Spectrographic Determination of Metallic Impurities in PuO₂

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Summary. An emission spectrographic method has been developed for the estimation of 22 metallic impurities in plutonium dioxide using carrier-distillation technique. Silver chloride at 5% concentration in a charge of 100 mg has been used as the carrier. Mixed oxide standards containing 10% PuO₂ have been used for the analysis of matching composition of plutonium samples. Precision and accuracy determinations of the synthetic samples indicate 7-16% deviation for most of the elements. The work described includes analysis of reference samples and matrix effect studies. The method is suitable for the chemical quality control analysis of plutonium oxide to be used for Fast Breeder Test Reactor (FBTR) fuel.

Key words: Analysis of Plutonium dioxide; Spectroanalyse, Trägerdestillation; 22 Verbindungen.

1. Introduction

Emission-spectrographic analysis of common metallic impurities in plutonium oxide forms an important aspect of the chemical quality control programme of fuel materials. It can be carried out either by directly arcing the sample along with some carrier or by chemically separating the impurities from the major matrix, pre-concentrating them and then using either direct arc or spark excitation techniques. The chemical separation method for the analysis of these impurities cannot be adopted as a routine method because of the longer analysis time, extensive handling of the sample and the need for high purity reagents in the separation stage.

The well-known “carrier distillation” technique developed for uranium base materials by Scribner and Mullin [16] can be adopted for the analysis of PuO₂ samples without chemically separating the metallic impurities. A detailed survey of the literature indicates that the methods used for the analysis of PuO₂ by various laboratories can be classified in two broad groups: (i) those using 100% PuO₂ standards and samples [4-6, 14, 15] and (ii) those mixing 5-10 mg of the PuO₂ sample with major fraction of pure U₃O₈ and then carrying out the analysis using standards with U₃O₈ matrix [2,12]. For the analysis of PuO₂, Mound Laboratory [7] has recently reported the use of 36% PuO₂ and 36% U₃O₈ in a sample charge of 80 mg and matching standards.

In the present work, a method based on “carrier-distillation” techniques has been developed for the analysis of PuO₂. In this method, 10% PuO₂ sample is mixed with 5% AgCl carrier, 0.01% Pd internal standard and balance amount of U₃O₈ to form a charge of 100 mg and the impurities are estimated using matching standards. The method enables the analysis of 22 metallic impurities in PuO₂ in the spectral region photographed in one setting.

Precision and accuracy of the method were determined for intermediate concentrations of the impurities from ten replicate analysis of the four synthetically prepared samples. Three plutonium dioxide reference samples obtained from C.E.A.-France have been analysed, and a close agreement with the certified values has been obtained by the proposed method. The matrix effect on
the estimation of various impurities in PuO₂ samples has also been studied by analysing one of the reference samples with respect to both U₃O₈ [13] and mixed oxide standards containing 10% PuO₂. The precision of the results obtained from these studies confirm the need for matching of standards and samples.

The analytical procedure for the estimation of metallic impurities in PuO₂ has been developed for the chemical quality control analysis of the Fast Breeder Test Reactor (FBTR) fuel. Hence, more emphasis was put on meeting the fuel specification limits with high degree of precision rather than on achieving lower detection limits.

2. Experimental

2.1. Apparatus

Spectrograph: Hilger 3.4 M Ebert, E-546, grating ruling 1200 grooves/mm, dispersion 2.5 Å/mm in 1st order.

Power supply: Hilger Source Unit FS-131 with Timer FS-106.

Microphotometer: Hilger non-recording microphotometer L-503, with galvoscule FR-333.

Electrodes: Lower electrode (anode), standard carrier distillation type electrode, ASTM designation: E-130-66, type S-2 used on type S-1 pedestal. Upper electrode (cathode), 0.120 dia preformed pointed electrode. ASTM designation: E-130-66 type C-1.

Sieve: Nylon cloth, 200 mesh supplied by M/s. SPEX Industries, Inc. U.S.A.

Plate Calibration: Hilger Seven step sector (ratio 2 : 1) with iron spectrum.

Calculator: Aristo Respektra.

2.2. Preparation of Standards

High purity uranium metal, received from Uranium Metal Plant was converted to U₃O₈ by heating it in air in a silica muffle furnace for 1 h at 850 °C. The uranium oxide, thus formed, was ground to a fine powder, passed through a nylon sieve of 200 mesh and then used in the preparation of standards. The 200 mesh sieve at every stage in the preparation of standards ensured that the particle size was less than 75 μm. The choice of 200 mesh sieve was based on the results obtained by Martell [10], which indicated that the intensity ratios for the different elements remained independent of particle size when it was less than 75 μm.

High purity plutonium oxide prepared in the laboratory [1] by repeated anion-exchange separations and peroxide precipitations was used in the preparation of standards.

A mixture of all the impurity elements, most of them as oxides, was thoroughly ground with an agate mortar and pestle and passed through the sieve. A fraction of this mixture was mixed with U₃O₈ to make a 20 g master standard (A). Silver chloride and palladium [in the form of (NH₄)₂PdCl₄] were ground together to make a carrier-distillation standard (B).

A series of eight standards each of 10 g was made by mixing graded amounts of master standard (A), 502.67 mg of mixture (B), 1 g of PuO₂ and balance amount of U₃O₈. The impurity concentrations between successive standards varied by a factor of 2 or 2.5.

2.3. Preparation of Sample

The plutonium dioxide sample was first heated at 900 °C for 1 h in air in a platinum crucible in the silica muffle furnace to remove traces of moisture, oxalate and nitrate which could affect the extraction of impurity elements. The fraction of the heated sample, weighing 50 mg was then mixed with 25.13 mg of mixture B and balance amount of pure U₃O₈ to make 500 mg total mixture necessary for five charges. The mixture was ground for 30 min in an agate mortar to have a homogeneous charge. No sieve was used in the preparation of sample. However the grinding time of 30 min ensured the particle size to be much less than 75 μm [10] thus matching with the particle size in the standards.

2.4. Spectrographic Procedure

The standards and the samples in duplicate, each weighing 100 mg, were loaded in the craters of standard “carrier-distillation” electrodes. Each electrode after heating under infra-red lamp to remove possible traces of moisture, was vigorously tapped so as to evenly spread the charge in the crater and a vent hole was made in the charge with a stainless steel venting tool. A d.c. arc was used as an excitation source to obtain the spectra of standards and samples. The detailed experimental conditions are given below:

<table>
<thead>
<tr>
<th>Spectral region</th>
<th>2200-3400 Å (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc current (d.c.)</td>
<td>12.5 A</td>
</tr>
<tr>
<td>Slit width</td>
<td>15 μ</td>
</tr>
<tr>
<td>Analytical gap</td>
<td>4 mm (not kept constant during arcing)</td>
</tr>
<tr>
<td>Exposure time</td>
<td>25 s</td>
</tr>
<tr>
<td>Photographic emulsion</td>
<td>Kodak Spectrum Analysis No. 1, two plates 25.4 × 10.2 cm</td>
</tr>
<tr>
<td>Plate development</td>
<td>For 3 min at 18°C in Kodak D-19 developer and fixed in Kodak acid fixing salt solution for 3 min.</td>
</tr>
</tbody>
</table>

The intensity ratios for all the analysis lines were calculated and the estimations for the samples were made from the working curves. In order to estimate precision and accuracy of estimation, 4 PuO₂ samples with intermediate concentrations of impurities in the analytical range were synthetically prepared and analysed. The precision data were obtained from ten replicate spectra for each sample.

Determination of metallic impurities in three reference samples of PuO₂ viz. Beaujolais (B), Champagne (C) and Durette (D) supplied by C.E.A.-France with certified values of impurity concentrations were made by the procedure described here from triplicate spectra.

In order to study the matrix effect on the estimation of different metallic impurities in PuO₂ samples, the reference sample “Durette” (D) was analysed with respect to U₃O₈ standards prepared earlier [13] as well as with mixed oxide standards containing 10% PuO₂. The precision was calculated from ten replicate spectra.

3. Results and Discussion

3.1. Estimation Limits and Precision

The analytical lines used for different impurity elements, the internal standard lines and the estimation ranges covered by them are shown in Table 1. Palladium lines 2448 Å and 3027.9 Å were used as internal standard lines in the entire spectral region of interest. Some of the typical working curves obtained for B, Be and Cd elements are shown in Figure 1.

A comparison of the lower estimation limits obtained here for different elements in PuO₂ and those reported in literature [2, 4–7, 14, 15] as shown in Table 2, indicates...