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REGULATORY GUIDE

DIRECTORATE OF REGULATORY STANDARDS

REGULATORY GUIDE 5.6

STANDARD METHODS FOR CHEMICAL, MASS SPECTROMETRIC, AND SPECTROCHEMICAL ANALYSIS OF NUCLEAR-GRADE PLUTOMIUM DIOXIDE POWDERS AND PELLETS AND NUCLEAR-GRADE MIXED OXIDES ($[U, Pu]O_2$)

A. INTRODUCTION

Section 70.22(b) of 10 CFR Part 70, "Special Nuclear Material," requires an applicant for a license to possess certain quantities of special nuclear material in an unsealed form to describe, among other things, his procedures for control of and accounting for special nuclear material. This guide identifies acceptable methods for chemical, isotopic, and impurity analyses which an applicant may specify as part of his procedures for accounting for special nuclear material.

B. DISCUSSION

Committee C-26 on Fuel, Control, and Moderator Materials for Nuclear Reactor Applications of the American Society for Testing and Materials (ASTM) has developed standards containing methods for the chemical analysis of (1) nuclear-grade plutonium dioxide powders and pellets, and (2) nuclear-grade mixed oxides. These standards are ASTM Standard C 697-72, "Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Plutonium Dioxide Powders and Pellets,"[1] and ASTM Standard C 698-72a, "Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Mixed Oxides ($[U, Pu]O_2$)."[1] As used in these standards, *nuclear grade* material means material that is to be used *exclusively* for the fabrication of nuclear fuel.

Plutonium Dioxide

The standard C 697-72 was approved by the ASTM on March 3, 1972, and published in May 1972. Included in this standard are three methods for the determination of plutonium:

a. Controlled-Potential Coulometry. The optimum quantities of plutonium to be determined are 2 to 6 mg with a stated precision of 0.14 percent relative standard deviation (RSD).

b. Ceric Sulfate Titration. stated precision of 0.27 percent RSD.

c. Amperometric Titration with Iron (II). The optimum quantities of plutonium to be determined are 10 to 20 mg with a stated precision of 0.03-0.06 percent RSD and a bias of 0.02 percent or less.

This standard also includes a method for the determination of the absolute isotopic composition of plutonium dioxide allowing for the use of reference standards to determine bias. The stated precision of the method for Pu-239 at the 91% concentration level is 0.034% RSD; for Pu-240 at the 7.9% concentration level, 0.182% RSD; for Pu-241 at the 0.63% concentration level, 0.978% RSD; and for Pu-242 at the 0.033% concentration level, 4.6% RSD. Various impurities such as nitrogen, carbon, chloride, fluoride, sulfur, rare earths, trace elements and impurities, and moisture can be determined using the methods that are included in the standard.

Section 6.1 of ASTM Standard C 697-72 states that plutonium dioxide is very hygroscopic. It must be noted that some forms of PuO_2 are not very hygroscopic. Therefore, if the form of PuO_2 being analyzed is of the non-hygroscopic variety, the dry atmosphere mentioned would not be needed.

Mixed Oxides ($[U, Pu]O_2$)

The standard C 698-72a was approved by the ASTM on May 30, 1972, and published in July 1972. Included

[1] Copies may be obtained from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

in this standard are two methods for the analysis of plutonium in the presence of uranium:

a. Controlled-Potential Coulometry. The optimum quantities of plutonium to be determined are 2 to 6 mg. The method may be used for samples in which the U/Pu ratio varies within the limits of 0.1 to 10, with a stated precision for a single measurement of 0.14% relative standard deviation (RSD); and

b. Amperometric Titration with Iron (II). The optimum quantities of plutonium to be determined are 10 to 20 mg in mixed oxides with a plutonium content varying between 4 and 27 mass %. The method has a stated precision of 0.03 to 0.06% RSD and a bias of 0.02% or less.

One method for the analysis of uranium in the presence of plutonium is included in this standard: Controlled-Potential Coulometry. The optimum quantities of uranium to be determined are 3 to 10 mg. The method may be used for samples in which the U/Pu ratio varies within the limits of 0.1 to 10, with a stated precision for a single measurement of 0.27% RSD.

The standard also includes a method covering the determination of the absolute isotopic composition of plutonium or uranium or both by mass spectrometry utilizing solvent extraction techniques. The accuracy of the method depends primarily on the accuracy of the calibration standards of suitable isotopic composition. Precision of the measurements is dependent on the relative abundance of each isotope.

Various impurities such as nitrogen, carbon, chloride, fluoride, sulfur, tungsten, moisture, rare earths, trace elements and impurities, and total gas can be determined using the methods that are included in the standard.

Another method for the determination of uranium in the presence of various impurities that has been well characterized and found to be accurate, precise, and versatile which can be used as an alternate to the Controlled-Potential Coulometric procedure is the AEC New Brunswick Laboratory titrimetric method for uranium, NBL-252, "Titrimetric Determination of Uranium in Product, Fuel, and Scrap Materials after Ferrous Ion Reduction in Phosphoric Acid."[2]

C. REGULATORY POSITION

The analytical methods for the measurement of nuclear-grade plutonium dioxide powders and pellets contained in ASTM Standard C 697-72 and the analytical methods for the measurement of nuclear-grade mixed oxides ($[U, Pu]O_2$) contained in ASTM Standard C 698-72a are generally acceptable and provide an adequate basis for the assay, isotopic measurement, and impurity analysis of nuclear-grade plutonium dioxide powders and pellets and nuclear-grade mixed oxides subject to the following:

1. Precision and Accuracy Statements. The listed statements provide guidance to the levels of performance which may be attained using the described methods. The actual precision and accuracy of a method applied within a selected laboratory can only be determined through a well-planned quality control program.

2. Sample Handling Conditions. Section 7.1 of C 697-72 recommends that all sampling and critical weighings be performed in an atmosphere with a dew point no greater than -23°C. In some cases this may contribute to a sample sorption of water, especially in the case of low-fired oxide that has been held in an unsaturated condition. Therefore, an atmosphere containing less than 10 ppm of moisture should be established. It is especially important for the analyst to know the sample's history in order to assure a sample representative of the process batch before proceeding with various degrees of atmospheric moisture control since this information enables him to duplicate the conditions in which the oxide was handled. When sampling hygroscopic PuO_2, materials that are non-permeable to water should be used for sampling vials.

3. Sample Dissolution. Depending upon the process of manufacture including the temperature at which the material was fired (low-fired, high-fired), various degrees of difficulty in dissolution will be encountered. The dissolution techniques described in Section 30.1 of C 697-72 and Section 28.1 of C 698-72a are acceptable for preparing samples to be analyzed using the analytical methods set forth in C 697-72 and C 698-72a provided the proper matrix for the analytical methods can be obtained once the material is dissolved. The proper control of the dissolution techniques to assure complete dissolution and preclude the formation of method-incompatible plutonium species is extremely difficult and important; therefore, as a part of the laboratory quality control program, the complete and proper dissolution of the material should be verified.

4. Calibration and Standardization. The standards should be prepared in the same matrix as the samples, and the calibration points should bracket the estimated range of the samples.

5. Safety. Procedures involving the use of perchloric acid in radiochemical hoods and glove boxes should be performed with caution because of the potential explosion and fire hazard.

6. NBL-252. The AEC New Brunswick Laboratory titrimetric method for uranium, NBL-252, is an acceptable alternative to the Controlled-Potential Coulometric procedure in ASTM Standard C 698-72a for the determination of uranium.

[2] Copies may be obtained from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22151.