WESTINGHOUSE MATERIALS
COMPANY OF OHIO

DOE/OR/21600--T23

Method No: 4011
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ANALYTICAL LABORATORIES

DE88 012278

RADIOMETRIC DETERMINATION OF URANIUM-232 IN
URANIUM BEARING MATERIALSRevision: 0
Date: 1/14/87

1.0 SCOPE

The method is designed for use on recycled uranium materials and is applicable to materials that will yield at least 100 mg of uranium. Typical analysis time is 24 to 30 hours. U-232 can be measured to a lower limit of detection of 1 ppb (U-235 basis).

2.0 PRINCIPLE

Recycled uranium materials are purified with an ethyl acetate liquid-liquid extraction from a nitric acid media. Uranium is precipitated from the aqueous solution after TTA/Xylene purification. The uranium is then oxidized by heat to triuranium octoxide (U_3O_8), weighed, dissolved in 5% nitric acid (HNO_3) and evaporated on a stainless steel planchet. The alpha activity of the sample is measured on a Si surface barrier detector and the absolute weight of the U-232 is determined. If the amount of U-232 measured is to be based on the amount of U-235, a U-235 value must be obtained by performing either a gamma, or a mass spectrometric analysis.

3.0 SPECIAL APPARATUS

- 3.1 Multichannel Pulse Height Analyzer, Northern Scientific model NS-715.
- 3.2 Si Surface Barrier Detector, ORTEC model BR-045-900-100.
- 3.3 Two-inch diameter, concentric-ringed, stainless steel planchets, WMCO Stores No. S-00215.
- 3.4 Glass Vials, 4 dram, Stock Room Item No. P-98.

4.0 REAGENTS

Note: All volumes are measured using an appropriately sized graduated cylinder, unless otherwise specified. All reagents are thoroughly mixed when they are prepared.

- 4.1 Nitric Acid (HNO_3) - concentrated (70% by weight).
- 4.2 HNO_3 (8M) - Add 510 mL of HNO_3 (Reagent 4.1) to 490 mL of distilled water.
- 4.3 HNO_3 (2M) - Add 127 mL of HNO_3 (Reagent 4.1) to 873 mL of distilled water.

MASTER

MP

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- 4.4 Ammonium Hydroxide (NH_4OH) - concentrated (29% NH_3 by weight).
- 4.5 Hydrogen Peroxide (H_2O_2) - concentrated (30% by weight).
- 4.6 Ethyl Acetate ($\text{CH}_3\text{CO}_2\cdot\text{C}_2\text{H}_5$) - Certified A.C.S. Grade.
- 4.7 Xylenes ($\text{C}_6\text{H}_4(\text{CH}_3)_2$) - reagent grade.
- 4.8 Thenoyltrifluoroacetone (TTA) - Eastern Chemical Co., no purity specification.
- 4.9 TTA (0.5M) - Add 220 ± 0.1 g of TTA (Reagent 4.8) to approximately 1L of xylene (Reagent 4.7) and mix thoroughly to effect dissolution using a glass rod. Transfer the solution to a 2L volumetric flask and adjust to volume with xylene (Reagent 4.7).
- 4.10 Aluminum Nitrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$) - reagent grade.
- 4.11 $\text{Al}(\text{NO}_3)_3$ Solution - Add 1L of distilled water to 2268 g (5 lbs.) of $\text{Al}(\text{NO}_3)_3$ (Reagent 4.10) placed in a 2L beaker and heat to complete dissolution. Stir vigorously with a glass rod while heating the reagent.
- 4.12 $\text{Al}(\text{NO}_3)_3$ Wash Solution - Add 1L of distilled water and 120 mL of HNO_3 (Reagent 4.1) to 2268 g (5 lbs.) of $\text{Al}(\text{NO}_3)_3$ (Reagent 4.10) placed in a 2L beaker and heat to complete dissolution. Stir vigorously with a glass rod while heating the reagent.
- 4.13 Acetone ($\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$) - reagent grade.
- 4.14 Cellulose Powder (Filter Aid), Whatman CF1, maximum ash 0.015%.
- 4.15 U-232 Primary Standard, 0.12 μCi (266,400 d/m), calibrated and certified by ORNL on 11-16-79, in 5 mL of 2M HNO_3 (Reagent 4.3).
- 4.16 U-232 Reference Standard (266.4 d/m-mL) - dissolve the U-232 Primary Standard (Reagent 4.15) in 2M HNO_3 (Reagent 4.3) and quantitatively transfer the solution to a 1L volumetric flask. Adjust to volume with 2M HNO_3 (Reagent 4.3).
- 4.17 Th-230 Reference Standard, Eberline Instrument Co. #S-11423, 0.0061 μCi on 9-8-81.

5.0 SAFETY PRECAUTIONS

- 5.1 WEAR SAFETY GLASSES IN THE LABORATORY AT ALL TIMES.

6.0 SAMPLE PREPARATION**COMMENTS**

- 6.1 Start sample preparation at the appropriate step for the type of sample being analyzed:

- (a) Solid samples - Step 6.2
- (b) Liquid samples - Step 6.5

Submit the sample to the Chemical Analysis Group for a uranium analysis (in % U or Ug/L) if the uranium content is unknown and/or the U-232 content is to be expressed on a uranium basis.

USE A GRADUATED CYLINDER TO MEASURE OUT VOLUMES UNLESS OTHERWISE DIRECTED IN SECTION 6.0.

- 6.2 Slowly add enough sample to yield 9 grams of U_3O_8 to 100 mL of 8M HNO_3 (Reagent 4.2) which is in a 250 mL beaker. After the reaction subsides boil the solution for 5 minutes on a hotplate.

Use a Speedy-vap and boiling beads to prevent losses.

Calculate the amount of sample needed using:

$$\text{Amt.} = \frac{763.2}{\% \text{ U}} \pm 0.1 \text{ g}$$

- 6.3 Cool the solution, then vacuum filter the sample (if necessary) through a Whatman #40 filter paper in a Buchner funnel.

Collect the filtrate in a clean 600 mL vacuum flask.

- 6.4 Continue at Step 6.6.1.

- 6.5 Measure a sufficient sample volume to yield 9 grams of U_3O_8 into a 600 mL beaker.

Calculate the volume of sample needed using:

$$\text{Volume} = \frac{7632}{\text{U g/L}} \pm 1 \text{ mL}$$

- 6.6 Boil the sample to dryness on a hotplate. Cool and add enough concentrated HNO_3 (Reagent 4.1) to cover the residue (typically 50-100 mL).

Converts the sample to the nitrate form.

- 6.6.1 Again boil the sample to dryness on a hotplate and cool.

SAMPLE PREPARATION

COMMENTS

- 6.7 Add 100 mL of 8M HNO_3 (Reagent 4.2) to sample. Heat gently on a hotplate, if necessary to redissolve the solids.
- 6.8 Add 200 mL of $\text{Al}(\text{NO}_3)_3$ solution (Reagent 4.11) to the sample and transfer it to a 1000 mL separatory funnel.
- 6.9 Add 200 mL of ethyl acetate (Reagent 4.6) to the separatory funnel and shake it for 1 minute, venting as required to relieve the pressure. Shake the funnel gently at first and vent through the stopcock to relieve pressure.
- 6.10 Allow the phases to separate, then drain and discard the lower aqueous phase. Swirling the funnel aids in separating the residual aqueous solution.
- The uranium is now in the ethyl acetate phase.
- 6.11 Add 50 mL of $\text{Al}(\text{NO}_3)_3$ wash solution (Reagent 4.12) to the separatory funnel, vent, and shake the funnel for 30 seconds. Removes residual aqueous solution from the organic phase.
- 6.12 Allow the phases to separate, then drain and discard the lower aqueous phase.
- 6.13 Add 200 mL of distilled H_2O to the separatory funnel, vent, and shake the funnel for 30 seconds.
- 6.14 Allow the phases to separate. Drain the lower aqueous phase into a clean 600 mL beaker. The aqueous phase now contains the purified uranium.

SAMPLE PREPARATION

COMMENTS

6.15 Adjust the pH of the aqueous solution from the previous step to 1.0 ± 0.05 with NH_4OH (Reagent 4.4) and/or dilute HNO_3 (Reagent 4.3).

Use a pH meter which has been standardized to pH = 1.0.

6.16 Add the pH 1.0 solution to a 1000 mL separatory funnel containing 100 mL of TTA/Xylene (Reagent 4.9) and shake the solution for exactly 1 minute, venting as necessary.

Trace levels of decay products (Th, Pa) are transferred to the organic phase (TTA).

Decay products produce spectral interferences.

6.17 Allow the phases to separate, and drain the lower aqueous phase into a beaker containing 10 mL of H_2O_2 (Reagent 4.5) and 100 mL of H_2O .

Uranium is still in the bottom (aqueous) phase.

6.18 Mix the sample to precipitate uranium oxides. Vacuum filter the sample through a Whatman #42 filter paper placed in a Buchner funnel.

Filter aid (Reagent 4.14) may be used for fine precipitates.

Use filter aid sparingly, no more than 1 g/sample.

6.19 Wash the filter cake with acetone (Reagent 4.13) and allow it to dry. Transfer the cake to a numbered platinum crucible.

6.19.1 Record the crucible number and other sample information on the Sample Register (Attachment B).

6.19.2 Discard the filtrate down the drain with water.

6.20 Slowly place the dish in an $850 \pm 10^\circ\text{C}$ muffle furnace. Permit the flames to die down.

6.20.1 Heat the cake in the muffle furnace for 15 minutes.

This will convert the cake to U_3O_8 .

SAMPLE PREPARATION

COMMENTS

- 6.21 Cool, then transfer the U_3O_8 to a labelled glass vial (Special Apparatus 3.4).
- 6.22 Analyze the sample for U-235 (in wt%), if the U-232 is to be expressed on a U-235 basis, using Method 4000 or 4001.
- 6.23 Accurately weigh 0.1 ± 0.0005 g of sample (U_3O_8) and transfer it to a 50 mL beaker.
- 6.24 Cover the sample with 5 mL of concentrated HNO_3 (Reagent 4.1) and heat gently until dissolution is complete.
- 6.25 Transfer the solution to a 100 mL volumetric flask, washing the beaker several times with distilled water into the flask. Cool and adjust the solution to volume with distilled water.
- 6.26 Pipette 2 mL of the sample solution onto a planchet (Special Apparatus 3.3) and allow it to evaporate under a heat lamp.
- 6.27 Using a Fisher burner, flame the planchet to a dull red color and allow it to cool.
- 6.28 Identify the planchet with a self sticking label indicating the proper lab number, the analyte and the date plated.
- 6.29 Repeat Steps 6.26 through 6.28 for the U-232 Reference Standard (Reagent 4.16).

The label should be inscribed with lab number, analyte and date.

Avoid sample loss due to splashing.

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SAMPLE PREPARATION

COMMENTS

- 6.29.1 Identify the planchet with "Standard", "U-232", and the date.

7.0 PROCEDURE

COMMENTS

- 7.1 Count the sample until either the count in the highest U-232 peak channel reaches 1000, or 24 hours, whichever comes first.

See Method 4004 for alpha counting and readout.

- 7.2 Set the region-of-interest from background on the low energy side, to background on the high energy side of the 5.30 MeV U-232 alpha peak.

- 7.3 Print out the data channel contents and the gross counts for the region-of-interest.

- 7.4 To obtain background for the measurement: average the background channels and multiply the average times the number of channels in the region-of-interest.

For example, if the background counts were 298 and 302 the average background would be 300 counts. If there were 20 channels in the peak (including background channels) the measurement background would be $300 \times 20 = 6000$ counts.

- 7.5 To obtain the net counts/minute subtract the background count from the gross count and divide by the counting time in minutes.

For example, if the gross count for the peak was 10,000 counts and the background was determined to be 6,000 counts, then the net counts would be 4,000 counts. If these counts were measured for 1,000 minutes then the net counts/minute would be $4000/1000 = 4$.

- 7.6 Use the net c/m and Equation 9.1 to calculate the U-232 concentration of an unknown sample.

8.0 STANDARDIZATION

- 8.1 The alpha spectrometer counting efficiency is determined by counting the Eberline Th-230 reference standard (S#11423). The activity of the reference standard on 9-8-81 was 13,500 d/m (0.0061 uCi) and the uncertainty of the value at the 99% C.L. is $\pm 2.44\%$. The spectrometer's counting efficiency is used to calculate the activity of an unknown sample (See Attachment A).

9.0 CALCULATIONS

- 9.1 The concentration of U-232 (on a U-235 basis) is calculated using the following relationship (See Attachment A for equation derivation):

$$\text{U-232 (U-235 Basis)} = \frac{(1.2402)(Cx)}{(E)(I)} \text{ ppb}$$

Where,

Cx = Measured net count rate for the sample (c/m)
 E = Counting Efficiency Fraction (measured Th-230 c/m divided by 13,500 d/m)
 I = U-235 concentration of the sample (wt % U-235 on a uranium basis)

- 9.1.1 The above formula assumes 2 mg of U_3O_8 are deposited on the planchet.
- 9.1.2 Either a mass spectrometric, or gamma spectrometric U-235 concentration value may be used.
- 9.2 To convert U-232 ppb (U-235 basis) to a uranium basis, multiply the result from Step 9.1 by the wt% U-235 and divide the answer by 100.
- 9.3 Example calculation:

	<u>Sample</u>	<u>Standard</u>
Counting Time (minutes) =	1,450	30
Gross Count =	1,635	41,917
Peak Channels =	35	40
Average Background =	5	120
Counts/Channel		
Net Count =	1,460	37,117
Net Counts/minute =	1.0069	1237.23

I = 1.253 wt % U-235

$$E = \frac{1237.23}{13500} = 0.0916$$

$$\text{U-232} = \frac{(1.2402)(1.0069)}{(0.0916)(1.253)} = 10.88 \text{ ppb (U-235 Basis)}$$

9.4 If the value calculated was for a routine sample it would be rounded to two significant figures and reported as 11 ppb (U-235 basis).

9.5 If the value calculated was for an ALQA sample it would be rounded to three significant figures and reported as 10.9 ppb (U-235 basis).

10.0 PRECISION AND ACCURACY

10.1 The relative precision (95% C.L.) of the procedure at the 10 ppb level is 29.5%.

11.0 QUALITY ASSURANCE

11.1 An internal reference standard (Reagent 4.16) is processed with each group of samples. If available, an ALQA control and/or recycle sample is processed with each sample, or group of samples.

12.0 REFERENCES

12.1 Humphrey, H.W., "Radiometric Procedure for U-232 Determination by Alpha Spectrometry", prepared March 15, 1978.

12.2 Humphrey, H.W. and Fritz, K.M., Quantitative Alpha Spectrometric Determination of U-233, U.S. A.E.C. Report, NLCO-1048 (Special), February 1970.

13.0 ATTACHMENTS

13.1 Attachment A - U-232 Equation Derivation.

13.2 Attachment B - Sample Register - Isotopic Analysis.

Revision 0, prepared by E.L. Adkins and H.W. Humphrey, 1/14/87.
Prepared on HP-Touchscreen, HP-Wordprocessor.

Approvals:

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9-29-87
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ATTACHMENT A

U-232 EQUATION DERIVATION

Counting efficiency "E" is defined as:

$$E = \frac{\text{Measured net count rate (C)}}{\text{Actual Disintegration Rate (D)}} \quad \frac{\text{c/m}}{\text{d/m}} \quad (1)$$

If Equation (1) is rearranged we can solve for "D",

$$D = \frac{C}{E} \quad \text{d/m} \quad (2)$$

The net U-232 count rate for an unknown sample "C_x" is measured and the efficiency "E" is determined using a Th-230 standard. The efficiency for Th-230 and U-232 are virtually identical.

Equation (2) gives the activity for the portion of the sample which is deposited on the planchet. To put the sample on a uranium basis, Equation (2) must be divided by the weight of uranium plated "W". Or,

$$D_x = \frac{C_x}{E \cdot W} \quad \text{d/m-gU} \quad (3)$$

where, "W" is expressed in grams.

U₃O₈ contains 0.848 g of uranium per gram of U₃O₈. From Step 6.18 a 0.1 g subsample of U₃O₈ was taken for analysis. A portion of this weight (2/100) was then plated and counted (Steps 6.20 and 6.21). Or, the amount of uranium on the plate is,

$$W = (0.1 \text{ g U}_3\text{O}_8)(0.848 \text{ g U/g U}_3\text{O}_8) \left(\frac{2}{100} \right) = 0.001696 \text{ g} \quad (4)$$

Substituting this value of "W" into Equation (3) we have,

$$D_x = \frac{C_x}{(0.001696) E} \quad \text{d/m-gU} \quad (5)$$

The weight (in ppb) equivalent to the activity determined by Equation (5) is determined by recalling that,

$$\text{U-232 ppb (U Basis)} = \frac{\text{U-232 ng}}{\text{Ug}} \quad (6)$$

ATTACHMENT A (Continued)

U-232 EQUATION DERIVATION

The specific activity of U-232 is 47,544 d/m-ng. If Equation (5) is divided by the U-232 specific activity we have,

$$\text{U-232 (U Basis)} = \frac{C_x}{(0.001696)(47,544)(E)} \text{ ppb} \quad (7)$$

or,

$$\text{U-232 (U Basis)} = \frac{C_x}{(80.6346)(E)} \text{ ppb} \quad (8)$$

To express the U-232 concentration on a U-235 basis, Equation (8) must be multiplied by (100/wt% U-235). Or,

$$\text{U-232 (U-235 Basis)} = \frac{C_x}{(80.6346)(E)} \cdot \frac{100}{(I)} \text{ ppb} \quad (9)$$

where "I" is the measured wt% U-235 value for the unknown sample. Consolidating constants we have the final form.

$$\text{U-232 (U-235 Basis)} = \frac{(1.2402)(C_x)}{(E)(I)} \text{ ppb} \quad (10)$$

The counting efficiency "E" is determined using the Th-230 standard and applying Equation (1),

$$E = \frac{\text{Measured net Th-230 count rate}}{13,500} \frac{\text{c/m}}{\text{d/m}} \quad (11)$$

where, the standard is counted on the same alpha spectrometer as the sample.