can also vary significantly. To reliably ascertain the total mercury content bauxite ore and bauxite residue, a robust method was developed using microwave digestion and flow injection mercury system (FIMS) on the resulting solution. The main challenges in the development of the procedure are the presence of trace and variable amounts of mercury and complex matrix of bauxite and bauxite residue.

2. Experimental

2.1. Reagents

Deionised water (greater than 1.0 M Ω cm resistivity) was used to prepare the solutions. All reagents were of analytical grade and checked for trace mercury contamination. A 1.2% (w/v) SnCl₂ reagent was freshly prepared by dissolving 12.0 g SnCl₂·2H₂O in 30 mL HCl and diluted up to 1 L with deionised water. Mercury stock solution 1000 mg·L⁻¹ in 10% (v/v) HNO₃ was supplied by Perkin Elmer Australia. Other stock solution was prepared by diluting this mother stock solution with deionised water and 1 mL BrCl as a preservative for 50 mL solution. Mercury calibration solutions (0.5 to 20 $\mu\text{g}\cdot\text{L}^{-1}$) were prepared from dilution of the mother stock solution prior to each experiment. Hydrogen peroxide (30% w/w) was supplied by Fluka Analytical, and used as such without further dilution. Bromine monochloride solution was prepared by first mixing 5.4 g of KBr (Sigma Aldrich) in 50 mL HCl for 1 h, 7.6 g KBrO₃ (Sigma Aldrich) was then added slowly over a period of approximately 5 min to produce the BrCl solution. Hydroxylamine hydrochloride was prepared by dissolving 15 g NH₂OH.HCl in deionised water to a final volume of 50 mL. Aqua regia (3 HCl + 1 HNO₃ by volume) was prepared immediately prior to digestion. Argon gas with >99.95% purity (Core gas) was used in all experiments.

The concentrated acids (HCl-37%, H₂SO₄-95%, HNO₃-70 (w_{acid}/w_{solution}) %) were supplied by Sigma Aldrich. They are used without dilution unless specified. When diluted, the percentage specified throughout the paper refers to volume percentage: 100% * (V_{concentrated solution} / V_{diluted solution}).

2.1.1. Reference material

Validation of the method described in the present work was performed using zinc concentrate reference material BCR®-109 (Institute for Reference Material and Measurements).

2.2. Instrumental

2.2.1. Microwave digester

For the digestion process a speed wave®4 (Berghof products) + instruments GmbH Germany, digester with DAK-100 pressure vessels was used. The pressure vessels are made of TFM-PTFE which has a high chemical resistance and hydrophobicity. The vessels are rated up to 100 bars with a maximum temperature of 300 °C. To provide a comfortable safety margin, the maximum temperature applied in this procedure was 230 °C. The pressure is monitored continuously by a contact free, optical system along with temperature by an external infrared based estimate. The microwave digestion of bauxite and bauxite residue was carried out in stages, in the first stage, the reactor contents were heated to 120 °C (maximum pressure 60 bars) for 6 min with a ramp up time 3 min followed by heating at 200 °C for 5 min with ramp up time of 3 min. In the third stage, the solutions were heated at 230 °C for 16 min with a ramp up time of 5 min. The total time required for digestion is about 45 min (including cooling time in the microwave digester).

2.2.2. Flow injection mercury system (FIMS)

A Perkin Elmer FIMS 400 flow injection mercury system is employed for the determination of mercury content of the diluted digestion liquor. This instrument uses a high performance single beam optical system, solar blind detector and low pressure mercury lamp. This flow injection system consists of two peristaltic pumps (P1, P2), a 24 cm long absorption cell with removable quartz window, electrically heated mantle to maintain the cell temperature at approximately 50 °C. The flow injection switching valve has five ports with variable length sample loops. The tubing is made of PTFE and the gas liquid separator is a membrane also made of PTFE. FIMS is a combination of the flow injection technique with atomic absorption detection. The hardware was controlled using the Perkin Elmer Win Lab 32 for AA system software. The instrumental operating conditions are given in Table 1. SnCl₂/HCl was used as reductant and argon gas was used as a carrier of mercury vapour to the absorption cell.

2.3. Sample collection and nature of samples

Three different bauxite and two different bauxite residue samples were collected from various alumina refineries and mining sites. Samples were collected and placed in plastic containers and transported to the lab.

2.4. Characterization of bauxite residue and bauxite

The main components of bauxite and bauxite residue samples were quantified by XRF (X-ray fluorescence), the bauxite content was 44–53% Al₂O₃, 14–27% Fe₂O₃, 3.8–7% SiO₂, 2–2.5% TiO₂ as wt.% and

Table 1
Characteristic parameters of FIMS.

FIMS	
Wave length	253.7 nm
Lamp	Electrodeless discharge mercury lamp (EDL)
Measurement	Peak height
FIAS prefill time	15 s
FIAS fill time	10 s
FIAS inject time	15 s
Read delay	0 s
Read time	15 s
Reductant	1.2% (w/v) SnCl ₂ in 3% (v/v) HCl
Carrier	3% (v/v) HCl
Carrier gas stream	Argon
Carrier gas flow rate	50 mL · min ⁻¹
Cell temperature	50 °C
Sample loop	500 μL (can be variable)

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