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QUANTITATIVE ALPHA SPECTROMETRIC
DETERMINATION OF ^{232}U

Special Report

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ABSTRACT

A method was developed for determining the concentration of ^{232}U in uranium materials to a low limit of 10 ppb on a ^{235}U basis with a relative precision of $\pm 28.2\%$ at the 95% confidence level. The method consists of an ethyl acetate extraction followed by a measurement of the 5.298 Mev (average weighted value) alpha peak of ^{232}U utilizing a Frisch grid ionization chamber. A mass spectrometric ^{235}U value is then used to determine the $^{232}\text{U}/^{235}\text{U}$ weight relationship.

INTRODUCTION

The analytical determination of many of the minor isotopes of uranium is gaining importance due to the enhancement of these isotopes in high neutron fluxes and their subsequent influence upon nuclear reactor parameters as they are recycled in fissile feed materials. Isotopes such as ^{232}U , for example, if allowed to accumulate in sufficient quantities in recycled materials, could require the use of remote handling and fabrication techniques.

In the past ^{232}U was not a problem since the two processes by which it is produced in slightly enriched uranium were closely controlled.¹ The precursors of ^{232}U (^{232}Th and ^{236}U) were kept at a minimum level in a thermal reactor. Today, ^{232}U and ^{237}Np are deliberately allowed to build to higher levels in feed materials since they are needed for use in radioisotopic heat sources.

Large amounts of recycled reactor fuels are processed at this site; therefore an analytical method was desired which would permit a rapid quantitative determination of the ^{232}U level. Since ^{232}U is radioactive and emits alpha particles with a half life of 74 years, the authors undertook to establish a procedure which incorporated the measurement of this activity.

SUMMARY OF RESULTS

Several means of determining ^{232}U were investigated using samples previously analyzed by Nuclear Fuels Services (NFS), West Valley, New York. NFS routinely analyzes their feed materials shipped to this site for ^{232}U on a ^{235}U basis. The method ultimately selected for use at this site employs an absolute radiometric determination of ^{232}U on a total uranium basis; a highly precise and accurate weight percent ^{235}U value is obtained from gas-type mass spectrometric analysis.

Ten replicate analyses were made on prepared solutions at two extremes in concentration level: 10 ppb and 370 ppb ^{232}U (^{235}U basis). After a 4-hour count, the limits of error on individual results at the 95% confidence level were $\pm 28.2\%$ and $\pm 18.9\%$, relative, for the 10 ppb and 370 ppb samples, respectively. A 16-hour counting time at the 10 ppb level did not significantly improve the precision at that level.

A uranium sample can be analyzed for ^{232}U in 6 hours using this procedure, which incorporates an ethyl acetate extraction similar to that used by Kelley and Twitty.²

The effect of thorium on the precision of the method was quantitatively investigated, but no spectral interference was encountered.

EXPERIMENTAL

To facilitate the comparison of our results with those of NFS, it was necessary to express the concentration of ^{232}U on a ^{235}U basis, as NFS did. Since NFS had not published their ^{232}U procedure and subsequent telephone inquiries were unfruitful, the authors considered the feasibility of the following three approaches to the analysis: (1) the weight ratios for ^{232}U and ^{235}U could be determined by alpha spectrometry, (2) the weight percent ^{235}U could be determined by some other means and then used with the alpha analysis of ^{232}U to obtain the desired weight, or (3) the ratio of $^{232}\text{U}/^{238}\text{U}$ could be determined by alpha spectrometry and the $^{235}\text{U}/^{238}\text{U}$ ratio could be determined by thermal mass spectrometry. The first approach was ruled out because past experience indicated that the alpha analysis of ^{235}U is rather insensitive, except in rare cases, due to the long half life of ^{235}U and its multiple alpha peaks. Since most shipments received from off-site are analyzed here for weight percent ^{235}U prior to acceptance, the second approach to the analysis of ^{232}U was considered both feasible and desirable. The third approach, utilizing the thermal mass spectrometer also seemed feasible since ^{233}U was also being analyzed by this instrument, and the various uranium isotopic weight ratios had to be obtained prior to a ^{233}U determination. It must be kept in mind, however, that the thermal mass spectrometric results are, for the most part, not as accurate as gas-type mass spectrometric results.

Somewhat similar to this approach is the method used by R. C. Shank of Phillips Petroleum Company where the $^{232}\text{U}/^{234}\text{U}$ ratio is determined by alpha spectrometry, and the abundance of ^{234}U is determined mass spectrometrically.³ Since the ionium (^{230}Th) peak (4.666 Mev*) would present a definite spectral interference with ^{234}U (4.754 Mev*) and would, hence, require an additional extraction, this method was not investigated.

INSTRUMENTATION

Description

The instruments used for the alpha spectrometric evaluation were: (1) a Radiation Instrument Development Laboratories (RIDL) 400-channel pulse-height analyzer, model 34-12B; (2) a custom made Frisch grid ionization chamber designed by E. Fairstein of ORNL; (3) a Hamner Electronics Company high-voltage power supply, model N-4035; and (4) a solid state F.E.T. preamplifier designed and built at this laboratory by M. R. Bailey. This preamplifier improves the pulse shape and enhances the signal-to-noise ratio. The circuit consisted of one F.E.T. input transistor and three additional transistors for amplification of the signal pulse. The circuit is schematically illustrated in Figure 1. Power for the preamplifier (-12 volts) is supplied by the RIDL analyzer.

*Calculated on the basis of a weighted average.

Operating Conditions

Previous experience with the RIDL 400-channel pulse-height analyzer indicated that the alpha spectrum of uranium could be established at the following settings:

Conversion gain	- 2 volts/100 channels
Coarse gain	- 1/32
Fine gain	- 0
Threshold	- 0 volts
Window	- 10 volts
Input signal	- positive direct

The detector used throughout the study was the Frisch grid ionization chamber operated at a positive pressure of 2.5 psig P-10 gas (90% argon - 10% methane) and a potential of 2500 volts dc. The ionization chamber was twice purged with P-10 gas which was then allowed to flow dynamically through a bubbler assembly before each sample was counted. A semiautomatic sequential programming device (designated and fabricated by J. Kramer of our Electronics Section) controlled the chronological operations of purging, evacuating, bubbling, etc., and energized the high voltage circuit.

Calibration

To determine the exact location of the ^{232}U peak, a series of standards with known energies was used to establish a calibration curve. Using a weighted energy, since the two

peaks of ^{232}U are unresolved, the location of the 5.298 Mev peak of ^{232}U was determined.

A sample was obtained which had previously been analyzed by NFS and was reported to contain approximately 400 ppb ^{232}U (^{235}U basis). Figure 2 illustrates the relative size and position of the ^{232}U peak compared with the other alpha emitters in this recycled uranium.

METHOD

The second approach was investigated first because it appeared to offer the most interference-free measurement of ^{232}U , as was seen in Figure 2, in addition to the fact that a measurement in this area would be less sensitive to sample preparation and electronic incongruities. The following theoretical relationship applies to the absolute measurement of $^{232}\text{U}/^{235}\text{U}$ on a weight basis:

$$\frac{^{232}\text{U}}{^{235}\text{U}} = \frac{^{232}\text{U}/\text{U}}{^{235}\text{U}/\text{U}} = \frac{\text{CAT}}{0.693 (\text{WINGE}) \times 10^{-2}}$$

where,

C = net counts per minute due to ^{232}U

A = atomic weight of ^{232}U (in grams)

T = half life of ^{232}U (in minutes)

W = equivalent fractional weight* of U_3O_8 deposited on counting planchet (in grams)

*Since U_3O_8 is normally the purification end product, this weight is the most usable practically. Uranium, however, is plated from a uranyl nitrate solution throughout this procedure.

I = weight percent ^{235}U *

N = Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$)

G = gravimetric factor (0.84802 from $\text{U}_3\text{O}_8 \rightarrow \text{U}$)

E = efficiency of detection system for 5.298 Mev alpha particles.

Evaluating the constants for our system:

$$\text{ppb } ^{232}\text{U} (^{235}\text{U} \text{ weight basis}) = \frac{(6.613 \times 10^{-3})C}{WI}$$

The efficiency was assumed constant over the energy range from ^{232}U (5.298 Mev**) to ^{241}Am (5.463 Mev**). Using the ^{241}Am alpha standard, the efficiency was determined to be 38.6% for our detection system and alpha particle energy.

A stock solution containing 0.848 g U/l was prepared from the 400 ppb ^{232}U (^{235}U basis) NFS sample and 5% HNO_3 v/v. One milliliter (containing 0.848 mg uranium) of this solution was pipetted onto a 2-inch diameter stainless steel planchet, and the solution was allowed to evaporate to dryness. The sample so prepared was then counted for 1 hour, and the peak area of ^{232}U was linearly corrected for background. A value of 360 ppb ^{232}U (^{235}U basis) was obtained based on an isotopic ^{235}U value of $0.6470 \pm 0.0007 \text{ wt } \%$ determined mass spectrometrically. Although the 1-hour counting time was not optimum, the isotopic ^{232}U value assayed approximately 90% of the value reported by NFS. This difference between laboratories was considered insignificant, and a precision study was conducted at this level of concentration.

*This value should be obtained by the most precise means available; in our case this was gas-type mass spectrometry with a precision of $\pm 0.0007 \text{ wt } \%$ ^{235}U at the 95% confidence level for isotopic values in the range of 0.71 to 0.94 wt % ^{235}U .

**Energy calculated from a weighted average.

A series of 10 planchets was prepared from the NFS reference sample stock solution, since there was an insufficient number of routine samples available at this time for evaluation purposes. Each planchet was prepared to contain 0.848 mg uranium, and each was counted for 4 hours. The results of this study are summarized in Table I.

Since the lower detection limit for ^{232}U analysis was expected to be 10 ppb ^{232}U (^{235}U basis), a 1-to-40 isotopic dilution of the stock solution was prepared from U_3O_8 containing no measurable ^{232}U (the lowest detectable level was calculated to be 2.5 ppb ^{232}U) in order to determine the precision at this level. The resulting new stock solution contained 0.6954 g U/liter. Ten stainless steel planchets were again prepared in the manner previously described, and each was counted for 4 to 16 hours. It was felt that the longer counting times might be beneficial due to the extremely low count rate. The relatively small size of the ^{232}U peak can be seen in Figure 3 as compared with ^{234}U and ^{238}U after a counting time of 4 hours.

A value of 0.7773 ± 0.0007 wt % ^{235}U was determined by mass spectrometric analysis for the diluted stock solution. The results of the subsequent precision study are presented in Tables II and III. The 16-hour count did not significantly improve the precision over the 4-hour count. This is probably due to electronic instability of the instrumentation with time at the low count rates (approximately 0.9 counts per minute) encountered at the 10 ppb ^{232}U level. Since there was no significant improvement in

precision with a 16-hour count at the lower limit of detection, a routine method was established incorporating a 4-hour count for all levels.

DISCUSSION

As previously mentioned the $^{232}\text{U}/^{235}\text{U}$ weight ratio can also be determined by utilizing an alpha spectrometric $^{232}\text{U}/^{238}\text{U}$ weight relationship in conjunction with a mass spectrometrically determined $^{235}\text{U}/^{238}\text{U}$ weight value. Such an approach is inherently less accurate due to the measurement of two peak areas instead of one and the subsequent measurement of background in an area of the spectrum that is very sensitive to fluctuations in resolution. One other shortcoming of this approach is the use of the $^{235}\text{U}/^{238}\text{U}$ weight ratio. Using our present equipment and methods, such a value had to be obtained by a thermal emission mass spectrometer which is less precise than the gas-type instrument previously utilized. Since initial results, using the same conditions as described earlier, indicated a high bias it was felt that the method did not warrant further investigation.

To ensure that there was no thorium spectral interference, a thenoyltrifluoroacetone extraction⁴ was employed to remove any traces of elemental thorium that might be present in the reference NFS sample. The ^{232}U concentration so assayed differed by less than 9% from the previously established value indicating that thorium was not a problem in ^{232}U determinations. The TTA

extraction was incorporated into the final procedure to eliminate the possibility of thorium interference in routine samples. This is an ever-present possibility since thorium and uranium are both processed at this site.

^{232}U determinations are being performed routinely in less than 6 hours. The procedure includes purification, planchet preparation, activity determinations, and calculation of results. The major part of the analytical time (4 hours) is required for counting due to the low count rates of the samples. To keep the count rate at a high enough level to maintain statistical integrity, a sample size of approximately 848 micrograms was employed. Although this sample size is not optimum, its use was justified by the relatively interference-free peak location of ^{232}U . The empirical correction factor used in the ^{232}U assay also took into account the slight self-absorption of the larger sample size. Optimization of the sample size evaporated on the counting planchet should enhance the resolution of the alpha spectrum. Although the resolution could have been enhanced by electro-deposition or vapor plating, it was felt that the increased time and complexity of these techniques would offset any potential benefits realized from better resolution.

The ^{232}U analysis here presented incorporates the use of a weight percent ^{235}U value; it is important that this value be determined by the most accurate and precise means available since errors in this assay will directly affect the $^{232}\text{U}/^{235}\text{U}$ weight ratio.

It should be noted that the reported precision studies apply only to instrumental error on standard solutions. There was insufficient sample available at the time this work was performed to enable multiple weighings; hence, the results do not reflect analytical preparational errors which would normally be included. Past experience has shown that the bulk of the error in alpha analysis is due to counting and planchet preparation. The stated precisions may therefore be applied in most practical cases to the determination of ^{232}U .

Although it is not mandatory to the analysis, it would be desirable to enhance the resolution of the uranium spectrum as well as to optimize the various other parameters of the assay. Future work will be directed toward these ends. Also, it is anticipated that a calibrated ^{232}U standard will be obtained in the near future from another laboratory as an additional reference.

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TABLE I

PRECISION DATA FOR THE NFS REFERENCE SAMPLE
WITH A 4-HOUR COUNTING TIME

<u>Planchet No.</u>	<u>$^{232}\text{U}/^{235}\text{U}$ (in ppb)</u>
1	340
2	330
3	390
4	411
5	401
6	379
7	385
8	336
9	335
10	389
Average	370 ± 22
LE_x^*	$\pm 70 (\pm 18.9\%)$

*Limit of error at the 95% confidence level for an individual analysis.

TABLE II

PRECISION DATA OF THE LOW DETECTION LEVEL
WITH A 4-HOUR COUNTING TIME

<u>Planchet No.</u>	<u>$^{232}\text{U}/^{235}\text{U}$ (in ppb)</u>
1	13.1
2	11.1
3	9.7
4	11.9
5	10.2
6	11.2
7	9.4
8	8.7
9	9.5
10	10.6
Average	10.5 ± 0.9
LE_x^*	$\pm 3.0 (\pm 28.2\%)$

*Limit of error at the 95% confidence level for an individual analysis.

TABLE III

PRECISION DATA AT THE LOW DETECTION LEVEL
WITH A 16-HOUR COUNTING TIME

<u>Planchet No.</u>	<u>$^{232}\text{U}/^{235}\text{U}$ (in ppb)</u>
1	9.9
2	7.2
3	9.6
4	7.9
5	7.8
6	8.5
7	8.0
8	6.5
9	9.0
10	9.2
Average	8.4 ± 0.8
LE_x^*	± 2.4 ($\pm 29.2\%$)

*Limit of error at the 95% confidence level for an individual analysis.

Figure 1. Schematic Diagram of the Frisch Grid Ionization Chamber Preamplifier.

Figure 2. Typical Alpha Spectra of Recycled Uranium Counted for 4 Hours. The Relative Size of the ^{232}U Peak Corresponds to a Concentration of Approximately 370 ppb on a ^{235}U Basis.

Figure 3. Typical Alpha Spectrum of Uranium Counted for 4 Hours. The Relative Size of the ^{232}U Peak Corresponds to a Concentration of Approximately 10 ppb on a ^{235}U Basis.