

Determination of mercury traces in products of TiO₂ manufacturing

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Abstract. A simple method for the determination of mercury traces in co-products and final products of titanium (IV) oxide manufacturing was developed. It was shown that different procedures recommended for the total digestion of such materials (using mixtures of HF, HNO₃, HCl and HClO₄) could be efficiently replaced by a unique partial digestion method based on mercury leaching from sample by HNO₃. Partial digestion method was much quicker and more sensitive than total digestion methods. Mercury was detected with cold vapour atomic fluorescence spectroscopy and a detection limit of 10 pgHg/g was achieved. The method was validated using certified reference materials PACS-1 (NRCC) and maroccan phosphate rock (BCR). Regarding mercury content in analysed samples from the point of view of the ecological risk, only residual material after first digestion of raw material with H₂SO₄ were found to contain mercury concentrations higher than accepted background value for sediment and soils (0.1 µgHg/g). All other co-products as well as the final product titanium (IV) oxide were almost free of mercury (< 0.01 – 30 ngHg/g).

Key words. Mercury traces – partial digestion by nitric acid – titanium dioxide.

Introduction

Stricter requirements on industrial materials, both from environmental and technological points of view, have caused a growing interest for trace analysis in such products. Titanium (IV) oxide plays an important role in various fields of technology for which a high-purity material is required [1]. Trace characterisation of titanium (IV) oxide is done for numerous metals, but data for mercury content in such materials are not found in literature [1,2]. In the process of manufacturing titanium (IV) oxide by the so called sulphate route, different co-products are generated. A simultaneous analysis of mercury and other trace metals in such samples could be difficult to achieve for two possible reasons. First, some of applied total digestion procedures may not be appropriate for the determination of volatile elements such as mercury (as they include step of evaporation to dryness). Second, multielemental analytical techniques used for the analysis of other metals are usually insufficiently sensitive for the determination of mercury traces [2], therefore, a more sensitive detection method, such as CV AFS (cold vapour atomic fluorescence spectroscopy), should be applied for mercury determination.

Speciation of mercury varies in different kind of samples which greatly influence method of sample preparation and digestion [2]. The most common methods for digestion of mineral samples (sediment, soil, rocks, ores) include digestion with a mixture of acids promoted by conventional [2–4],

or microwave heating [2,5]. Some authors insist on the total digestion of geological samples [6], although others have found that for mercury analysis a partial digestion was sufficient [3]. Digestion of solid samples with HNO₃, assisted by conventional [6], or microwave heating [7] proved to be sufficient for the quantitative extraction of mercury from a large number of environmental matrices (sediment, soil or biological samples). However, partial digestion of samples by HNO₃ for mercury analysis in industrial materials has not yet been tested.

The aim of this work was to develop a cost effective and simple method for the determination of mercury traces in co-products and final products of titanium (IV) oxide manufacturing. With the intention to develop a unique digestion method for all types of samples (regardless of their composition), partial digestion of samples with HNO₃ was compared with different wet digestion procedures (by mixtures of HF, HNO₃, HCl and HClO₄) involving total sample decomposition.

Material and methods

Samples origine

Samples of TiO₂ and co-products formed during TiO₂ manufacturing by so-called sulphate procedure are taken during 1996 from different units of the factory Tioxide-Europe,

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Calais, France, as described in more detail in [8]. Types of samples analysed, including their composition, are given in Table I.

Reagents

Acids used were of analytical quality (HNO_3 p.a., HCl p.a., HClO_4 p.a., Merck, Germany and HF p.a., Prolabo, France) or suprapur grade (HCl and HF , Merck). Mercury standard was prepared from stock standard solution (1 g/L, Merck). A standard solution was prepared weekly in 10% HNO_3 and 0.01% of $\text{K}_2\text{Cr}_2\text{O}_7$, whereas reference standard solutions were prepared daily in 1% HNO_3 . A reductant solution (5% SnCl_2 in 10% HCl) was prepared by dissolving SnCl_2 (Prolabo or Merck) in concentrated HCl and diluting with MQ water. The certified reference materials used for verification were marine sediment PACS-1 obtained from the National Research Council of Canada (NRCC) and Moroccan phosphate rock obtained from the Community Bureau of Reference (BCR).

Instruments

For mercury detection a CV AFS method was used. First, Vapour Generation Accessory VGA-77 (Varian) connected with the atomic fluorescence detector (PSA 10.023 Merlin) was used, which enabled detection of 10 ngHg/L in the final solution. Afterwards, more sensitive equipment consisting of vapour generator (PSA 10.003), a gold platinum trap (PSA 10.501 Galahad) and AFS detector was used. This combination enables detection of 1 ngHg/L in the final solution and is described in detail elsewhere [9].

Procedures

Total digestion was made by a method recommended for each type of material by the manufacturer. It consisted in digestion with a different mixture of acids suitable for each

kind of material (Tab. I). Partial digestion was made with HNO_3 , by a conventional heating or by applying a microwave irradiation. For digestion by conventional heating the sample (0.1 – 1g) was heated in 5 mL of HNO_3 for 4 hours at 150 °C in tightly closed 20 mL PFE vial. Open vessel microwave digestion was performed in a Microdigest 300 (Prolabo, France) focused microwave system with a maximum power of 300 W. A sample (0.1 – 0.5 g) was irradiated in 10 mL of HNO_3 for 5 min at a power of 10% in a glass digestion vessel. After cooling and centrifugation, if necessary, an aliquot of HNO_3 was diluted in MQ water to the concentration which could be optimally measured by the detection method used.

Results and discussion

According to their solubility characteristics, the products of TiO_2 manufacturing could be divided into three groups (Tab. I), those which are soluble in HCl , those which are soluble in HF and those which are soluble in a mixture of acids (HNO_3 , HCl , HClO_4 and HF). Preliminary results showed that mercury level in most of the commercial acids of analytical quality grade (HCl , HClO_4 , HF) was too high (0.5 – 5 $\mu\text{gHg/L}$) to obtain detection limit required for analysis of such samples, therefore, suprapur acids had to be used. Only in HNO_3 p.a. (Merck) mercury level was enough low (0.01–0.05 $\mu\text{gHg/L}$) as it could be used without further purification. A specific problem was encountered with HF for which mercury content, even in suprapur HF (Merck), was too high (5 $\mu\text{gHg/L}$) to be used for the digestion of TiO_2 samples. This acid had to be purified by passing through an anionic exchange resin (Dowex, Biorad, chloride form) which retained most of the mercury present in the anionic fluoride complex.

For first type of material soluble in HCl (salts), the mercury level was extremely low (< 10 pg/g) and even by the

Table I. Procedures for the total digestion of different types of analysed samples.

| Sample type | Composition | Digestion procedure |
|---------------------|---|---|
| Salts | 90% metal sulphates | HCl or H_2O (at 150 °C for 3h) dilution in 5% HNO_3 |
| Neutralised salts | metal sulphates + $\text{MgO}+\text{CaO}$ | $\text{HCl}/\text{H}_2\text{O}$ (5:1) (at 150 °C for 3h) dilution in 5% HNO_3 |
| Titanium (IV) oxide | TiO_2 | HF/HNO_3 (2:1) (at 150 °C for 3h) dilution in H_2O |
| Metal oxides | 50% Fe_2O_3 +20% $\text{MgO}+$ 10% TiO_2 +residue | $\text{HF}/\text{HNO}_3/\text{H}_2\text{O}$ (5:2.5:1) + HClO_4 (0.5) -evapor. till dry + dissolution in 15% HCl |
| Digestion residue | 25% TiO_2 +25% SiO_2 + residue | $\text{HF}/\text{HNO}_3/\text{H}_2\text{O}$ (5:2.5:1) + HClO_4 (0.5) -evapor. till dry+ dissolution in 15% HCl |

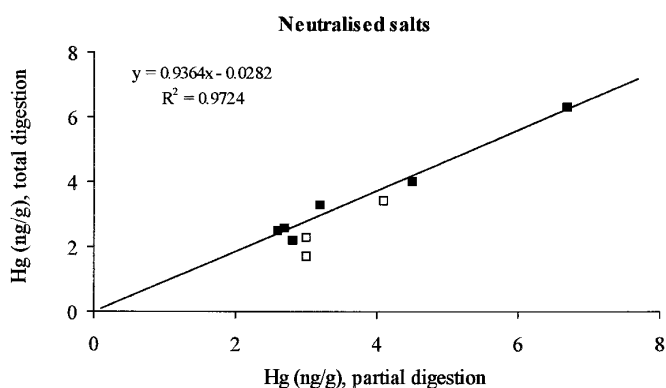


Fig 1. Comparison of mercury concentrations obtained after partial and total digestion of neutralised salts samples. (Open symbols denote samples for which lower results were obtained with total digestion, see text for explanation).

digestion of 5 g of sample it was not possible to detect mercury in any analysed sample. In the second type of samples soluble in HCl (neutralised salts), mercury content was also very low, lower than 10 ng/g (Fig. 1). A very good agreement between total and partial digestion was obtained in most of these samples. However, some samples demonstrated a lower mercury concentration after digestion with HCl (Fig. 1). This could be a consequence of the interfering effect of HCl on the mercury reduction when using tin (II) chloride as reductant. Namely, the peak of mercury standard was significantly suppressed already in 2 mol/L HCl, whereas, even 6 mol/L HNO₃ could be used as working solution without such effects. Interfering effect of HCl on mercury reduction was already observed by other authors and was explained by the formation of chlorine which leads to the loss of volatile mercury chlorides [4]. The lower mercury values observed in completely dissolved samples could be also a consequence of interfering effects of some other metals present in the solution [3].

The results of mercury analyses in samples soluble in HF or mixture of HF and HNO₃ (titanium dioxide) are given in figure 2. The level of mercury, although slightly higher than in the previous group of samples, was also very low, in the

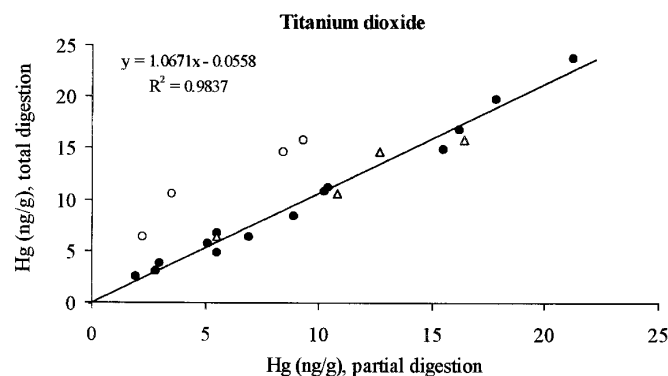


Fig 2. Comparison of mercury concentrations obtained after partial and total digestion of titanium (IV) oxide samples. (Open circles denote samples for which lower results were obtained by partial digestion with conventional heating, and open triangles results obtained by partial digestion in open microwave system, see text for explanation).

range of 5 – 25 ng/g of solid. A very good agreement between partial and total digestion has been obtained in most of the samples (Fig. 2). However, in some samples mercury concentration obtained after HNO₃ digestion was too low, even when heating time was prolonged up to 12 hours. However, by substituting conventional with a more powerful microwave heating, the complete leaching of mercury with HNO₃ also from these samples was obtained (Fig. 2) providing a very rapid digestion method (5 minutes instead of 4 hours).

For the last group of samples for which total digestion includes a step of evaporation up to dryness, a comparison of the partial and the total digestion was not possible, because the reproducibility of the total digestion was inadequate (Tab. II). Mercury concentrations obtained after partial digestion of metal oxides with HNO₃ (Tab. III) were of the same order of magnitude as in TiO₂ samples (2 – 30 ng/g). For samples of digestion residues containing higher mercury levels (up to 300 ng/g) two types of partial digestion were compared (Tab. IV). The results of two digestion methods were comparable indicating that HNO₃ efficiently leach mercury from this type of materials. Partial digestion with HNO₃ has also been tested on some Certified

Table II. Comparison of mercury concentration in some samples after partial digestion with HNO₃ and total digestion which include evaporation up to dryness.

| Sample | Digestion residue 3* | Digestion residue 4 | Metal oxide 8 |
|-----------------------------|----------------------|---------------------|----------------|
| Partial digestion Hg (ng/g) | 240 ± 27 (4)** | 331 ± 16 (4) | 30.1 ± 3.4 (5) |
| Total digestion Hg (ng/g) | 69; <1; 52 | 9; 12; <1 | <1; <1 |

* Sample numbers correspond to numbers given in Table 3 for metal oxides and Table 4 for digestion residues.

** Arithmetic mean, standard deviation and number of samples analysed are given.

Table III. Mercury concentration in samples of metal oxides after partial digestion with HNO₃.

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|-----------------------------|------------------|------------------|------------------|------------------|-------------------|-------------------|-------------------|-------------------|
| Partial digestion Hg (ng/g) | 1.7 ± 0.1 (2) | 1.8 ± 0.2 (2) | 2.6 ± 0.4 (2) | 5.7 ± 0.1 (2) | 10.8 ± 0.9 (2) | 11.5 ± 1.3 (2) | 17.7 ± 2.0 (5) | 30.1 ± 3.4 (5) |

Table IV. Comparison of mercury concentration in samples of digestion residue after partial digestion with HNO₃ (I) and partial digestion by a mixture of acids (II).

| Sample | 1 | 2 | 3 | 4 |
|--------------------------------|------------|--------------|--------------|--------------|
| Partial digestion I Hg (ng/g) | 63 ± 8 (3) | 110 ± 12 (5) | 240 ± 27 (4) | 331 ± 16 (4) |
| Partial digestion II Hg (ng/g) | 70 | 120 | 190 | 350 |

Partial digestion II: mixture of H₂SO₄ and HNO₃ at 70 °C and dilution/oxidation in KMnO₄ performed by another laboratory (INRA).

Reference Materials, PACS-1, marine sediment (certified mercury value 4.57 ± 0.12 µg/g) and maroccan phosphate rock (certified mercury value 55 ± 11 ng/g). The obtained values for PACS-1 (4.50 ± 0.26 µg/g, the average from 16 analyses) and phosphate rock (59.1 ± 2.5 ng/g, the average from 12 analyses) were in very good agreement with the certified values, proving that HNO₃ successfully extracted mercury from abiotic samples such as sediments and rocks.

Regarding mercury content in the analysed samples from the point of view of the manufacturing procedure and ecological risk it is evident that only residual material after first digestion of raw material with H₂SO₄ (digestion residue) contains elevated mercury concentration, if compared with accepted background values for sediment and soils of 0.1 µgHg/g [10]. Mercury in these samples probably originates from H₂SO₄ which may contain significant amounts of mercury [11]. All other co-products as well as the final product titanium (IV) oxide are almost free of mercury, probably as a consequence of the loss of this volatile element during the manufacturing process which include heating of materials at high temperatures.

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