Standard Guide for the Determination of Iodine-129 In Uranium Oxide[1]

This standard is issued under the fixed designation C 1638; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the determination of iodine-129 (^{129}I) in uranium oxide by gamma-ray spectrometry. The method could also be applicable to the determination of ^{129}I in aqueous matrices.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 1402 Standard Guide for High-Resolution Gamma-Ray Spectrometry of Soil Samples

D 1193 Specification for Reagent Water

D 3648 Standard Practices for the Measurement of Radioactivity

D 3649 Standard Test Method for High-Resolution Gamma-Ray Spectrometry in Water

3. Summary of Practice

3.1 An aliquot of uranium oxide is dissolved in dilute nitric acid and the iodine is selectively extracted via liquid-liquid extraction. The iodine is further purified by selective precipitation and counted by gamma-ray spectrometry.

3.2 Gravimetric tracer recoveries using this method are typically between 75 and 90 %.

3.3 The minimum detectable activity (MDA) will vary with chemical yield, sample size, instrument background, counting time and counting efficiency. For a sample size of 100 mg U

oxide, using a well shielded detector, a 1000 minute counting time, and 32 % detector efficiency at 30 keV, a MDA of ≤0.74 Bq/g (20 pCi/g) oxide was achieved.

4. Significance and Use

4.1 The determination of ^{129}I is not typically requested in nuclear fuel specifications however it is commonly requested for disposal of the spent fuel, or for disposal of excess uranium from national weapon complexes. This practice can provide results of sufficient quality for waste disposal repositories.

5. Interferences

5.1 Incomplete removal of uranium and its ^{234}Th/^{234m}Pa daughters could lead to elevated Compton background in the low energy region of the gamma-ray spectrum, where the ^{129}I x-rays are counted.

5.2 Because the iodine yield monitor is added after the oxide dissolution, any loss of ^{129}I during the dissolution step will not be monitored and may lead to results that are biased low. To minimize any iodine loss, avoid prolonged heating of the sample and minimize the time the sample is in an acidic state.

6. Instrumentation

6.1 Extended-range or low-energy gamma ray spectrometry system. See C 1402, D 3648 or D 3649 for a general description of gamma-ray spectrometry systems. The system used to measure the low-energy x-rays from ^{129}I should have a thin window to allow the efficient penetration and measurement of the low-energy x-rays.

7. Terms and Definitions

7.1 *ROI:* Region-of-Interest; the channels, or region, in the spectra in which the counts due to a specific radioisotope appear on a functioning, calibrated gamma-ray spectrometry system.

7.2 *Reagent blank:* reagent water processed the same as the samples; used in the determination of the minimum detectable activity.

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[1] This guide is under the jurisdiction of ASTM Committee C26 on the Nuclear Fuel Cycle and is the direct responsibility of subcommittee C26.05 on Methods of Test.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

8. Apparatus

8.1 *Plastic bottles*, 30 and 60-ml, or separatory funnels

8.2 *Filter paper*—25-mm diameter, 0.45μm pore size

8.3 Vacuum filter apparatus

8.4 pH paper with unit resolution

9. Reagents and Materials

9.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available[3].

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I water as defined in Specification D 1193.

9.3 *1M Hydroxylamine-hydrochloride*—commercially available solution or dissolve 70 g of the powder in 500 mL of water, dilute to 1 litre final volume.

9.4 Iodide carrier, 20 mg I⁻ per millilitre as KI.

9.5 Nitric Acid, concentrated, ~16M

9.6 *0.1M Nitric Acid*—Add ~6 mL of concentrated HNO_3 to 950 mL of water, dilute with water to a final volume of 1 litre.

9.7 *8M Nitric Acid*—Add 500 mL of concentrated HNO_3 to 450 mL of water; dilute with water to a final volume of 1 litre.

9.8 p-xylene.

9.9 *Palladium carrier*—~10 mg/mL, dilute a commercially prepared solution to the correct concentration

9.10 *Sodium bisulfite, 0.1M*—dissolve 10.4 g of powder in 500 mL of water, dilute to a final volume of 1 litre

9.11 *Sodium Carbonate, 2M*—dissolve 212 g of powder in 500 mL of water, dilute to 1 litre final volume.

9.12 *Sodium Hydroxide, 4M*—dilute a commercially prepared solution or dissolve 160 g of pellets in 700 mL of water, dilute to a final volume of 1 litre. This is a very exothermic reaction. The use of an ice bath can mitigate the magnitude of the exothermicity.

9.13 Sodium Hypochlorite.

10. Calibration and Standardization

10.1 The gamma-ray spectrometry system should be calibrated for energy, resolution and efficiency according to the manufacturer instructions. The background counting rate for the instrument should be measured at a frequency determined by the user. See C 1402, D 3648 or D 3649 for additional information. A typical spectrum for ^{129}I is shown in Fig. 1.

10.2 Confirm the concentration of the I⁻ carrier by adding 1.00 mL of the carrier solution to 15 mL of water. Add 1 mL of the 0.1M $NaHSO_3$, mix, heat gently and then add 2 mL of the Pd^{+2} carrier. Collect the precipitate (PdI_2) on a tared 25-mm filter paper. Dry and reweigh the filter paper to confirm the expected precipitate weight. Repeat this confirmation several times to increase the precision of the determination.

10.3 Prepare an efficiency curve for the 30 keV x-rays comparing the relative efficiency versus weight of PdI_2 by precipitating equal quantities of ^{129}I with various weights of PdI_2. A typical curve for a Ge well detector is shown in Fig. 2; note that this curve shows the net count rate versus weight of PdI_2 rather than calculated efficiency (the ^{129}I activity used to prepare this graph was 2.2 Bq (60 pCi)).

11. Procedure

11.1 Weigh out no more than 100 mg of uranium oxide into a small beaker.

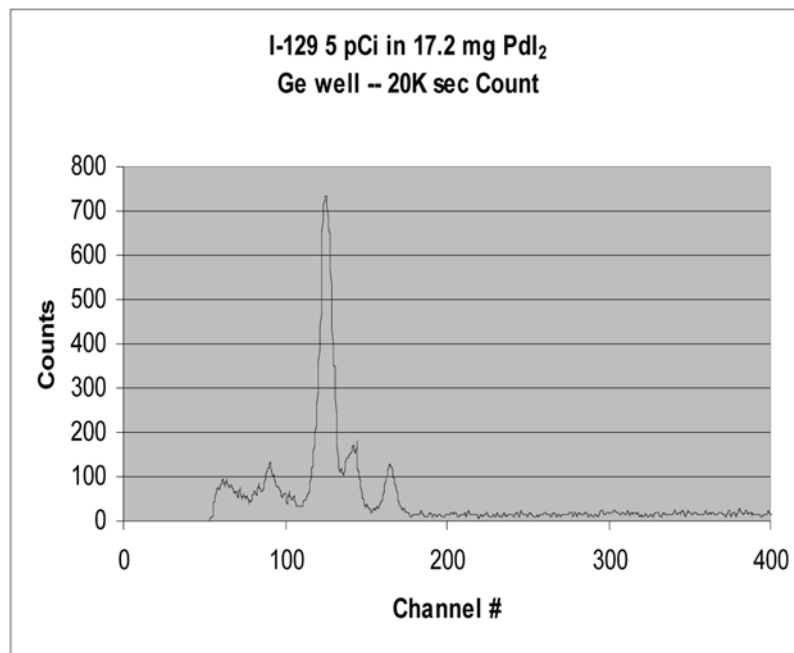[3] "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington DC.

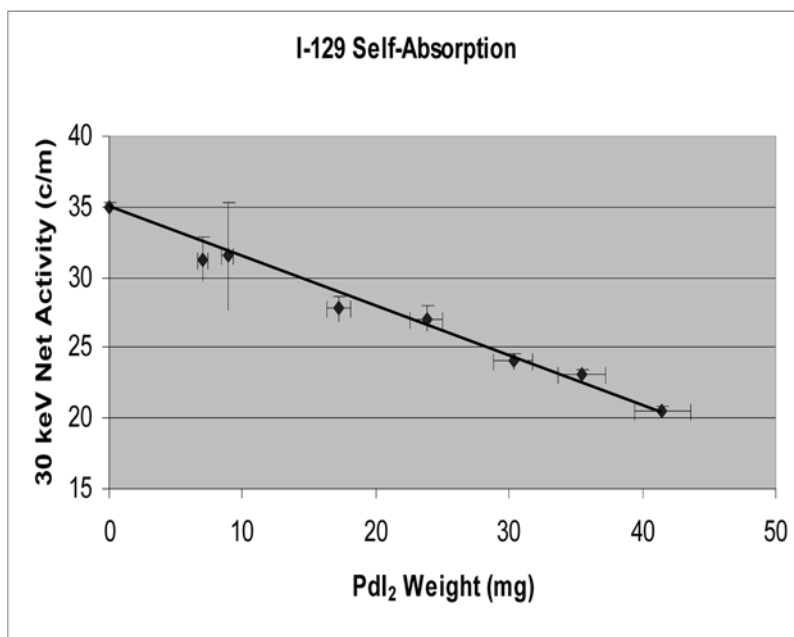**FIG. 1 Low-Energy Photon Spectrum of I-129 on a Ge Well Detector**

I-129 Self-Absorption

FIG. 2 Self-Adsorption of 30 keV X-ray versus Weight of PdI$_2$·H$_2$O

11.2 Dissolve the oxide in about 20 mL of 0.1M HNO$_3$. Heat gently, if required, to complete the dissolution.

NOTE 1—Avoid prolonged heating to minimize any iodine volatilization and possibly avoid heating altogether if only a small portion of the sample remains undissolved. Also, proceed directly to the next steps to minimize the time the sample is held under acidic conditions without the tracer present. Addition of the tracer prior to dissolution may not be appropriate since the sample iodine may not be in the same form and oxidation state as the tracer iodine.

11.3 Add 1 mL of the 4M NaOH. Swirl the solution to mix and check the pH. The solution should be strongly basic.

11.4 Add 1 mL of the 2M NaCO$_3$. Swirl to mix the solution

11.5 Add 1.00 mL of the 20 mg/mL I$^-$ carrier. Swirl to mix.

11.6 Add 1 mL of the NaHClO$_3$ solution to the beaker to oxidize the iodine to periodate (IO$_4^-$). Swirl to mix. Place the beaker on a hotplate and heat the solution to just below boiling. Remove from the hotplate and cool to room temperature.

CAUTION: The beaker and solution must be cool prior to the next step.

11.7 Carefully add 1 mL of the 8M HNO$_3$. Swirl the solution then check the pH. The solution should be strongly acidic.

11.8 Transfer the solution to a 60-mL plastic bottle or separatory funnel. Rinse the beaker a few times with small portions of water and add to the bottle.

11.9 Add 10 mL of p-xylene to the bottle.

11.10 Add 3 mL of 1M NH$_2$OH-HCl to the bottle to reduce the periodate to iodine (I$_2$). Swirl to mix. The solution should be red-purple in color at this point.

11.11 Cap the bottle and shake for several minutes to extract the iodine into the organic layer. Let the solution stand and allow the organic layer to separate from the aqueous layer.

11.12 Remove the cap and draw off the top, organic layer with a disposable pipette. Transfer the organic layer to a 30-mL plastic bottle or clean separatory funnel.

11.13 Add 15 mL of water to the organic in the 30-mL bottle. Add 1 mL of the 0.1M NaHSO$_3$ to the bottle to reduce the iodine to iodide (I$^-$). Cap the bottle and shake for one minute until the organic layer is colorless. Let the solution stand and allow the organic layer to separate from the aqueous layer.

11.14 Draw off the upper, organic layer and discard.

11.15 Transfer the aqueous layer to a 100-mL beaker and gently warm the solution on a hotplate.

11.16 Add 2 mL of the Pd^{+2} carrier solution to the beaker.

11.17 Allow the PdI$_2$ to precipitate and then filter the solution through a tared 25-mm filter paper.

11.18 Allow the filter paper to dry and then reweigh to determine the chemical yield of the separation.

11.19 Count the filter on an extended range or low-energy gamma-ray spectrometry system for the length of time required to meet the requested detection limit. Set the ROI for ^{129}I to monitor the 29-34 keV Xe K x rays.

12. Calculation

12.1 CALCULATION OF CHEMICAL YIELD

Y = mg PdI$_2$ recovered/mg PdI$_2$ expected based on calibration (10.2)

12.2 CALCULATION OF ACTIVITY

$$A_i = [(G_i - B_i) / (Y * E * AB_i * W)] \qquad (1)$$

where
A_i = activity of ^{129}I in Bq per gram U oxide
G_i = gross counts per second in the ^{129}I ROI
B_i = background counts per second in the ^{129}I ROI
Y = yield calculated above expressed as a fraction
E = detector efficiency for the 29-34 keV x-rays, expressed as a fraction, based on the weight of the PdI$_2$
AB_i = branching ratio for ^{129}I, expressed as a fraction
W = weight of U oxide analyzed in grams

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If the weight of uranium per gram of oxide is known the sample activity may be reported as Bq of [129]I per gram of uranium by multiplying by the correct ratio.

12.3 CALCULATION OF MINIMUM DETECTABLE ACTIVITY

$$MDA_i = (4.65 * s_B + 2.71) / (E * Y * T * AB_i * W) \qquad (2)$$

where

MDA_i = minimum detectable activity (Bq/g)
s_B = standard deviation of the reagent blank counts in time T
T = sample counting time in seconds

13. Keywords

13.1 Gamma-ray spectrometry; liquid-liquid extraction; x-ray