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Determination of uranium in uranium dioxide powder and pellets — Iron(II) sulfate reduction/potassium dichromate oxidation titrimetric method

Dosage de l'uranium dans la poudre et les pastilles de dioxyde d'uranium — Méthode titrimétrique par réduction par le sulfate de fer(II) et oxydation par le dichromate de potassium

Reference number
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Foreword

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1 Scope

1.1 This International Standard specifies an analytical method for the determination of uranium in uranium dioxide powder and pellets.

1.2 The method recommends that the aliquot of sample is weighed and that a mass titration is used, in order to obtain adequate precision and accuracy. This does not preclude the use of any alternative technique which can be shown to give an equivalent performance.

As the performance of some steps of the method is critical, the use of certain automatic devices has some advantages, mainly in the case of routine analyses.

2 Principle

2.1 Uranium(VI) is reduced to uranium(IV) in concentrated phosphoric acid solution by reaction with iron(II) sulfate. The excess iron(II) sulfate is subsequently oxidized by nitric acid in the presence of molybdenum, and the uranium(IV) is determined by mass titration with standardized potassium dichromate solution to a potentiometric end-point.

2.2 A portion of sample containing about 0,2 g of uranium in nitric acid solution is diluted with orthophosphoric acid containing a little dichromate to oxidize any reducing species which may be present. An excess of iron(II) sulfate solution is then added to reduce all the uranium to the quadrivalent state. Amidosulfuric acid is added to remove oxides of nitrogen formed at this stage.

The excess of iron(II) sulfate is destroyed by oxidation with nitric acid, catalysed by molybdenum, in a time and temperature controlled operation. After dilution, the uranium is determined by mass titration with standardized potassium dichromate solution to a potentiometric end-point. To improve precision, the end-point is approached using dilute potassium dichromate solution and the titration is performed in the presence of vanadium(IV), which increases the rate of equilibrium attainment and enhances the potential step at the equivalence point.

2.3 The standard potassium dichromate solution is checked either against an internationally recognized uranium standard using the same potassium dichromate titration procedure.

3 Reactions

Under the given experimental conditions, the principal reactions are as follows.

3.1 In concentrated phosphoric acid solution

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ \longrightarrow U^{4+} + 2Fe^{3+} + 2H_2O$$

$$3Fe^{2+} + NO_3^- + 4H^+ \xrightarrow{Mo} 3Fe^{3+} + NO + 2H_2O$$

$$Fe^{2+} + NO_3^- + 2H^+ \xrightarrow{Mo} Fe^{3+} + NO_2 + H_2O$$

3.2 In diluted phosphoric acid solution

$$U^{4+} + 2Fe^{3+} + 2H_2O \longrightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$

$$Fe^{2+} + VO^{2+} + 2H^+ \longrightarrow Fe^{3+} + V^{3+} + H_2O$$

The overall reaction may be represented:

$$U^{4+} + 2VO^{2+} \longrightarrow UO_2^{2+} + 2V^{3+}$$

3.3 On titration with potassium dichromate solution

$$Cr_2O_7^{2-} + 6V^{3+} + 2H^+ \longrightarrow 2Cr^{3+} + 6VO^{2+} + H_2O$$

which is equivalent to the titration of U^{4+} with dichromate:

$$Cr_2O_7^{2-} + 3U^{4+} + 2H^+ \longrightarrow 2Cr^{3+} + 3UO_2^{2+} + H_2O$$

4 Interferences

This procedure is less subject to interference from foreign ions than most other methods of determining uranium. Ions and metals which do not interfere in any reasonable concentration include fluoride, perchlorate, sulfate, nitrate, peroxide, Al, Be, Si, Zr, Nb, Ti, Cr, Fe, Co, Ni, W, Cu, Pb, Pu, Th, the rare earths, the alkali metals and the alkaline earth metals. Molybdenum interferes only if large amounts of nitrate are also present and vice versa. Bromide, oxalate, Au, Sn, Mn and some platinum group metals interfere slightly. Interference from iodide, iodate, Ag, V and Tc is more severe. There is inadequate information on the effect of chloride, Hg, As, Sb, Np and Am and further studies are required.

5 Reagents

Use only reagents of recognized analytical grade and distilled or deionized water.

5.1 Hydrofluoric acid, ρ 1,13 g/ml.

5.2 Nitric acid, ρ 1,42 g/ml.

5.3 Orthophosphoric acid, ρ 1,75 g/ml.

5.4 Sulfuric acid, 50 % (*V/V*) solution.

Add 100 ml of sulfuric acid (ρ 1,84 g/ml) slowly and carefully to 100 ml of water, whilst stirring.

5.5 Iron(II) sulfate, 280 g/l solution

Add 50 ml of sulfuric acid (ρ 1,84 g/ml) slowly and carefully to 300 ml of water in a 2 litre beaker with constant stirring. Add 140 g ± 1 g of iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and stir until it is dissolved. Dilute to 500 ml and mix. This solution should not be used more than one month after preparation.

5.6 Oxidizing reagent

Dissolve 4,0 g ± 0,1 g of hexaammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$] in 500 ml of water. Add 500 ml of nitric acid (5.2) and mix well. This solution should not be used more than one week after preparation.

5.7 Amidosulfuric acid, 150 g/l solution

Dissolve 150 g of amidosulfuric acid in 1 litre of water at room temperature. This solution is almost saturated; heating would tend to decompose the amidosulfuric acid.

5.8 Vanadium(IV) oxide sulfate, 1,25 g/l solution

Weigh 1,25 g ± 0,01 g of vanadium(IV) oxide sulfate ($VOSO_4{\cdot}2H_2O$) and dissolve it in 900 ml of water containing 25 ml of the sulfuric acid solution (5.4). Dilute to 1 litre and mix well. This solution should not be used more than one week after preparation to minimize oxidation to vanadium(V).

5.9 Potassium dichromate solutions

5.9.1 Concentrated potassium dichromate solution (0,2 mol/l)

Weigh a clean, dry, 1 litre volumetric flask to 0,01 g (m_1). Weigh out about 9,81 g of dried potassium dichromate ($K_2Cr_2O_7$) to 0,000 1 g (m_2) and dissolve it in water. Transfer to the tared flask, dilute to 1 litre with water, weigh the flask plus contents to 0,01 g (m_3) and finally mix well. Calculate the concentration of dichromate, in millimoles of 1/6 $K_2Cr_2O_7$ per gram of solution, in the solution (F_1), correcting for the purity and applying a buoyancy correction to the mass of solid dichromate but not to the mass of solution (since the apparent mass of the latter is used in 8.1), where

$$F_1 = \frac{m_2}{0{,}049\,03\,(m_3 - m_1)}$$

5.9.2 Dilute potassium dichromate, solution

Weigh a clean, dry, 2 litre volumetric flask to 0,02 g (m_4). Weigh approximately 150 g of concentrated potassium dichromate solution (5.9.1) in a weighing bottle to 0,001 g (m_5) and transfer the bulk of the solution to the 2 litre flask. Reweigh the weighing bottle and any remaining contents to the nearest 0,001 g (m_6). Adjust the volume of solution in the flask to 2 litres with water and weigh the flask and contents to the nearest 0,02 g (m_7). Mix.

Calculate the factor F_2 using the expression

$$F_2 = \frac{m_5 - m_6}{m_7 - m_4}$$

without applying any buoyancy corrections.

5.9.3 Verification of the concentration

The concentration of the potassium dichromate solution should be verified by comparison with an appropriate internationally recognized uranium reference material. Either pure uranium metal (for example, NBS SRM 960 or BCR-MU-1) or pure U_3O_8 (for example, NBS SRM 950b), or sintered uranium dioxide of known purity may be used. The comparison should be made by taking at least three separate portions of the selected reference material through the following procedure.

Weigh 1,0 g to 1,2 g of the reference material to 0,000 1 g (m_8) into a 400 ml tall-form beaker. Add 10 ml of water, 30 ml of nitric acid (5.2) and 1 drop of hydrofluoric acid (5.1) and place the beaker covered with a watch glass on a boiling water bath to maintain a steady reaction. When dissolution is complete, allow to cool, and transfer the solution quantitatively to a clean, dry 50 ml volumetric flask weighed to 0,000 5 g (m_9). Dilute to 50 ml with water and weigh the flask plus contents to 0,000 5 g (m_{10}). Take a weighed aliquot of the solution through the procedure described in clause 7 as if the solution was a sample, calculating the uranium concentration of the solution (U_1) as in 8.1.

Calculate the measured uranium content of the reference material (U_2) from the expression

$$U_2 = U_1 \times \frac{m_{10} - m_9}{m_8}$$

applying a buoyancy correction to m_8 only.

Compare the mean result with the certified uranium content; the dichromate concentration (F_1) is acceptable if the agreement is better than 0,1 %. If it is not, repeat the procedure.

Alternatively, the potassium dichromate solution may be verified by direct comparison with potassium dichromate NBS SRM 136 C, by analysis of a pure uranium solution using this standard method.

6 Apparatus

Normal laboratory equipment and

6.1 Millivoltmeter: a high impedance millivoltmeter (100 MΩ input resistance) with a digital read-out capable of discriminating to 1 mV is most suitable.

6.2 Platinum wire or **spade electrode,** of surface area 0,1 cm^2 to 1 cm^2

The performance of the electrode should be checked regularly by analysis of a control solution. If the response of the electrode at the titration end-point begins to deteriorate, the electrode should be cleaned by immersion in boiling nitric acid (ρ 1,42 g/ml) containing a little potassium dichromate, followed by thorough rinsing with distilled water. It is also possible to heat the electrode to red heat in an open flame that is free from sulfur.

6.3 Calomel reference electrode.

6.4 Sample weighing bottle: a stoppered weighing bottle with delivery spout, of capacity 20 ml, is suitable.

6.5 Titration weighing bottle for use as a mass burette: a weighing bottle with teat and delivery spout, of capacity 40 ml, is suitable.

6.6 Microdispenser, capable of delivering 0,1 ml of solution rapidly and repeatedly, with a precision of ± 1 % or better, and capable of being weighed.

6.7 Magnetic stirrer and plastics-coated stirring bars.

7 Procedure

7.1 Weigh the titration weighing bottle (6.5) containing concentrated potassium dichromate solution (5.9.1) to 0,000 1 g (m_{11}).

7.2 Weigh the microdispenser (6.6) containing dilute potassium dichromate solution (5.9.2) to 0,001 g (m_{12}).

7.3 Prepare the test sample of UO_2 pellets as follows.

Crush or break the sample without producing excessive amounts of fine particles.

7.4 Analyse UO_2 powder samples without any further preparation.

7.5 Dissolve the test sample of UO_2 pellets as follows.

Weigh out, to the nearest 0,000 1 g, 0,20 g to 0,25 g of the test sample (m_{19}) into a 400 ml tall-form beaker. Add 3 ml of nitric acid (5.2) and 1 drop of hydrofluoric acid (5.1). Cover the beaker with a watch glass and heat on a boiling water bath to maintain a steady reaction. When dissolution is complete, remove the watch glass and evaporate to dryness. Redissolve in 10 ml of water.

7.6 Dissolve the test sample of UO_2 powder as follows.

Weigh out, to the nearest 0,000 1 g, 0,20 g to 0,25 g of the test sample (m_{19}) into a 400 ml tall-form beaker containing 10 ml of water. Add 3 ml of nitric acid (5.2) and 1 drop of hydrofluoric acid (5.1). Cover the beaker with a watch glass. Allow the reaction to subside and then heat on a boiling water bath. When dissolution is complete, remove the watch glass and evaporate to dryness. Redissolve in 10 ml of water.

NOTE 1 A buoyancy correction is required if the corresponding plant measurement is on an absolute weight basis.

7.7 Add 5 ml of sulfuric acid solution (5.4) to the sample solution, insert a stirring bar and 0 to 100 °C thermometer and place the beaker on the magnetic stirrer (6.7).

7.8 Stir the solution and add the following reagents in the order stated, allowing to mix between each addition: 40 ml of orthophosphoric acid (5.3), 0,2 ml of potassium dichromate solution (5.9.1), 5 ml of amidosulfuric acid solution (5.7) and 5 ml of iron(II) sulfate solution (5.5).

NOTES

2 Alternatively, an equivalent amount of potassium dichromate can be added to the bulk stock phosphoric acid, to destroy reducing impurities.

3 The iron(II) sulfate should be added from a pipette directly into the sample solution, without splashing the walls of the beaker.

4 1 ml of hydrofluoric acid (5.1) can be added in some circumstances to improve the electrode response.

7.9 Continue stirring the solution for a minimum of 1 min and adjust the temperature to within the range 35 °C to 40 °C. Using a pipette, add 10 ml of oxidizing reagent (5.6), using it to wash down the inside walls of the beaker. A dark colour is produced in the sample solution on addition of the oxidizing reagent but this colour shall not persist for longer than about 40 s.

NOTE 5 The beaker should be temporarily transferred to a magnetic stirrer hotplate or cooling bath if temperature adjustment is required.

7.10 Stir for a further 2 min 30 s and stop the stirrer. Allow the solution to stand unstirred for 30 s and immediately add 100 ml of the vanadium(IV) oxide sulfate solution (5.8).

To avoid significant error, the titration shall be either

a) completed within 7 min of adding the vanadium(IV) oxide sulfate solution; or

b) carried out by adding 100 ml of water and 125 mg of solid vanadium(IV) oxide sulfate instead of the solution (5.8).

7.11 Insert the platinum and calomel reference electrodes (6.2 and 6.3) into the solution and commence rapid stirring without splashing. The potential reading is normally 350 mV to 400 mV. Add concentrated potassium dichromate solution (5.9.1) from the titration weighing bottle until a potential difference of 450 mV to 480 mV is indicated.

7.12 Add dilute potassium dichromate solution (5.9.2) in 0,1 ml increments from the microdispenser (6.6), recording the millivolt reading, when it is stable, after each addition.

NOTE 6 The reading is regarded as being stable when it does not change by more than 1 mV in 5 s.

7.13 Continue the addition of dilute potassium dichromate solution until the equivalence point of the titration (indicated by a sharp inflection in potential at about 550 mV to 600 mV) is reached. Make one further addition.

7.14 Record the number (n) of additions of dilute potassium dichromate solution at this stage.

7.15 Weigh the titration weighing bottle to the nearest 0,000 1 g (m_{15}).

7.16 Weigh the microdispenser to the nearest 0,001 g (m_{16}). At the end of the titration, the 400 ml beaker shall be thoroughly washed to remove all traces of uranium and vanadium before it is reused.

8 Expression of results

8.1 Method of calculation

8.1.1 Calculate the mass of dilute potassium dichromate solution (5.9.2) used in the titration, using the second differential of the millivolt recordings as in the following example.

$K_2Cr_2O_7$ 0,1 ml unit additions	mV	First differential	Second differential
$n-3$	$E1$		
$n-2$	$E2$	$(E2-E1)$	$(E3-E2)-(E2-E1)$
$n-1$	$E3$	$(E3-E2)$	$(E3-E2)-(E4-E3)$
n	$E4$	$(E4-E3)$	

The mass of dilute potassium dichromate solution used in the titration (m_{17}) is given by

$$m_{17} = \left[(n-2) + \frac{(E3-E2)-(E2-E1)}{(E3-E2)-(E2-E1)-(E4-E3)}\right] \times \frac{m_{12}-m_{16}}{n}$$

8.1.2 Calculate the equivalent total mass of concentrated potassium dichromate solution (5.9.1) used in the titration (m_{18}), using the factor (F_2) (see 5.9.2) and the expression

$$m_{18} = (m_{11} - m_{15}) + (F_2 \times m_{17})$$

8.1.3 The relative atomic mass, A_r, of the uranium may be calculated from the isotopic composition [% (m/m)] using the expression

$$A_r = \frac{100}{\frac{\%^{234}U}{234{,}041\,0} + \frac{\%^{235}U}{235{,}043\,9} + \frac{\%^{236}U}{236{,}045\,6} + \frac{\%^{238}U}{238{,}050\,8}}$$

8.1.4 Calculate the uranium content (U_3), in milligrams of uranium per gram, of the sample using the expression

$$U_3 = \frac{m_{18} \times F_1 \times A_r}{2m_{19}}$$

where

m_{18}, F_1 and A_r are as expressed in 8.1.2, 5.9.1 and 8.1.3;

m_{19} is the mass, in grams, of the sample (see 7.3.2).

8.2 Repeatability

The coefficient of variation for a single determination is better than 0,1 % when the method is applied to a pure uranium solution on the open bench.

8.3 Bias

The bias of the method is less than 0,1 % when applied to pure uranium solutions.

9 Test report

The test report shall include the following information:

a) identification of the sample;

b) reference of the method used;

c) the results and method of expression used;

d) any unusual features noted during the test;

e) any operations not included in this International Standard or regarded as optional.