



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca



Direct determination of total mercury in phosphate rock using alkaline fusion digestion

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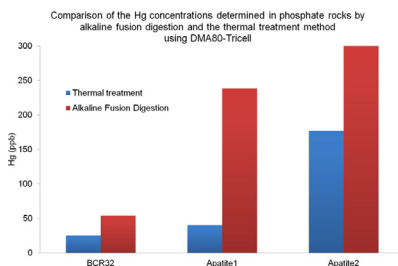
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HIGHLIGHTS

- Determination of total mercury concentration within phosphate rock by alkaline fusion digestion.
- Digestion by alkaline fusion salts mixture which melts at 400 °C.
- Total Hg determination by atomic absorption spectrophotometry comply with EPA method 7473.
- Comparison of Hg recovery between EPA method 7473 and alkaline fusion digestion method.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 21 June 2014

Received in revised form 14 September 2014

Accepted 15 September 2014

Available online xxx

Keywords:

Mercury

Alkaline fusion digestion

Apatite

Phosphorite

EPA method 7473

ABSTRACT

The aim of this work was to develop a new method to determine the mercury (Hg) concentrations in phosphate rock using a dedicated analytical instrument (the DMA80 Tricell by Milestone) that employs an integrated sequence of thermal decomposition followed by catalyst conversion, amalgamation and atomic absorption spectrophotometry. However, this instrument underestimates Hg concentrations when phosphorite and apatite rocks are investigated with a classic thermal decomposition treatment that complies with US EPA method 7473.

Therefore, to improve the recovery of total Hg, we performed alkaline fusion digestion (AFD) directly inside the furnace of the instrument, using BCR(32) as a certified reference material (Moroccan phosphate rock – phosphorite). The salts used for the AFD were a mixture of Na₂CO₃, K₂CO₃ and Li₂CO₃, which melt at about 400 °C, due to their ability to form a ternary eutectic and to decompose the phosphorite matrices at 700 °C. By adopting this analytical approach, the Hg recovery in BCR(32) was about 100%, compared to 40% when the reference material was analysed without using the alkaline fusion salt. We suggest that the AFD allowed the decomposition of the sample matrix and that some Hg compounds linked with other functional groups may be transformed in carbonates that sublimate at lower temperatures than other Hg compounds. This original method was tested on a number of different geological samples to compare the differences between the AFD method and the thermal treatment in order to verify the working range and to check the robustness of the new approach.

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1. Introduction

The determination and monitoring of very low concentrations of mercury (Hg) have always been of crucial importance in the field

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of trace-metal analysis. Mercury determination in rocks poses major problems, because its abundances are generally extremely low. Mercury is known to be widely distributed in nature, and the average amount of it in the Earth's crust ranges between 15 and 500 ng g⁻¹ [1,2]. It is mainly present in sulphides, cinnabar and metacinnabar. By accepting that Hg occurs mainly in the elemental state inside rocks, it can hardly be expected to occupy specific structural sites in most rock-forming minerals, but is instead thought to be distributed in a more random fashion in lattice defects, dislocations and imperfections [3,4,7]. In a series of heating experiments with rocks and minerals, Jovanovic and Reed [3] suggested that Hg was loosely held in labile sites and could easily escape and be volatilised at a few hundred degrees, whereas Hg trapped in more retentive crystal structure sites requires a higher temperature to bring about its diffusion to the surface.

Recently, a technique has been developed that, along with the integrated sequence of thermal decomposition, catalyst conversion, amalgamation and atomic absorption spectrophotometry, permits the determination of the total Hg content in liquid and solid samples at nanogram levels without any pre-treatment. This analytical technique and method has been designated as US EPA method 7473 [5]. In contrast, other classic approaches, such as ICP-OES, ICP-MS, and CVAAS, need the complicated and time-consuming preparation of samples and generally a reduction to the liquid form.

Herein, we present a new analytical approach for total Hg determination in rocks, soils and sediments using alkaline fusion digestion (AFD) directly inside the furnace of the same analytical instrument. This is because we believe that in different geological

samples Hg is to be linked with other compounds that sublime at temperatures greater than 700 °C.

2. Materials and methods

The salts used in the mixture, namely Na₂CO₃, K₂CO₃ and Li₂CO₃ (VWR distribution), were all in the anhydrous form and had previously been heated in the oven overnight at 700 °C to ensure that they were Hg free.

Calibration of the instrument was performed using an Hg standard solution (1000 µg mL⁻¹) by the Czech Metrology Institute Analytika. The dilutions of the standard were performed with Milli-Q water (>18 MΩ) that had previously been tested to ensure that it was Hg free.

The instrument used to determine the Hg concentration was a DMA80 Tricell provided by Milestone.

A D8 Discover Bruker Diffractometer, with a Bragg–Brentano configuration and equipped with a Sol-X energy-dispersive detector, was utilised.

The main certificate reference material (CRM) used in this work was BCR(32) (Sigma–Aldrich). This is a Moroccan phosphate rock (phosphorite) with an Hg concentration of 55 ± 11 ng g⁻¹. Other CRMs analysed were: NCS DC77302 and NCS DC77301 soils from the China National Analysis Centre (for iron and steel); BIR rock from the USGS reference materials; MESS-3 and PACS-2 marine sediment from the Canadian National Research Council; and JA-1a igneous rocks from the Geological Survey of Japan.

The geological samples analysed in this work were marlstone, limestone, quartz sand, claystone and two different apatite

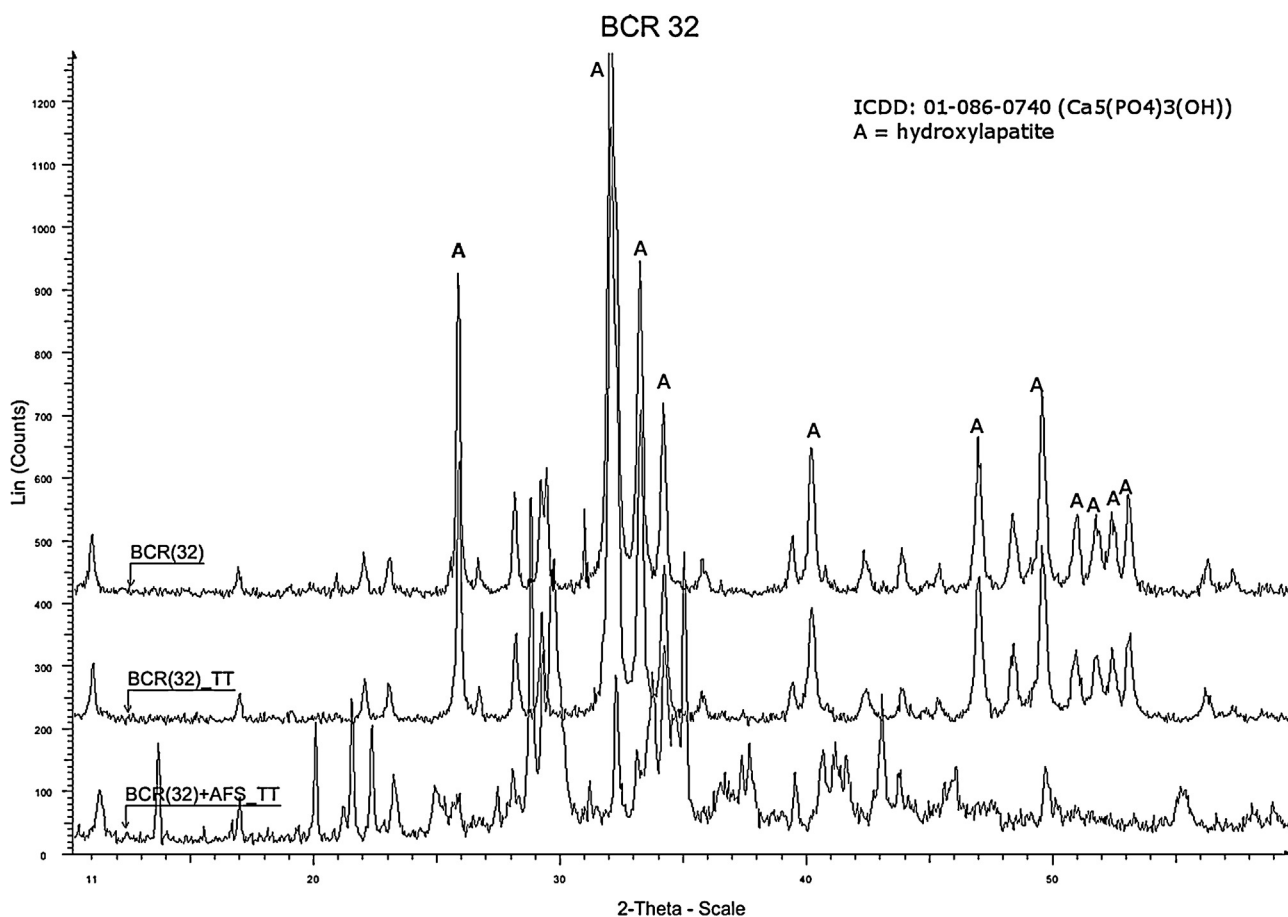


Fig. 1. XRD of BCR(32), BCR(32)_TT (thermal treated) and BCR(32)+AFS_TT (with AFS and thermally treated).

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