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TITLE A STATE-OF-THE-ART PASSIVE GAMMA-RAY ASSAY SYSTEM

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A STATE-OF-THE-ART PASSIVE GAMMA-RAY ASSAY SYSTEM FOR ^{235}U IN SOLUTION

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Abstract

We report details of the development of a high-accuracy, high-precision system for the non-destructive assay of ^{235}U in solution. The system can measure samples with concentrations ranging from 0.0001-500 g ^{235}U/ℓ using 200-mℓ samples at low concentrations, 30-mℓ samples at high concentrations, and 1000-s measurement times. The accuracy and precision goals of 0.1% were essentially attained for concentrations above 100 g/ℓ. This on-line system, designed for a production plant environment, represents a significant improvement in the state of the art.

1. Introduction

In 1982, the Los Alamos National Laboratory Safeguards Assay Group was asked to develop a new assay system for ^{235}U in solution form; successful completion of the project required a significant advancement in the state of the art.

We chose transmission-corrected passive gamma-ray assay of the 185.7-keV gamma ray from ^{235}U as the measurement technique, with a ^{169}Yb source for transmission measurements and an ^{241}Am source for rate-loss corrections.

This paper describes the system's performance and development. We assume familiarity with the principles of transmission-corrected passive gamma-ray assay applied to ^{235}U solutions.

2. System Design and Performance Parameters

The design and performance parameters provided by the user that influenced system design are listed below:

^{235}U Concentration Range
- 0.1 mg/ℓ to 500 g/ℓ

Sample Size
- 30 mℓ -- 1 to 500 g/ℓ
- 200 mℓ -- 0.1 mg/ℓ to 10 g/ℓ

Counting Time
- 1000 s per sample, all samples

Accuracy and Precision
- 0.1% relative, for high concentrations

Sample Vial
- commercial source

Sample Filling
- automatic fillers, thus a variable sample depth

Sample Transport
- pneumatic rabbit system

The ^{235}U concentration range of nearly 7 orders of magnitude interacted with the user's desire to provide minimum sample volumes (to reduce waste) resulting in a system with two measurement heads (detectors). One detector measures high-level or more concentrated solutions in a 30-mℓ sample; the low-level or low-concentration measurements are made on 200-mℓ samples.

The counting time of 1000 s naturally influences the attainable statistical precision. The goal of 0.1% accuracy (defined here as the difference between the measured value and the true value) is strongly influenced by the consistency of the calibration standards available.

The properties of the sample vials also influence the accuracy. High precision requires the highest possible sample counting rates, which means small sample-to-detector distances (a few cm for high-level solutions, even less for low-level solutions). The small distances increase the sensitivity of the assay to variations in sample dimensions and sample position arising from manufacturing tolerances in the sample vial dimensions.

The sample vials were manufactured from polypropylene, which has less rigidity and dimensional stability than some other plastics; $1/r^2$ effects from sample vial dimensional variations increased problems with assay accuracy.

Variable sample depths posed another difficult problem. The automatic sample filling system reduces labor costs over the alternative of accurate pipetting, but causes variable sample depths. The transmission-corrected passive assay technique can handle this problem if the sample depth is either constant or known. A separate device was needed to accurately measure the sample depth.

3. Performance Development

Counting Configuration

The two choices for a counting configuration were an up-looking geometry or a side-looking geometry. These two configurations measure fundamentally different quantities.

The up-looking geometry views the bottom of a cylindrical solution sample, viewing the entire sample volume. It measures the ^{235}U mass in the total sample solution volume. Coupled with a mass measurement of the sample solution, it yields a result in g ^{235}U/g sample. With g ^{235}U/g sample determined, the batch mass can be found from the batch density and batch volume.

The side-looking geometry views a collimator-defined portion of solution contained in a parallel-sided vial. Because all of the solution is not viewed, this technique has to be calibrated in terms of solution concentration, g ^{235}U/ℓ. The batch volume can then be used directly to get the batch ^{235}U mass.

Advantages of up-looking geometry (g ^{235}U/g sample)

1. The entire sample is viewed providing the most efficient use of the limited sample volume and the best statistical precision for a given total sample size as much as a factor of 2 better than the alternative
2. A 1% deviation from the stated sample depth results in 0.15-0.25% deviations in the ^{235}U assay for sample-to-detector distances of 5 cm to 2 cm[1]. For a 3-cm sample-to-detector distance, the sample depth variation must be less than 0.1 mm to keep assay errors from this effect below 0.1%. This assumes a 20 cm^2 x 1.5-cm deep sample (30 mL)
3. The sample and batch temperatures may be different. Only total mass is being measured
4. Geometry is more compact, taking less plant space

Disadvantages of up-looking geometry (g ^{235}U/g sample)

1. The sample depth and diameter must be fixed or known. The sample-to-detector distance must be constant. For a 3-cm distance, a 1% change in the distance results in about 0.8% change in the assay. This sensitivity is the geometry's biggest disadvantage and means that sample-to-detector distances must be held to about ±0.04 mm to keep the assay error below 0.1%
2. Sample depth must be accurately measured or fixed by careful pipetting
3. Sample transport through the pneumatic rabbit may cause some solution to hang up in the threads because of a poor seal. This can perturb the sample geometry and cause an assay error

Advantages of side-looking geometry (g ^{235}U/L)

1. Ease of sampling is the biggest advantage. The sample volume needs only exceed that required to fill the volume defined by the collimator
2. Small variations in the sample-to-collimator distance have little effect on the assay

Disadvantages of side-looking geometry (g ^{235}U/L)

1. Less efficient use of limited sample volume gives poorer precision than alternative method
2. Sample thickness must be constant or known. Assay error is approximately 1:1 with sample thickness error. Thus thickness tolerances must be on the order of ±0.04 mm to keep the assay error from this effect below 0.1%
3. Corrections must be made for any temperature differences between the sample and the batch. Differences of a few tens of degrees Celsius can lead to errors of several tenths of a percent. Expansion coefficients as well as temperatures must be known to correct this effect

We chose the up-looking (g ^{235}U/g sample) geometry primarily because it offered the only possibility of attaining 0.1% RSD precision in 1000-s count times for >100-g/L solutions.

Sample Vial Characteristics

After choosing the counting configuration we specified sample vial dimensions. These systems are most efficient when the greatest sample volume is closest to the detector, but the sample diameter should not greatly exceed the detector crystal diameter. We chose the sample diameter to be nearly equal to the detector diameter and accepted the sample depth that came with it. This gave sample solution dimensions for the high-level (1-500 g/L) system of 5.05 cm diam (20 cm^2) by 1.5 cm deep (30 mL) and a low-level solution diameter of 6.68 cm, with a depth of 5.71 cm (200 mL).

Bottles are made of polypropylene with screw-top lids, with bottom thickness for both high- and low-level bottles of 1.5 mm.

We carried out extensive tests on pilot runs of the commercially manufactured bottles, carefully measuring the deviation from flatness in the bottle bottoms. Variations in this flatness can cause assay errors because of the changing solution-to-detector distance. Typical bowing in the center of the bottle bottom is 0.004-0.005 in. (0.10-0.13 mm). But is not expected to be a problem unless it changes from bottle to bottle. Figure 1 shows the distribution of the average bowing for a sample of 25 bottles. We do not expect the distribution from -0.002 to -0.005 in. to be a problem. However, the two outliers around -0.007 in. could be a problem. These would cause an assay error of nearly 0.3%. This error could be significant when compared with the requested accuracy of 0.1%.

We also measured the transmission of the empty bottles at 186 keV to determine if variations would significantly affect the sample transmission measurement. These results showed an assay error of about 0.08% from sample bottle transmission variability. It is clear that the sample vials limit our ability to attain 0.1% accurate assays.

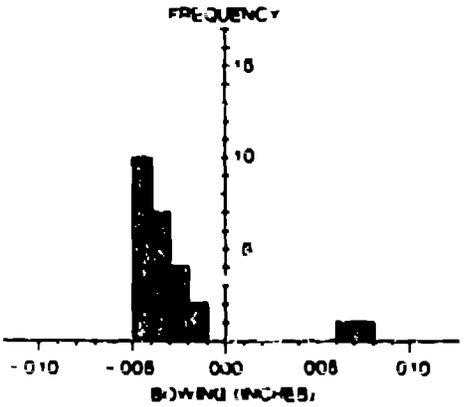

Fig. 1. - Distribution of bowing for a sample of 25 bottles for high-level measurements

Electronic Improvements

The measurement sequence chosen was that typically called a two-pass assay. In this approach the shutter is opened and the transmission source is counted. Only the transmission data are analyzed from this spectrum. Then, in a second pass, the shutter is closed and the passive signal from the ^{235}U sample is counted without interference from the transmission source. The total 1000-s count time is divided between the two measurements. It is clear that the more time devoted to the passive measurement, the better the final statistical precision will be, provided the precision of the transmission measurement is also adequate. This requires counting at high rates during the transmission measurement to obtain the best precision in a minimum time. High rates also require a rate high enough in the 60-keV ^{241}Am reference source peak to prevent its statistical precision from contributing significantly to the overall assay precision. These requirements lead to stronger ^{169}Yb transmission sources, stronger ^{241}Am reference sources, and gross high-level system count rates in the range of 50-100 kHz.

Most of the pileup and dead-time losses arise in the main amplifier. We found that a 1-μs amplifier time constant allowed adequate resolution and minimized pileup losses. For shorter time constants the resolution was unacceptable. The resolution of commercial US gated integrator amplifiers was too poor at the low energies of these measurements to use.

A 450-MHz clock rate, Wilkinson type ADC coupled with data collection in only 1024 channels reduces dead time from the ADC digitization process so that the presence of the ADC is transparent to the system.

The final electronic improvement was the use of new generation digital gain and zero stabilization modules, which enabled us to computer-control the stabilizer settings, a necessary feature for the sophisticated, two-pass measurement procedure.

Count-Time Optimization

Optimizing the division of the total counting time between the shutter-open and shutter-closed measurements is desirable because (1) passive count rate varies with solution concentration, and (2) transmission count rate varies with time (32-day half-life of ^{169}Yb transmission source) and with solution concentration.

The sample assay is proportional to the product of two independent factors: (1) the total corrected passive 186-keV count rate (corrected for pileup and dead time), and (2) the sample attenuation correction factor. If the statistical precision of these two factors is known for a given count time, then an expression can be derived that gives the division of the total counting time that minimizes the statistical precision of the sample assay. Implementing this approach leads to a modified assay sequence:

1. Close shutter, count passive sample 100 s, and save data in MCA
2. Open shutter and count transmission source for 100 s
3. Compute precision of corrected passive rate and attenuation correction factor from the 100-s measurements. Use these in algorithm to obtain optimum count-time division.
4. Continue open-shutter count of transmission source (if needed) for remainder of optimum count time
5. Close shutter, recall passive data, and continue passive sample count for remainder of its optimum fraction
6. Compute final assay result

Figure 2 shows a typical optimum count time variation for solution samples of 93% ^{235}U using a well-decayed ^{169}Yb transmission source.

This count time optimization applies primarily to high-level solutions. For low-level solutions below about 0.1 g/ℓ, the division is nearly always 100 s shutter open and 900 s shutter closed.

Background Reduction

Some special background reduction methods were necessary to improve detection sensitivity for very low concentration (solutions <1 mg/ℓ). Several sources of background were identified:

1. Natural background
2. The americium reference source, taped to the detector end cap, contributes background from weak gamma rays with energies >186 keV
3. The ^{169}Yb transmission source has gammas up to 300 keV, which can penetrate the tungsten shutter.
4. Activated impurities in the Yb_2O_3 and its aluminum capsule can produce high-energy gamma rays that can easily penetrate the shutter. High-energy gamma rays from iron, nickel, zinc, manganese, cobalt, scandium, europium, and lutetium have been observed.

We took the following steps to reduce background from these sources:

1. Two-in.-thick, high-purity lead shielding reduced natural background. The same shield is also used for high-level detectors.
2. A weaker ^{241}Am reference source is used for the low-level detectors. The weaker source does not cause precision problems because the measurement precision, in this case, is completely dominated by the 186-keV ^{235}U count rate.
3. We increased the tungsten shutter thickness from 1.9 cm to 2.5 cm on the low-level heads.
4. We used ultra-pure Yb_2O_3 (99.999%) in the source capsules.
5. We fabricated the source capsules from research grade, ultra-high-purity aluminum (99.9995+ %).
6. We used a larger collimator opening to allow a lower ytterbium activity and thus less impurity activation.

The ultra high-purity aluminum in the source capsule seemed to provide the greatest background reduction when coupled with the increased shutter thickness.

The steps described above reduced the background continuum from ~0.25 count/s to

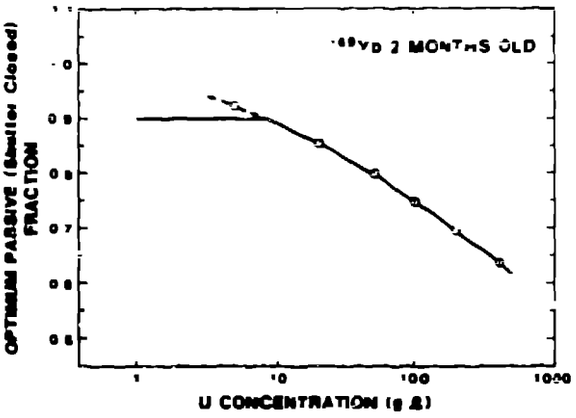

Fig 2 – Typical variation of optimum count-time division as a function of concentration.

~0.05 count/s in 186-kev peak window. This compares very favorably with the ~0.04 counts/s observed in heavily shielded detectors not set up for solution assay. The 0.05-counts/s background gives a 3 σ, 1000-s detection limit of about 0.1 mg ^{235}U/ℓ in a 200-mℓ sample. These background count rates at Los Alamos (2200 m altitude) are about twice those at sea level.

Transmission Correction

Acc rate transmission or attenuation corrections accounting for self-absorption of the assay gamma ray in the sample are essential for 0.1% measurement accuracy. Low-level solutions have a transmission of around 0.45 independent of uranium concentration. The transmission of high-level solutions ranges from 0.3 at 400 g/ℓ to about 0.8 at 1 g/ℓ.

The transmission correction formalism uses a numerical integration technique that accounts for the finite extent of both the sample and detector. A procedure developed by Cline[2] characterizes the detector efficiency as a function of energy and source position. This characterization was done once for a detector similar to those used in this system. The same efficiency parameters are used for both high- and low-level detectors. The primary parameters needed for the correction are sample radius, sample depth, sample transmission, and sample-to-detector distance. The requirement for accurate knowledge of the solution depth arises from its use in this correction factor calculation, which takes about 12 s on a Micro PDP/11 computer.

4. Performance Testing

High-Level Detectors

For accurate calibration, the system needs standards made in an analytical chemistry laboratory. The system can measure relative ^{235}U mass of different solutions of similar concentration with extremely high precision (<0.05% RSD) under laboratory conditions. Calibration standards are necessary to place these measurements on an absolute scale.

The calibration constant is expressed in units of total corrected count rate at 186 kev per gram ^{235}U. This constant is not expected to vary as a function of solution concentration. Any variation from a constant value should be small (a few tenths of a percent) and monotonic with concentration. When we observe variations of ≥0.5%, we first suspect two items: (1) bottle variations and (2) errors in the solution standards. It is difficult to unravel these two effects. But we can try by measuring the standards at large sample-to-detector distances (10-20 cm) "far-field" geometry measurements. Reference 1 shows that 1/r^2 effects from variations in bottle dimensions and solution depths significantly decrease as the sample-to-detector distance increases. If the same relative pattern among standards persists in far-field measurements, the solution standards are probably in error. If the pattern changes as the samples are moved closer to the detector, a bottle variation error is probably present.

These far-field measurements are extremely lengthy. Obtaining a statistical precision of <0.1% RSD for a concentration of 10 g/ℓ may take several days of measurement time. Measurements at 20 cm are impractical at concentrations below 10 g/ℓ.

Figure 3 compares results from two sets of standards (solid squares and open circles). These are measurements in the normal assay geometry. Not only does the solid square set seem to be consistent (max spread <0.2%), it indicates which standards of the open circles are likely to be in error, that is 6.3 g/ℓ, 20 g/ℓ and 400 g/ℓ. Far-field measurements confirmed that these were solution standard errors, not bottle variations. These data (squares) indicate that the goal of 0.1% accuracy (data show a spread of 0.07% RSD about their mean) is achievable under careful conditions: all bottles were hand selected and the solution depth was known and constant. These conditions are not likely to be present in routine use.

Low-Level Detectors

For the concentration range 10^{-4} to 10^{-1} g U/ℓ, the 1000-s measurement precision is expected to be significantly poorer than the

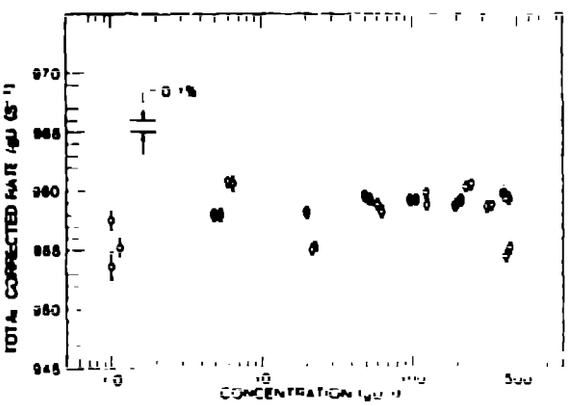

Fig 3 – Comparison of data from two calibration solution sets

achievable assay accuracy. The potential assay accuracy for low-level solutions is nearly as good as that for high-level solutions, however bottle variation effects are expected to be more severe because of the closer sample-to-detector distance (~0.5 cm). For a constant matrix the sample transmission is independent of uranium concentration from 1 to 10^{-4} g U/ℓ, which potentially makes accurate low-level assays easier than high-level assays. Transmission variations will arise from matrix composition variations, but the effects will change the transmission only about 10%.

It is also difficult to obtain accurate solution standards in the low-concentration range. Dilution techniques used to produce the samples can rapidly compound uncertainties, and analytical techniques are less accurate for low concentrations. Calibration to an accuracy of 1% RSD should be achieved. Indeed, the low-level measuring system is probably superior to most chemical techniques in accuracy, precision, and cost for appropriate solutions.

Figure 4 shows the consistency of calibrating a low-level system over a concentration range of five orders of magnitude. Note the dual scale on the ordinate: it expands a factor of 10 between 0.99 and 1.01. Data from two nominally identical systems are shown.

The 16 points plotted for 0.01 through 1.0 g U/ℓ show an RSD about their mean of less than 0.3%. It is very likely that the high values for 10 g U/ℓ result from an error in the solution standard. The measurements at 0.001 g U/ℓ and below are fairly imprecise. The measurement accuracy at 10^{-4} g U/ℓ is uncertain. This is at the system limit of detection and background subtraction is a large (20%-50%) effect.

In addition to verifying the calibration accuracy, we also verified the insensitivity of the system to fill-height variations (as long as the variable fill height is known). Figure 5 shows that accuracy is maintained as fill height is varied over 60% for a 1 g U/ℓ sample.

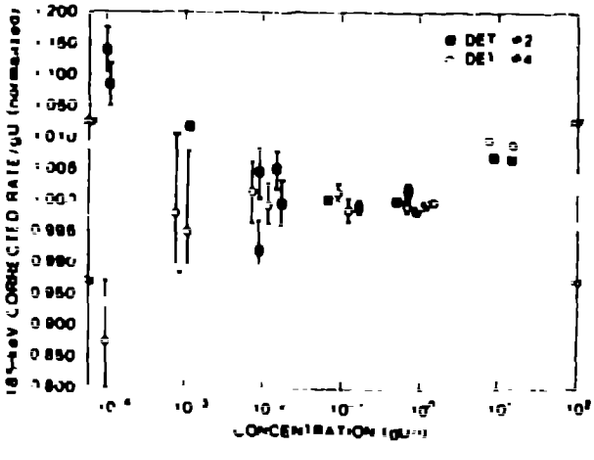

Fig. 4 - Variation of calibration constant as a function of concentration for two low-level assay systems. Dual scale on ordinate is expanded a factor of 10 between 0.99 and 1.01.

Measurement Precision

We define assay measurement precision as pure repeatability, where variations arise only from counting statistics.

The user's goal for measurement precision was 0.1% RSD for high-concentration solutions in a 1000-s measurement time. Figure 6 displays the precision for high-level and low-level solution measurements and shows that this goal was essentially attained for concentrations >200 g U/ℓ.

Count Rate Bias Effects

We have mentioned several effects that can bias measurements. Bottle dimension changes, calibration solution errors, and incorrect sample depth specification. Another effect may cause short-term biases. On some occasions the system calibration has shifted when the ^{169}Yb transmission source is changed. This is likely a counting-rate effect, which shows up most prominently in the measured sample transmission. With a new ytterbium source, the counting rate for the straight-through portion of the transmission measurement may be 2-3 times its value before the source change, typically a count rate change from 30 kHz to 90 kHz. This causes the peak widths

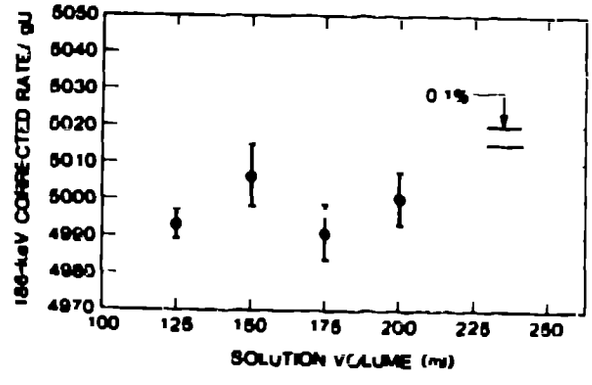

Fig. 5 - Immunity of low-level system to assay errors arising from known fill-height variations. Sample was 1 g U/ℓ.

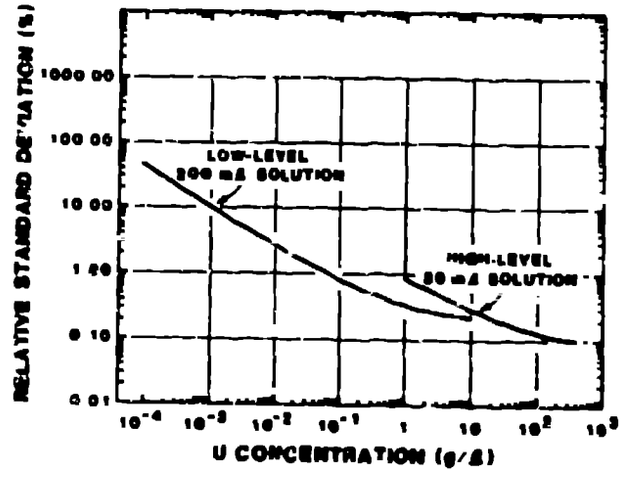

Fig. 6 - Assay precision for both high- and low-level detectors over entire assay range.

to broaden and may slightly bias the peak area determination. The magnitude of this effect is about 0.1-0.2%, which is further complicated by the presence of 195-keV and 202-keV ^{235}U peaks surrounding the 198-keV ^{169}Yb transmission peak.

5. Summary

This paper outlines the development of a state-of-the-art assay system for ^{235}U in solution form. The goal was to produce a system that would operate over a concentration range spanning nearly seven decades and be two to five times more accurate and precise than previous systems.

The sample-detector geometry greatly influences measurement precision for fixed-sample volumes. We selected an up-looking detector geometry that provided the best measurement precision for the specified sample volume. However, this selection may cause problems from sample container variability, particularly variability that affects the solution-to-detector distance.

Careful application of current generation nuclear electronics enabled us to maximize system count-rate throughput. A unique count-time optimization technique also improved the measurement statistical precision.

Several background reduction techniques reduced low-level detector backgrounds to nearly the level of natural radiation.

We applied a more rigorous attenuation correction factor calculation than used in previous systems.

We identified correct specification of the solution depth as necessary for accurate assays.

Under well-controlled laboratory conditions the assay accuracy of high-level solutions (1-500 g U/ℓ) can be 0.1% or better. In routine processing plant use, an accuracy of ~0.2%, similar to that expected from routine chemical analysis, should be achieved by conscientious system operators. The system is cheaper and faster than chemical analysis but must be operated with the same care needed in chemical analysis. For low-level solutions (10^{-4}-10 g U/ℓ) assay accuracy can be 0.3% above 10^{-2} g U/ℓ. It should be similar for lower concentrations but at 10^{-4} g U/ℓ background effects may contribute to errors as large as 10%. The minimum detectable concentration for a 200-mℓ sample and a 1000-s count is ~0.1 mg ^{235}U/ℓ.

Measurement precision is ~0.1% RSD above 200 g U/ℓ and can be better than 0.5% RSD for concentrations above 0.3 g U/ℓ in 1000-s counting times.

We identified several small effects that can bias measurements on the order of 0.1%. Slightly reduced targets for measurement precision may reduce these potential biases. Relaxing the measurement precision requirements to 0.15-0.2% would allow larger sample-to-detector distances (which would reduce bottle and sample depth effects), the better resolution of a 2-μs time constant, and maybe 2048 channels of data collection. These effects would improve resolution and possibly reduce the count-rate effects. This situation would probably improve overall nuclear material accountability. An illustration and photograph of the system is shown in Fig. 7.

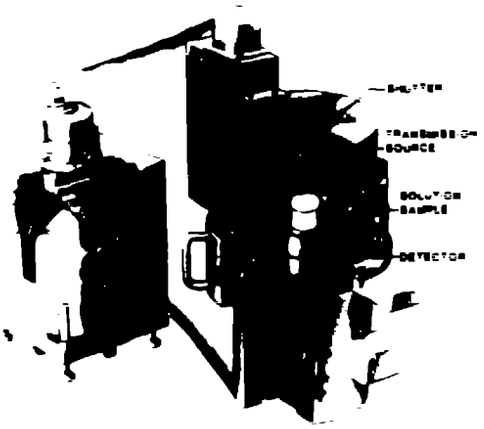

Fig. 7(a) - Artist conceptions of system measurement head

Fig. 7(b) - A single measurement system with high- and low-level detector heads and terminals

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