International Standard 7097

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Determination of uranium in reactor fuel solutions and in uranium product solutions — Iron(II) sulfate reduction/potassium dichromate oxidation titrimetric method

Dosage de l'uranium dans les solutions de combustibles pour réacteurs et dans les solutions de produits à base d'uranium — Méthode titrimétrique par réduction par le sulfate de fer(II) et oxydation par le dichromate de potassium

First edition — 1983-12-15

UDC 621.039.54 : 543.242 : 791 **Ref. No. ISO 7097-1983 (E)**

Descriptors : nuclear reactors, nuclear fuels, tests, determination, uranium.

Price based on 5 pages

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 7097 was developed by Technical Committee ISO/TC 85, *Nuclear energy*, and was circulated to the member bodies in July 1981.

It has been approved by the member bodies of the following countries :

Austria	Germany, F. R.	Poland
Belgium	Hungary	Romania
Canada	Ireland	Spain
China	Italy	Sweden
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The member body of the following country expressed disapproval of the document on technical grounds :

USSR

Printed in Switzerland

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1 Scope and field of application

1.1 This International Standard specifies an accurate and precise analytical method for the determination of uranium in solutions of reactor fuels fed to reprocessing plants and in the uranyl(VI) nitrate product solutions from such plants.

1.2 This method can be used directly for the analysis of nitric acid solution of most uranium and uranium/plutonium oxide reactor fuels, either irradiated or unirradiated and to uranyl(VI) nitrate product solutions. Fission products equivalent to up to 10 % burn-up of heavy atoms do not interfere, and other elements which could cause interference are not normally present in sufficient quantity to affect the result significantly.

1.3 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 equivalent performance.

As the performance of some steps of the method is critical, the use of some automatic device has some advantages, mainly in the case of routine analysis.

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 dichromate titration procedure, or against NBS potassium dichromate, SRM 136 C.

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 :

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