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UNION CARBIDE

# GAMMA-RAY SPECTROMETRIC DETERMINATION OF $UF_6$ ASSAY WITH 1 PERCENT PRECISION FOR INTERNATIONAL SAFEGUARDS

## PART 1: PRODUCT AND FEED IN 1S AND 2S SAMPLE CYLINDERS

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## DISCLAIMER

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## ABSTRACT

A rapid gamma-ray spectrometric (non-destructive) method is described which can determine $^{235}U$ enrichment with a relative precision of 1 percent (or less) in $UF_6$ contained in 1S and 2S bottles. The method is based on counting the 186 keV gamma rays emitted by $^{235}U$ using a Pb-collimated Ge(Li) detector. The gamma-ray count rate, corrected for cylinder wall (nickel) attenuation, is converted to $^{235}U$ assay by comparison with standards.

Measurements of fifty $UF_6$ product and feed cylinders reveal the following precisions (i.e., percent relative standard deviations) which correspond to the counting times given in parenthesis: Product - 2S, 0.98 percent (600 sec); Feed - 2S, 0.48 percent (2500 sec); Product - 1S, 0.62 percent (1000 sec); Feed - 1S, 0.73 percent (3000 sec).

A 1 percent precision is desired for "variables - attributes" verification measurements of $^{235}U$ assay in $UF_6$ sample cylinders for safeguards inspections by the International Atomic Energy Agency (IAEA). Statistically, these measurements stand between fine, high-precision (or "variables") measurements and gross, low-precision (or "attributes") ones. The former are costly and time consuming but do not require analysis of all samples; the latter are inexpensive and simple but must be applied to all samples. Variables-attributes (or fine-attributes) measurements have precisions between variables and attributes measurements and retain the simplicity of attributes measurements. Because of their intermediate precisions, the variables-attributes measurements may not require analysis of all samples, and this could result in significant savings of IAEA inspector time.

Although the precision of the above results is satisfactory, the average relative differences between gamma-ray and mass-spectrometric determinations for the last two sets of measurements (1S cylinders) have positive biases. Research and development work is underway to understand and correct these biases. Also, a series of measurements of $UF_6$ tails in 1S and 2S bottles are currently being performed and evaluated.







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# I. INTRODUCTION

The International Enrichment Safeguards Program at Union Carbide Corporation - Nuclear Division (UCC-ND) is charged by the Office of Safeguards and Security of the Department of Energy (DOE/OSS) with the evaluation of potential safeguards strategies that may be applied at the Portsmouth Gas Centrifuge Enrichment Plant (GCEP). This report describes a potentially useful technique which could be applied as part of GCEP's international nuclear material accountability system if IAEA safeguards are to be applied.

## Material Accountancy Verification by the IAEA

According to INFCIRC/153,[1] the IAEA will draw a safeguards technical conclusion from verification measures it will perform for each material balance area (MBA) at the safeguarded facility. The purpose and operation of these verification measures are discussed in a comprehensive report currently being prepared by the Technical Support Organization at Brookhaven National Laboratory.[2] The facility operator would report his material-balance measurements and his MUF (Material Unaccounted For) to the IAEA, which would then verify them to detect, and thereby deter, the abrupt or protracted diversion of declared nuclear materials. For the Cascade MBA, this would include the detection of undeclared $UF_6$ through the Feed and Withdrawal facilities. To accomplish this, the IAEA will need to verify, among other quantities, the assay in $UF_6$ product, feed and tails samples. The Operator has two general strategies that he could use to divert material undetected from the material balance. He could report an unfalsified material balance (accurately reporting his own measurements) and divert an amount that would result in a reported MUF which was within the range of the uncertainty in his material balance. He would imply (or state) that this MUF arose from measurement uncertainties. This strategy is called "diversion into MUF." Alternatively, he could falsify his reported measurements so as to reduce his reported MUF.

It is convenient to define two levels of falsification: a defect and a bias. A "defected item" is an item whose reported $^{235}U$ content differs from its actual value by an amount which is significantly greater than the combined uncertainties of the operator's measurement and the inspector's most accurate measurement for that item. This means that a falsification would be very clearly indicated if the inspector decided to measure accurately a defected item. A "bias" is a falsification by an amount smaller than a defect.

To detect a bias the IAEA must use high-precision (or "variables") measurements, while gross, low-precision (or "attributes") measurements could suffice to detect a defect. An example of the former is mass spectrometry; one of the latter is non-destructive analysis (NDA), such as gamma-ray counting.

Variables measurements are costly and time consuming but do not require analysis of all samples; attributes measurements are simple but must be applied to all samples. In turn attributes measurements usually take two forms: (1) a gross attributes measurement which can be done quickly but has poor sensitivity, performed on a large fraction (possibly all) of the samples in order to detect large defects; (2) a fine attributes measurement (sometimes called a "variables-attributes" measurement), performed on a smaller fraction of the samples with better accuracy, in order to detect small defects.

## Verification of the $^{235}U$ Weight Percent

The verification of the $^{235}U$ assay by the IAEA would be accomplished using a combination of attributes and variables measurements. In this context, DOE/OSS contractors are developing NDA instrumentation for two alternative approaches to the attributes verification of the $^{235}U$ weight percent in $UF_6$. In one approach, the $^{235}U$ concentrations of the product and feed $UF_6$ streams would be measured via in-line enrichment monitors. In the second approach, the $^{235}U$ concentrations of feed, product and tails in 1S or 2S $UF_6$ sample cylinders[3] would be measured using gamma-ray spectrometry.* The in-line monitors would provide attributes verification measurements every 10-20 minutes, continuously and automatically. Thus, all the $UF_6$ which flows through them would be assayed with a low demand of IAEA inspector time. The gamma spectrometric measurements of 1S and 2S cylinders are expected to provide variables-attributes assay verification measurements of a fraction of the samples. This could result in significant savings of IAEA inspector time, in comparison with gross attributes gamma-spectrometry assay measurements of all the sample bottles.

## Technical Aspects

Model 2S sample cylinders[3] are most frequently used in U.S. enrichment plants, while Model 1S bottles are occasionally employed. It is understood, however, that sample bottles similar to the latter in shape and size are used extensively in Europe. The 1S cylinders are 1-1/2 in. (3.8 cm) in diameter and 11 in. (27.9 cm) long, containing up to 1 lb (0.454 kg) of $UF_6$, while the 2S bottles contain up to 4.9 lb (2.22 kg) of $UF_6$ and are 3-1/2 in. (8.9 cm) in diameter and 11-1/2 in. (29.2 cm) long.

Gamma-spectrometry assay measurements of large $UF_6$ cylinders are commonly performed using Ge(Li) detectors for domestic accountability verification purposes. Typically, precisions of 3 to 8 percent are obtained

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*Before using gamma-ray spectrometry for these measurements, attempts were made to measure assay by neutron counting using a random driver. However, long-term variations in count rate were experienced and the required 1 percent precision could not be attained.

in those measurements.[4] An accuracy and a relative precision of 1 percent or less (at the 68 percent confidence level) are considered necessary for variables-attributes assay verification measurements of 1S and 2S sample cylinders. UCC-ND is developing a gamma-ray spectrometry method that can achieve the prescribed accuracy and precision for those measurements.

Mathematically, the precision is measured by the relative standard deviation percent $\sigma$, which is given by the equations:

$$\sigma = \sqrt{\frac{\sum_i (D_i - \overline{D})^2}{n-1}}; \qquad \overline{D} = \frac{1}{n} \sum_i D_i; \qquad D_i = 100\ (I_{M,i} - I_{T,i})/I_{T,i}; \qquad (1)$$

where: $I_{T,i}$ is the mass spectrometric assay for sample i,

$I_{M,i}$ the gamma spectrometric assay for sample i,

$D_i$, the percent relative difference for that sample, and

$\overline{D}$, the mean relative difference percent (a measure of the accuracy).

Because mass spectrometry is one or two orders of magnitude more accurate than gamma-ray assay determinations, the mass spectrographic results were considered exact when evaluating the accuracy of the gamma-ray measurements.

This is the first of a two-part report. This part refers to assay measurements of $UF_6$ product and feed. The second part will treat measurements of tails and will report completion of the method's development. The experimental work described here was performed and published earlier by Eugene E. Clark of the ORGDP Technical Services Division.[5] This report places the method developed by Mr. Clark in the context of international enrichment plant safeguards. It draws heavily upon Reference 5 which frequently is repeated verbatim.

## II. EXPERIMENTAL

The assay determination is based on measurement of the characteristic 186 keV gamma rays of $^{235}U$ from an "infinitely thick" layer of $UF_6$. Thus, the gamma-ray count rate is proportional to the $^{235}U$ enrichment in this compound.[6] The development work proceeded along several steps. First, a cylinder-positioning/collimator system was designed and tested for reliability, and the thickness gauge was calibrated. Then the $UF_6$ assay measurements were calibrated against "standard" 1S and 2S cylinders in terms of $^{235}U$ assay versus count rate. The calibration of 2S cylinders was verified by determining assay in five additional "standard" cylinders. Finally, thirty 2S and twenty 1S sample cylinders containing $UF_6$ feed and product were measured to test the gamma-ray spectrometric method.

### Apparatus

A Ge(Li) detector coupled to a Nuclear Data 440 multichannel analyzer was used to obtain the gamma-ray counting data. The detector was an EG&G ORTEC Model 8101 coaxial Ge(Li) crystal.* It had an active volume of 59 cc and a relative efficiency of 9.8 percent (compared to a 7.6 cm x 7.6 cm NaI(Tℓ) detector) when measuring the 1.33 MeV peak of $^{60}Co$ at a distance of 25 cm. The resolution was 2.20 keV (full width at half maximum) at 1.33 MeV using a 3-μsec time instant. The resolution at 186 keV was 1.84 keV. The system gain was set at 0.77 keV/channel, and the 186 keV net count rates were evaluated by subtracting an average of the higher- and lower-energy backgrounds from the gross 186 keV count-rate.

The cylinder-positioning apparatus used in the measurements is sketched in Figure 1. This basic configuration was used to count both 1S or 2S sample cylinders, although different collimators were used. For the 1S cylinders (3.8 cm diameter) a collimator with a 1.6 cm bore diameter and a 1.9 cm length was used. The distance between the cylinder and detector was 3.1 cm. For the 2S cylinders (8.9 cm diameter), a collimator with a 2.5 cm bore diameter and a 5.0 cm length was used initially. The cylinder-to-detector distance was 6.3 cm. Ultimately, a 1.9 cm long collimator was used. The collimators were fabricated by boring and cutting standard-sized lead bricks.

Cylinder-wall thickness measurements (see next Section) were made using a Panametrics Inc. Model 5222 digital ultrasonic thickness gauge. Glycerine was used to couple the transducer to the cylinder wall. The manufacturer claims that the gauge is accurate to ±0.1 percent between 0.05 and 25 cm.

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*References to specific equipment or its selection for these experiments does not imply approval or recommendation by UCC-ND and DOE.

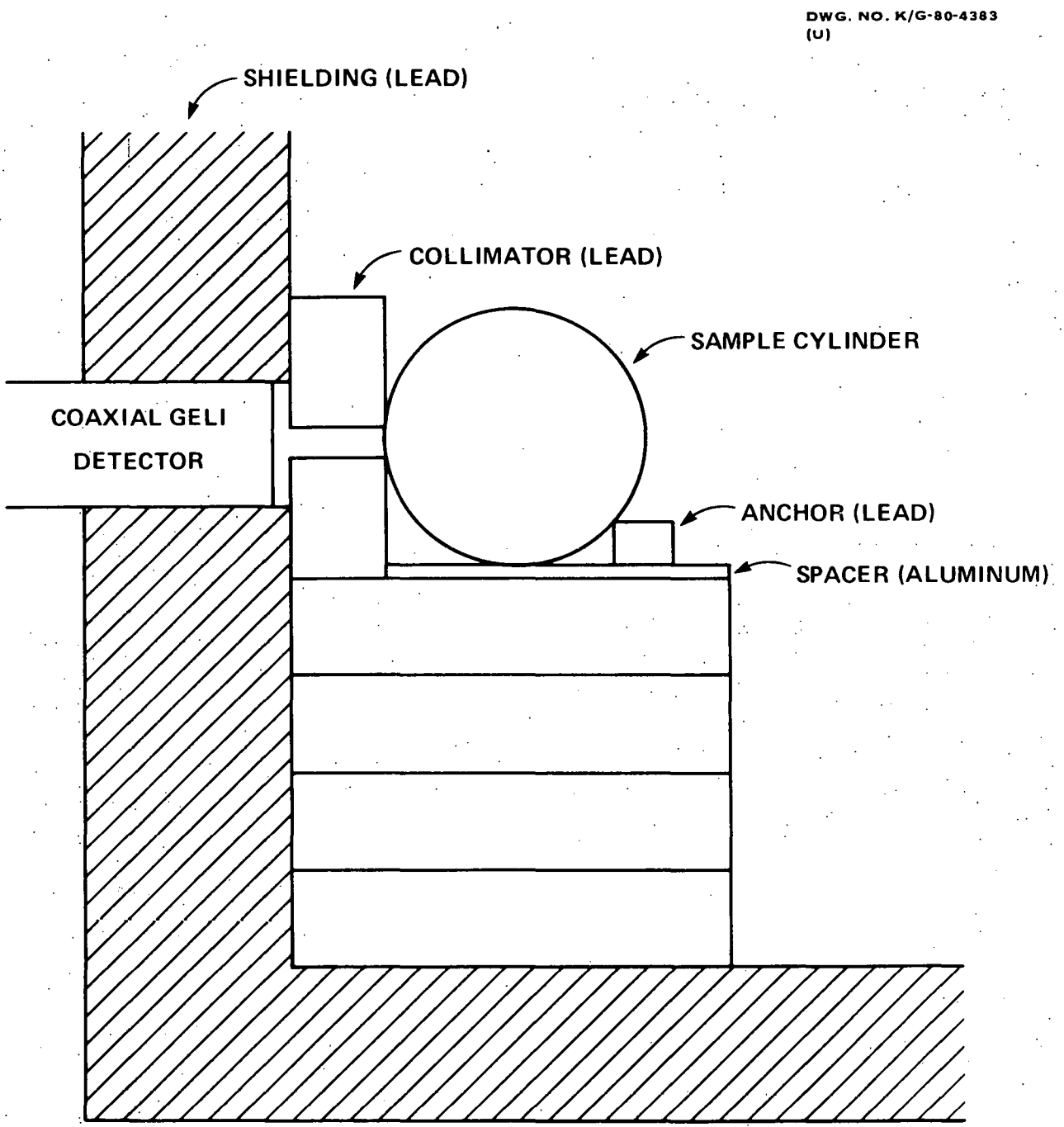


Figure 1
SAMPLE-CYLINDER POSITIONING APPARATUS

Cylinder Positioning and Wall Gamma-ray Attenuation

A 2S sample cylinder containing 1640 g of $UF_6$ (maximum net fill weight is 2220 g)(3) at a $^{235}U$ isotopic abundance of 3.007 weight percent was aligned in the positioning apparatus as shown in Figure 1. The gamma-ray radiation emitted from the cylinder was counted ten times for 3000 sec, with the cylinder repositioned between countings so that the same spot on the wall was exposed to the detector each time. The relative standard deviation (RSD) for the ten countings was 0.4 percent,* approximately equal to the theoretical counting precision. This test demonstrated that the cylinder-positioning technique is adequate for 2S cylinders. The attenuation of a monoenergetic gamma-ray beam as it passes through a material is given by the equation:

$$I = I_0 \exp(-\mu_m \rho t) \qquad (2)$$

where $I_0$ (in $sec^{-1}$) is the initial gamma-ray intensity, and I (in $sec^{-1}$) is the intensity after attenuation by an absorber of thickness t (in cm), density $\rho$ (in $g/cm^3$) and mass absorption coefficient $\mu_m$ (in $cm_2/g$, for the gamma-ray energy involved.) The relatively weak 186 keV gamma rays of $^{235}U$ are strongly attenuated as they pass through the nickel walls of the sample cylinder. Therefore, the thickness of the wall is measured with an ultrasonic thickness gauge (see Apparatus) and a gamma-ray absorption correction is applied. A 0.1 percent error in the wall-thickness measurement causes a 0.3 percent error in the corrected gamma-ray count rate. The mass absorption coefficient of nickel for the 186 keV gamma-ray energy is 0.162 $cm^2/g$, from least-squares interpolation[7] of data experimentally determined by the narrow-beam collimation method.[8] The ultrasonic thickness gauge was calibrated against a cylinder wall-thickness standard made by cutting a new 2S cylinder in half. The "standard" thickness (0.325 cm) was determined by measuring one spot of the cut cylinder wall several times with a micrometer.

Gamma-ray spectrometry measurements were also made of $UF_6$ samples contained in 1S cylinders. Wall-thickness measurements, made at two diametrically opposed positions on each of ten 1S cylinders, indicated differences as large as 0.028 cm at an average wall thickness of 0.185 cm. As mentioned above (Apparatus) the collimator was modified to accommodate the 1S cylinder. A cylinder containing 450 g of $UF_6$ with a $^{235}U$ isotopic abundance of 3.003 weight percent was counted ten times, for 600 sec each time, at a location 90° relative to the valve connection and 10 cm from the bottom of the cylinder. The sample cylinder was moved and returned to approximately the same position between countings as done for the 2S cylinders. The RSD for the ten countings was 0.5 percent, thus proving that the cylinder-positioning technique is also adequate for 1S cylinders.

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*This is the commonly used standard deviation (defined as the square root of the variance) which measures the deviation of a single counting. It is characterized here by RSD to avoid confusion with the value $\sigma$ of Equation 1.

## Calibration

The assay measurements of the 2S cylinders were calibrated using six 2S cylinders of $UF_6$ of increasing assays: 0.1976, 0.4990, 0.7108, 1.4982, 2.7310, and 3.1827 weight percent $^{235}U$ as determined by mass spectrometry. The cylinders were filled with approximately 2000 g to ensure that the thickness of $UF_6$ was at least 1 cm at the walls where the gamma-ray measurements were made.[6] For calibration purposes, each cylinder was counted for 25,000 to 50,000 sec at each of two diametrically opposed positions 5 cm from the bottom. There were no significant differences between the count rates at the two positions, so the two count rates were averaged for each calibration point. The experimental values were fitted using a linear least-squares method, which resulted in the equations:

$$Y = 14.29X + 0.6680, \quad \text{or} \quad X = 0.06999Y - 0.04676; \qquad (3)$$

where

Y is the 186 keV gamma-ray count rate ($sec^{-1}$), corrected for attenuation by the cylinder wall, and

X is the $^{235}U$ isotopic abundance (weight percent).

Using this calibration equation, the $^{235}U$ isotopic abundances of five additional cylinders were determined from eight 3000-sec counts on each cylinder. All readings were approximately 5 cm from the bottom of the cylinder, but 45° apart. This circumferential spacing of the counting positions thus included the effect of any significant variation in the compactness of the $UF_6$. Each total count was corrected for cylinder-wall attenuation, which amounted to a reduction of roughly 40 percent. Wall thickness variations of up to 0.025 cm were observed with the average thickness equal to 0.325 cm. The five routine cylinder samples were randomly selected and contained 1488 to 1971 g of $UF_6$. The average $^{235}U$ isotopic abundance results, with their respective 1σ limits, are compared with the mass spectral results in Table I. The average RSD for a single 3000-sec count is 0.5 percent at 3 percent $^{235}U$, and the bias is -0.4 percent relative to mass spectral results.

Although counting times longer than 3000 sec were used for 2S cylinders in positioning and calibration measurements, the counting time necessary to achieve the 1 percent precision α in routine measurements at 3 percent $^{235}U$ was determined to be 1500 sec. This time was reduced further by fabricating a shorter collimator which allowed the 2S cylinder to be positioned closer to the detector. The thickness of a lead brick was reduced from 5.0 to 1.9 cm, and a 2.5-cm-diameter hole was drilled through the center of the brick. With the shorter collimator the cylinder-to-detector distance was decreased from 6.2 to 3.1 cm, and the counting time was reduced from 1500 to 600 sec at 3 percent $^{235}U$.

Table I

URANIUM-235 ISOTOPIC ABUNDANCE OF
URANIUM HEXAFLUORIDE IN 2S CYLINDERS

| ORGDP Sample No. | Uranium-235 Isotopic Abundance, wt % | | Percent Relative Difference, $D_i$ (GS-MS) |
|---|---|---|---|
| | Mass Spectrometry (MS) | Gamma Spectrometry (GS) | |
| 968582 | 2.996 ± 0.0008* | 2.993 ± 0.004** | -0.1 |
| 968583 | 3.003 " | 2.998 ± 0.004 | -0.2 |
| 012712 | 3.112 " | 3.093 ± 0.006 | -0.6 |
| 012713 | 3.298 " | 3.265 ± 0.010 | -1.0 |
| 012714 | 3.104 " | 3.109 ± 0.003 | 0.2 |
| Average | 3.103 ± 0.0008 | 3.092 ± 0.005 | -0.4 ($\overline{D}$) |

*Average of four determinations.

**Average of eight 3000-sec countings at positions spaced equally about the circumference of the cylinder.

The system was recalibrated for 2S cylinders with the shorter collimator. The linear least-squares fitting of the calibration points resulted in the equations:

$$Y = 39.52X + 0.2200, \quad \text{or} \quad X = 0.02530Y - 0.005566,$$

where Y and X represent count rate and assay, respectively, as in Equation 3.

The sensitivity of the method, defined as the slope of the equation for Y (in terms of count rate per weight percent $^{235}U$), was thus increased by a factor of 2.8.

The gamma spectrometric method was calibrated for 1S cylinders by counting $UF_6$ with $^{235}U$ isotopic abundances of 3.003, 1.135, and 0.711 weight percent as determined by mass spectrometry. For calibration purposes, each cylinder was counted 2400 to 12,000 sec, depending on the weight percent $^{235}U$, at each of two diametrically opposed positions 10 cm from the cylinder bottom. The linear least-squares fit for the calibration points yielded the equations:

$$Y = 13.21X + 0.1110, \quad \text{or} \quad X = 0.07569Y - 0.008402,$$

where Y and X represent count rate and assay, respectively, as in Equation 3.

## III. RESULTS AND DISCUSSION

Thirty 2S and twenty 1S sample cylinders containing $UF_6$ feed and product were measured to test the gamma-ray spectrometric technique. To assure reliable analyses, two precautions were taken in the selection of cylinders. First, outer cylinder surfaces were observed to be reasonably free of dents which could cause erroneous wall thickness measurements and cylinder-to-detector distance variations. Second, "infinite" thickness of the $UF_6$ inside the cylinder at the point of measurement was ascertained. Sample cylinders were filled to near-maximum capacity and allowed to cool in an upright position to reduce the likelihood of a thin deposit or void at the point of measurement. Gain stability in the Ge(Li)-multichannel analyzer system was checked daily, and the ultrasonic thickness gauge was compared with a calibration standard before each use.

Twenty-two $UF_6$ product samples (approximately 3 percent $^{235}U$ assay) and eight $UF_6$ feed samples (0.711 percent assay), all in 2S cylinders, were analyzed using the 1.9-cm-long collimator. The sample cylinders were counted at each of two positions, 90° and 270° relative to the valve connection and approximately 5 cm from the bottom of the cylinder. The counting time for product samples was 600 sec, and for feed samples it was 2500 sec. Tables II and III list the results of these measurements and corresponding mass spectrometry results. The mean relative difference percent $\overline{D}$ and the relative standard deviation percent $\sigma$ at the bottom of columns 4, 6, and 8 in Tables II and III, are given by Equation 1.

Ten 1S cylinders containing $UF_6$ product (approximately 3 percent $^{235}U$) and ten 1S cylinders with $UF_6$ feed (0.711 percent $^{235}U$) were counted for 1000 and 3000 sec, respectively, at 90° and 270° relative to the valve connection and 10 cm from the bottom of the cylinder. Results are presented in Tables IV and V in the same format used for the 2S cylinders.

The results reported in Tables II through V show that the gamma-ray measurements easily can achieve the required precision $\sigma$ of 1 percent. To assess the method's accuracy, the mean $\overline{D}$ must be examined for a possible bias. It must be stressed, however, that $\sigma$ is not a measure of the mean's uncertainty. To establish whether a series of determinations is affected by a systematic error, the limit of error d for the mean must be determined by:[9]

$$d = t\sigma/n^{1/2} \qquad (4)$$

where t is a statistical quantity which can be found in "t-test" tables.[9,10] The d values calculated at the 95 percent confidence level for the four series of measurements of Tables II through V are listed with the corresponding $\overline{D}$ and $\sigma$ values in Table VI.

Table II

ASSAY OF $UF_6$ PRODUCT BY Ge(Li) GAMMA-RAY SPECTROMETRY
OF 2S CYLINDERS VERSUS MASS SPECTROMETRY ANALYSIS

| ORGDP Sample No. | $^{235}U$, wt % MS | $^{235}U$, wt % GS (90°)* | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % GS (270°) | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % Average GS (90°, 270°) | Percent Relative Difference, $D_i$ (GS-MS) |
|---|---|---|---|---|---|---|---|
| 014003 | 3.269 | 3.275 | 0.18 | 3.239 | -0.92 | 3.257 | -0.37 |
| 968569 | 3.202 | 3.168 | -1.06 | 3.210 | 0.25 | 3.189 | -0.41 |
| 968570 | 3.200 | 3.183 | -0.53 | 3.200 | 0.00 | 3.192 | -0.25 |
| 013383 | 2.722 | 2.647 | -2.75 | 2.714 | -0.29 | 2.681 | -1.51 |
| 013388 | 3.285 | 3.267 | -0.55 | 3.264 | -0.64 | 3.266 | -0.58 |
| 013391 | 3.287 | 3.310 | 0.70 | 3.281 | -0.18 | 3.296 | 0.27 |
| 013392 | 3.295 | 3.295 | 0.00 | 3.255 | -1.21 | 3.275 | -0.61 |
| 014006 | 3.285 | 3.346 | 1.86 | 3.283 | -0.06 | 3.315 | 0.91 |
| 008898 | 3.084 | 3.090 | 0.19 | 3.029 | -1.78 | 3.060 | -0.78 |
| 014011 | 2.778 | 2.801 | 0.83 | 2.798 | 0.72 | 2.800 | 0.79 |
| 014020 | 2.425 | 2.436 | 0.45 | 2.437 | 0.49 | 2.437 | 0.49 |
| 008913 | 3.047 | 2.951 | -3.15 | 2.963 | -2.76 | 2.957 | -2.95 |
| 014012 | 2.607 | 2.520 | -3.34 | 2.575 | -1.23 | 2.548 | -2.26 |
| 014013 | 2.619 | 2.600 | -0.72 | 2.614 | -0.19 | 2.607 | -0.46 |
| 014019 | 2.390 | 2.395 | 0.21 | 2.387 | -0.13 | 2.391 | 0.04 |
| 968574 | 3.280 | 3.288 | 0.24 | 3.273 | -0.21 | 3.281 | 0.03 |
| 014023 | 2.417 | 2.441 | 0.99 | 2.410 | -0.29 | 2.426 | 0.37 |
| 014024 | 3.300 | 3.253 | -1.42 | 3.282 | -0.54 | 3.268 | -0.97 |
| 014015 | 3.268 | 3.278 | 0.31 | 3.263 | -0.15 | 3.271 | 0.09 |
| 014016 | 3.281 | 3.285 | 0.12 | 3.293 | 0.37 | 3.289 | 0.24 |
| 014018 | 2.398 | 2.403 | 0.21 | 2.408 | 0.42 | 2.406 | 0.33 |
| 014008 | 2.602 | 2.613 | 0.42 | 2.644 | 1.61 | 2.629 | 1.04 |
| $\bar{D}$ | | | -0.31 | | -0.31 | | -0.31 |
| $\sigma$ | | | ±1.33 | | ±0.91 | | ±0.98 |

*Degrees indicate angle of counting location on cylinder relative to valve connection.

Table III

ASSAY OF $UF_6$ FEED BY Ge(Li) GAMMA-RAY SPECTROMETRY OF 2S CYLINDERS VERSUS MASS SPECTROMETRY ANALYSIS

| ORGDP Sample No. | $^{235}U$, wt % MS | $^{235}U$, wt % GS (90°)* | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % GS (270°) | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % Average GS (90°, 270°) | Percent Relative Difference, $D_i$ (GS-MS) |
|---|---|---|---|---|---|---|---|
| 178353 | 0.711 | 0.716 | 0.70 | 0.695 | -2.25 | 0.706 | -0.70 |
| 178351 | 0.711 | 0.715 | 0.56 | 0.715 | 0.56 | 0.715 | 0.56 |
| 178355 | 0.711 | 0.702 | -1.27 | 0.716 | 0.70 | 0.709 | -0.28 |
| 178371 | 0.711 | 0.722 | 1.55 | 0.705 | -0.84 | 0.714 | 0.42 |
| 178372 | 0.711 | 0.710 | -0.14 | 0.702 | -1.27 | 0.706 | -0.70 |
| 178366 | 0.711 | 0.718 | 0.98 | 0.701 | -1.41 | 0.710 | -0.14 |
| 178363 | 0.711 | 0.711 | 0.00 | 0.708 | -0.42 | 0.710 | -0.14 |
| 178379 | 0.711 | 0.711 | 0.00 | 0.715 | 0.56 | 0.713 | 0.28 |
| $\bar{D}$ | | | 0.30 | | -0.55 | | -0.09 |
| $\sigma$ | | | ±0.85 | | ±1.09 | | ±0.48 |

*Degrees indicate angle of counting location on cylinder relative to valve connection.

Table IV

ASSAY OF $UF_6$ PRODUCT BY Ge(Li) GAMMA-RAY SPECTROMETRY OF 1S CYLINDERS VERSUS MASS SPECTROMETRY ANALYSIS

| ORGDP Sample No. | $^{235}U$, wt % MS | $^{235}U$, wt % GS (90°)* | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % GS (270°) | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % Average GS (90°, 270°) | Percent Relative Difference, $D_i$ (GS-MS) |
|---|---|---|---|---|---|---|---|
| 966014 | 3.115 | 3.106 | -0.29 | 3.123 | 0.26 | 3.115 | 0.00 |
| 966016 | 3.398 | 3.413 | 0.44 | 3.405 | 0.21 | 3.409 | 0.32 |
| 966017 | 2.786 | 2.834 | 1.72 | 2.807 | 0.75 | 2.821 | 1.26 |
| 966019 | 2.485 | 2.484 | -0.04 | 2.515 | 1.21 | 2.500 | 0.60 |
| 966020 | 2.484 | 2.495 | 0.44 | 2.498 | 0.56 | 2.497 | 0.52 |
| 014016 | 3.281 | 3.342 | 1.86 | 3.266 | -0.46 | 3.304 | 0.70 |
| 014017 | 3.278 | 3.231 | -1.43 | 3.257 | -0.64 | 3.244 | -1.04 |
| 014039 | 2.514 | 2.488 | -1.03 | 2.559 | 1.79 | 2.524 | 0.40 |
| 014042 | 3.293 | 3.331 | 1.15 | 3.283 | -0.30 | 3.307 | 0.42 |
| 968574 | 3.280 | 3.307 | 0.82 | 3.314 | 1.04 | 3.311 | 0.94 |
| $\bar{D}$ | | | 0.36 | | 0.44 | | 0.41 |
| $\sigma$ | | | ±1.09 | | ±0.78 | | ±0.62 |

*Degrees indicate angle of counting location on cylinder relative to valve connection.

Table V

ASSAY OF $UF_6$ FEED BY Ge(Li) GAMMA-RAY SPECTROMETRY OF 1S CYLINDERS VERSUS MASS SPECTROMETRY ANALYSIS

| ORDGP (TSD) Sample No. | $^{235}U$, wt % MS | $^{235}U$, wt % GS (90°)* | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % GS (270°) | Percent Relative Difference, $D_i$ (GS-MS) | $^{235}U$, wt % Average GS (90°, 270°) | Percent Relative Difference, $D_i$ (GS-MS) |
|---|---|---|---|---|---|---|---|
| 1 | 0.711 | 0.725 | 1.97 | 0.735 | 3.38 | 0.730 | 2.67 |
| 2 | 0.711 | 0.727 | 2.25 | 0.729 | 2.53 | 0.728 | 2.39 |
| 3 | 0.711 | 0.728 | 2.39 | 0.719 | 1.12 | 0.724 | 1.83 |
| 4 | 0.711 | 0.714 | 0.42 | 0.722 | 1.55 | 0.718 | 0.98 |
| 5 | 0.711 | 0.719 | 1.12 | 0.723 | 1.69 | 0.721 | 1.41 |
| 6 | 0.711 | 0.713 | 0.28 | 0.718 | 0.98 | 0.716 | 0.70 |
| 7 | 0.711 | 0.726 | 2.11 | 0.726 | 2.11 | 0.726 | 2.11 |
| 8 | 0.711 | 0.712 | 0.14 | 0.716 | 0.70 | 0.714 | 0.42 |
| 9 | 0.711 | 0.719 | 1.12 | 0.720 | 1.27 | 0.720 | 1.27 |
| 10 | 0.711 | 0.715 | 0.56 | 0.725 | 1.97 | 0.720 | 1.27 |
| $\overline{D}$ | | | 1.24 | | 1.73 | | 1.50 |
| $\sigma$ | | | ±0.88 | | ±0.80 | | ±0.73 |

*Degrees indicate angle of counting location on cylinder relative to valve connection.

Table VI

SUMMARY OF STATISTICAL PARAMETERS FOR THE SERIES OF MEASUREMENTS OF TABLES II THROUGH V

| Measurement Series | Average Relative Difference Percent (GS-MS) | | |
|---|---|---|---|
| | Mean, $\overline{D}$ | Error Limit of Mean, d | Relative Standard Deviation %, $\sigma$ |
| Product - 2S Cylinders | -0.31 | ±0.43 | ±0.98 |
| Feed - 2S Cylinders | -0.09 | ±0.40 | ±0.48 |
| Product - 1S Cylinders | 0.41 | ±0.44 | ±0.62 |
| Feed - 1S Cylinders | 1.52 | ±0.52 | ±0.73 |

If the gamma-ray measurements had no systematic error, the mean $\overline{D}$ (i.e., the mean relative difference percent between their results and those from mass spectrometry) should be zero within its error limit d; or $|\overline{D}| \leq |d|$. This condition is satisfied by the data for 2S cylinder measurements in Table VI, but not by the Feed - 1S results. Although the precision $\sigma$ of the Feed - 1S results (± 0.73 percent) is better than the 1 percent target precision, the mean relative difference $\overline{D}$, between gamma-ray-spectrometry and mass-spectrometry results is 1.52 ± 0.52 percent. Thus, the error span of this difference lies in the realm of positive numbers (1.00 to 2.04 percent) and suggests a positive systematic error. This could also be the case for the Product - 1S data, where $|D| \sim |d|$. As the origin of this bias is not known, and its constancy cannot be ascertained, additional work is needed to identify the cause of this bias and eliminate it.

# IV. CONCLUSIONS AND RECOMMENDATIONS

A gamma-ray radiometric method to measure the $^{235}U$ assay in $UF_6$ contained in 1S and 2S cylinders is in the advanced stages of development. The target precision of 1 percent required for safeguards attribute verification measurements[2] has been attained. However, a positive bias has been found in the measurements of 1S cylinders. As the origin of this bias has not been found yet, its constancy cannot be ascertained. This systematic error, as well as assay measurements of $UF_6$ tails (0.2 to 0.3 percent $^{235}U$), is being investigated.

## Experimental Procedure

From the development work described in Section II (Experimental) a preliminary procedure for 1S and 2S sample cylinders has been developed. It consists of the following steps.

1. Select a cylinder filled to near-maximum capacity and allow it to cool in an upright position to ensure that an "infinitely thick" layer[6] of $UF_6$ is assured.

2. Position the cylinder in the apparatus of Figure 1 such that the wall facing the collimator is free of dents.

3. Measure the net count rate of the 186 keV photopeak of $^{235}U$.

   a. For 1S cylinders we recommend a collimator 1.9 cm long and 1.6 cm in diameter, facing the cylinder at 10 cm from its bottom; the product $UF_6$ (3 percent $^{235}U$) is counted for 1000 sec, and the feed (0.711 percent $^{235}U$) is counted for 3000 sec.

   b. For 2S cylinders we recommend a collimator 1.9 cm long and 2.5 cm in diameter, facing the cylinder at 5 cm from its bottom; the product $UF_6$ is counted for 600 sec, and the feed is counted for 2500 sec.

4. Perform the measurements of step 3 for diametrically opposite positions of the cylinder.

5. Determine the cylinder wall thickness at the two positions of steps 3 and 4 by means of a thickness gauge accurate to ± 0.1 percent. Calculate the corresponding attenuation of the 186 keV gamma-rays of $^{235}U$ by using Equation 2 ($\mu_m$ = 0.162 $cm^2/g$ for nickel).

6. Correct for attenuation and average the results of steps 3 and 4. Using a calibration equation (determined as in Section II), calculate the $^{235}U$ assay.

This procedure is termed "preliminary" because current research and development may suggest small modifications or additions, once tails assay is included, and the cause for the positive bias in 1S cylinder measurements is established.

Current work is directed toward finding the cause of the systematic error that affects the determination of assay in 1S cylinders and to eliminating this bias. Concurrently, the method is being extended to measure $UF_6$ tails (0.2 to 0.3 percent $^{235}U$) contained in 1S and 2S cylinders. Part II of this report will cover the systematic error and the tails studies.

The last phase of the experimental program is the design and manufacture of a prototype apparatus which can reliably measure assay in 1S and 2S $UF_6$ cylinders to at least 1 percent precision and accuracy. In accordance with Section III (Results and Discussion) these specifications mean $\sigma \leq 1$ percent with no systematic errors.

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