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The In-Plant Evaluation of a Uranium NDA System

by

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ABSTRACT

The Los Alamos Scientific Laboratory has an unirradiated enriched uranium reprocessing facility.

Various types of solutions are generated in this facility, including distillates and raffinates containing ppm of uranium and concentrated solutions with up to 400 grams U/l. In addition to uranyl nitrate and HNO_3, the solutions may also contain zirconium, niobium, fluoride, and small amounts of many metals.

A uranium solution assay system (USAS) has been installed to allow accurate and more timely process control, accountability, and criticality data to be obtained. The USAS assays are made by a variety of techniques that depend upon state-of-the-art high-resolution Ge(Li) gamma-ray spectroscopy integrated with an interactive, user-oriented computer software package.

Tight control of the system's performance is maintained by constantly monitoring the USAS status. Daily measurement control sequences are required, and the user is forced by the software to perform these sequences.

Routine assays require 600 or 1000 seconds for a precision of 0.5% over the concentration range of 2-400 g/l.

A comparison of the USAS precision and accuracy with that obtained by traditional destructive analytical chemistry techniques (colorimetric and volumetric) is presented.

KEYWORDS: Uranium Assay, Nondestructive

INTRODUCTION

The Los Alamos Scientific Laboratory (LASL) has operated an unirradiated enriched uranium reprocessing facility for 25 years. This facility generates solutions with uranium concentrations varying from 0.001-400 grams/liter. Until January of 1976 chemical analysis was used for accountability and a simple NaI-based single-channel analyzer was used for process control/criticality safety. Despite its accuracy, the chemical analysis was not timely enough for practical use, and despite its timeliness, the NaI-based system was not sufficiently accurate for practical use.

In December of 1975, the LASL safeguards technology group, Q-1, installed a Uranium Solution Assay System (USAS). After an initial calibration period the USAS went into routine operation in January of 1976. This instrument incorporated both the process control/criticality function and the accountability function into one device, which can measure the U solution concentrations to ± 1.0% (2-400 g/l) or better.

The following sections will describe the plant and its measurement points, the instrument and its operation, and an evaluation of the instrument's accuracy and precision.

THE URANIUM RECOVERY FACILITY[1]

The enriched uranium recovery is carried out by the Physical Chemistry and Metallurgy group, CMB-8. A section of this group operates two plants, a Concentration Plant that is primarily for head-end processing and solvent extraction and concentration and a Final Recovery and Purification Plant that is primarily for intermediate processing and final purification.

Virtually every solution generated in the chemical and physical manipulation during processing and purification is measured in the USAS as well as solutions obtained from other groups. Some of these solutions contain many materials besides uranyl nitrate and HNO_3, such as zirconium, niobium, aluminum, iron, sodium, phosphates, sulfates, or trace amounts of various metals. Some of these ions, iron, zirconium, and niobium in particular, interfere with the chemical analysis of uranium by the colorimetric method and must be removed prior to analysis by solvent extraction and electrolysis.

Graphitic materials (fuel rods and casting residues) are crushed, milled to a powder, and burned to remove essentially all the carbon. The ash is leached with hot 60% (13N) HNO_3 and the slurry is filtered. The filtrate is assayed for accountability and for process control/criticality. The uranium is typically in the 5-15 g U/l range. This filtrate is combined with filtrates from the H_2O_2 precipitation mentioned below, concentrated to about 20-25 g U/l (assays are done during the concentration for process control, and a final assay is done for accountability) and run through solvent extraction. The raffinate is measured for accountability and to determine if it can be discarded. Typical assays give 0.005-0.015 g U/l. The aqueous product is concentrated to about 200 g U/l and is analyzed for both accountability and process control. The distillate from this concentration step as well as others is also assayed for accountability and to determine if it can be discarded. Assays are typically in the range of 0.005-0.010 g U/l.

The concentrated aqueous product is filtered and the filtrate assayed for accountability and process control. The U is then precipitated with H_2O_2 and the resultant slurry is filtered. The precipitate is calcined to our final product, pure U_3O_8, and the filtrate is assayed (5-10 g U/l), combined with other filtrates, and recycled through solvent extraction.

Nongraphitic materials (rags, gloves, towels, etc.) are burned and the ash is leached successively with hot HNO_3 and a mixture of 10 M HF-1.7 M HNO_3 at 90-100°C. After cooling, the carbon filtrate is complexed with $Al(NO_3)_3$ and the slurry is filtered and assayed for process control. U assays will range from 1-15 g U/l. The filtrate, which is relatively uncontam, is run through solvent extraction and the aqueous product is treated as described above.

All other residual solids that have been previously leached with HNO_3 are treated the same as the ash from burning nongraphitic combustibles except that the leach with hot HNO_3 is left out.

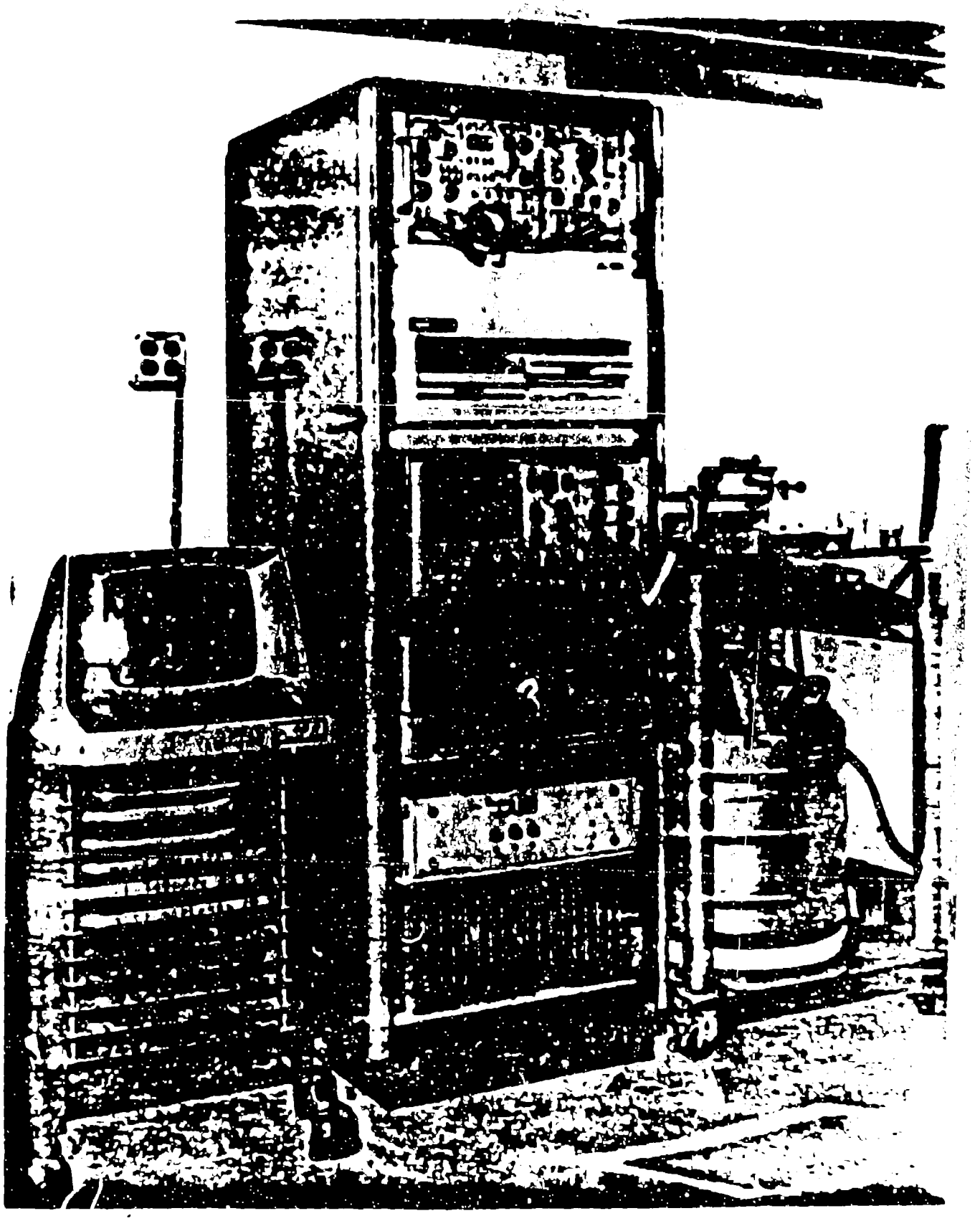
THE URANIUM SOLUTION ASSAY SYSTEM[3,4]

The USAS assays are made by a variety of techniques that depend upon state-of-the-art high-resolution gamma-ray spectroscopy integrated with an interactive, user-oriented computer software package. The USAS is shown in Fig. 1. The hardware cost of such a system is approximately $60K.

The design of the measurement station, Fig. 2, was determined by the wide range of uranium concentrations present in the process and the accuracies to which these must be measured. The concentration range, 0.001-600 g/l uranium, is divided into three material categories described below. Each category has a corresponding turntable measurement port into which is placed a plastic bottle containing the sample. The sample is rotated into the measurement position above the Ge(Li) detector for the assay.

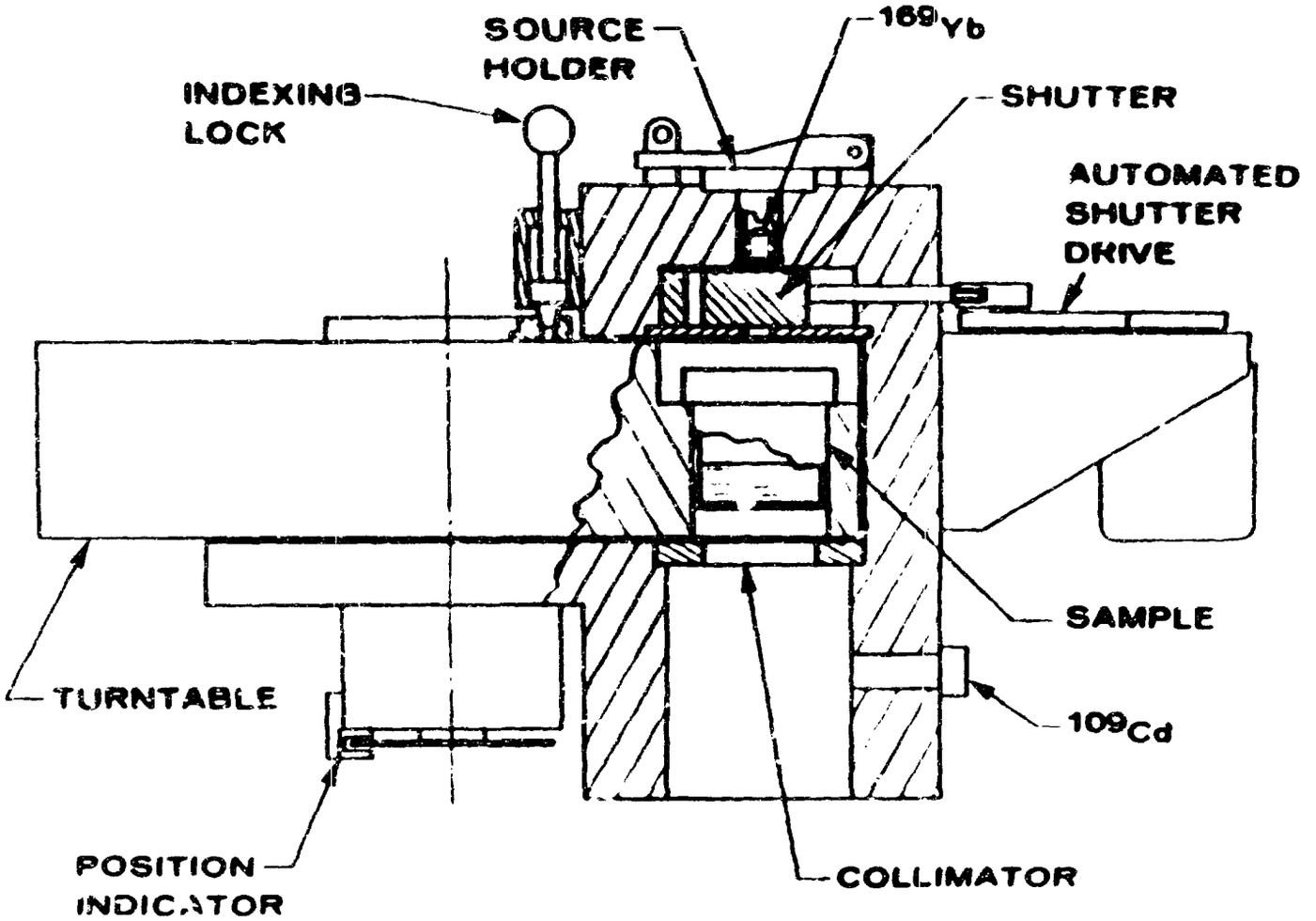
The Ge(Li) detector is a closed-end crystal with a diameter of 42 mm and a length of 30 mm. The relative efficiency and resolution at 1.33 MeV are 7% and 1.75 keV, respectively. The resolution at 122 keV is 0.8 keV.

Fig. 3, a cutaway drawing of the station top, shows a sample in the measurement position. The Index Lock positions and holds the sample accurately above the collimated detector. The position indicator is interfaced to the computer and checks that the assayist has placed the sample in the measurement port corresponding to the material category for which he is requesting an assay. The ^{169}Yb transmission source is mounted above the sample and may be isolated from it by an automated computer-controlled shutter. A ^{109}Cd



1. The Uranium Solution Assay System

2. The DBAS measurement station



3. A cutaway view of the measurement station

source is placed on the end of the indicated plug nearest the detector. The ^{109}Cd 88-keV gamma ray is used as the gain-stabilizing signal for the system electronics.

Standard high-resolution electronics are used to process the DFAS detector signals. The system is controlled by the minicomputer via a program written in BASIC. The program and the final results of each assay are stored on floppy diskettes. There are two CRT terminals for operator interacti and a hard-copy printer for the results.

During normal operation the user pushes the "request assay" button and then is prompted to enter a line of information on the CRT. This line consists of operator ID, sample ID, sample type, volume of material sample was drawn from, count time, and sample enrichment. When this information is sent to the computer, the assay begins.

Three gamma-ray assay techniques are used, each corresponding to a material category. The material category is determined by where the solution originates within the plant's process, which to a large degree also determines the uranium concentration range within a given category.

Material Type 1 (uranium concentrations of 0.001 to 2.5 g/l): These by-products normally contain a very small fraction of the total uranium processed, and therefore highly accurate assays are not required. However, data must be available at a 10% one-sigma level for a uranium concentration of 0.01 g/l in order to determine which solutions meet the disposal criterion.

The assay is made by pipetting 30 cc of the type 1 solution into an 80-cc sample bottle and positioning it above the detector. A spectrum is accumulated for 2000 s with the transmission shutter closed.

The concentration of uranium ρ_u is determined from these data by

$$\rho_u = \frac{I(186)/I(\text{Pulser})}{E}$$

where I(186) and I(Pulser) are the number of counts in the 186-keV and pulser peaks respectively, and E is a calibration constant determined from standards.

The results of a series of raffinate standard measurements are summarized in Fig. 4 where E is plotted versus log ρ_u. The distillate E value was found to be approximately 10% larger than for the raffinate. The computer software requires the assayist to identify the sample as a distillate or raffinate and uses the corresponding E value in the data analysis.

Material type 2 (uranium concentrations of 1 to 50 g/l): As with material type 1, the assay depends on the measurement of the ^{235}U 186-keV gamma-ray intensity. In addition, a transmission measurement, which accounts for the absorption of the 186-keV gamma ray in the sample, is required.

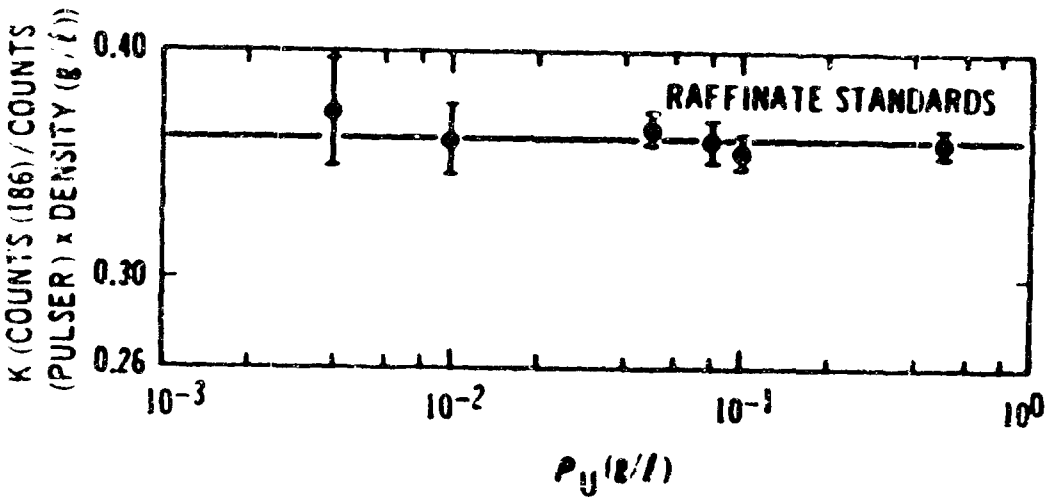
T, the transmission of a gamma ray at 186 keV, is determined by measuring the transmissions, T_1 and T_2, of the ^{169}Yb 177-keV and 198-keV gamma rays and linearly interpolating. The transmission T is then given by

$$T = T_1 \exp[-(186-177)/(198-177)(\ln T_1/T_2)] .$$

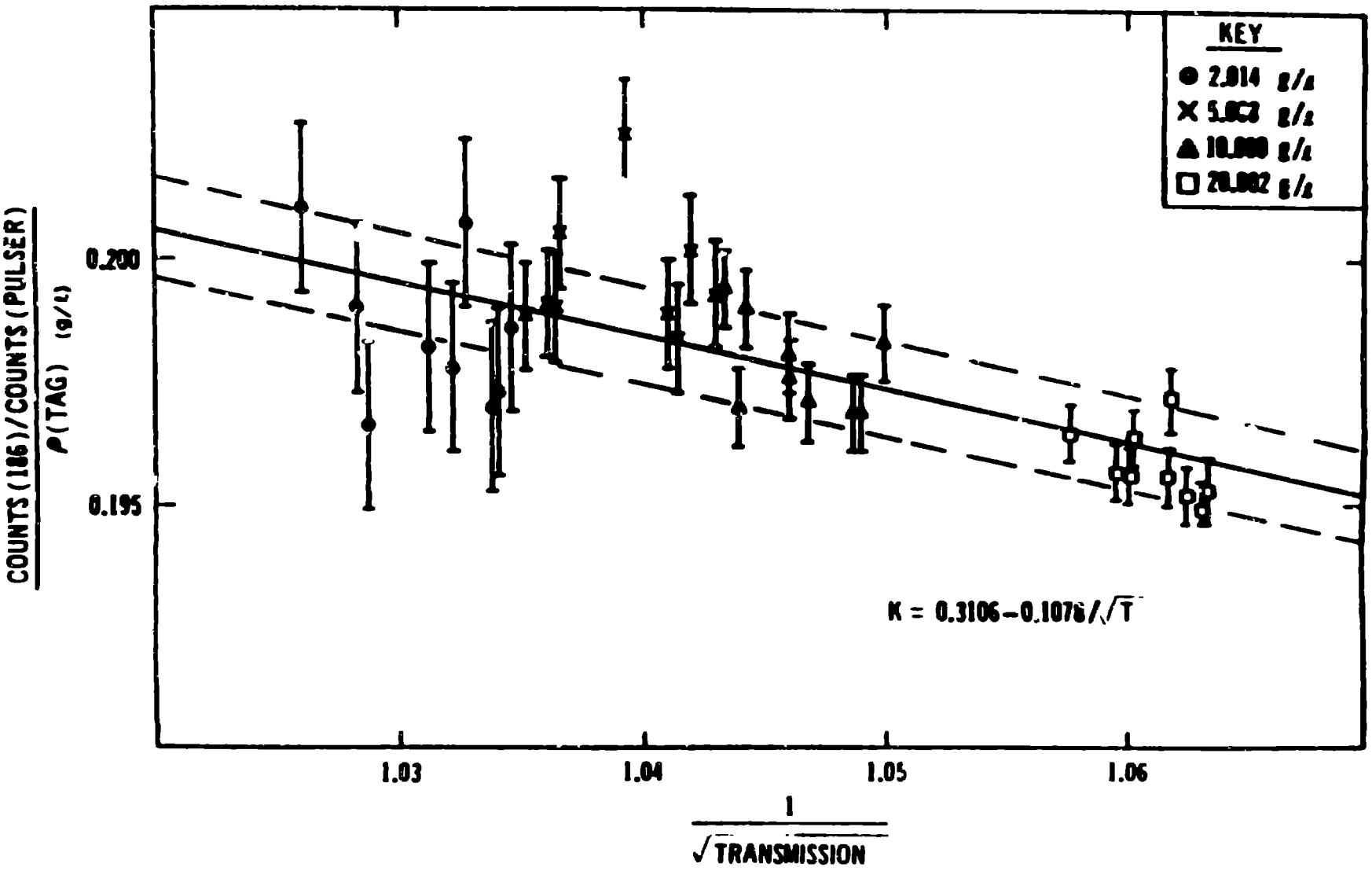
The assay is made by pipetting 20 cc of the type 2 solution into a 50-ml bottle, positioning the sample above the detector, and simultaneously counting the 186-keV and the transmission gamma rays for 400 seconds. The uranium concentration is obtained from these data by

$$\rho_u = \frac{I(186)/I(\text{Pulser})}{E(T)}$$

E(T) was determined using a set of standards with $2 \leq \rho_u \leq 50$ g/l. The transmissions were measured relative to an identical water sample. Typical results are shown in Fig. 5



4. A type I calibration



5. A type 2 calibration

where K is plotted versus 1/T. The solid line is a linear least squares fit to the data and gives K(T) for the T range of interest. The calibration function should not be extrapolated beyond this range as the linearity assumption will not hold for smaller T. The two dashed lines represent a ± 0.5% variation in K(T). The low concentrations (~2 g/l) demonstrate a ± 0.7% precision, while the higher concentrations (~20 g/l) demonstrate a ± 0.35% precision for the 400-s count times.

Material Type 3 (uranium concentrations of 100-400 g/l): Twenty-oc samples, placed in the 50-ml bottles, are assayed by an absorption-edge densitometry technique. The normal count time is 1000 seconds. The ratio of transmissions of two gamma rays from ^{169}Yb (110-keV and 130-keV gamma ray) with energies on either side of the uranium K-absorption edge (115.6 keV) is measured, relative to a water standard. The ratio of transmissions, R, is then given by

$$R = \frac{I(130)}{I(110)} \frac{I_w(110)}{I_w(130)} ,$$

where I(130)/I(110) is the ratio of the peak intensities transmitted through the sample and $I_w(110)$ $I_w(130)$ is the inverse of that ratio measured through the water standard. The latter is a constant for a given transmission source and needs to be measured only once. The total uranium concentration, ρ_u(g/l), is then given by

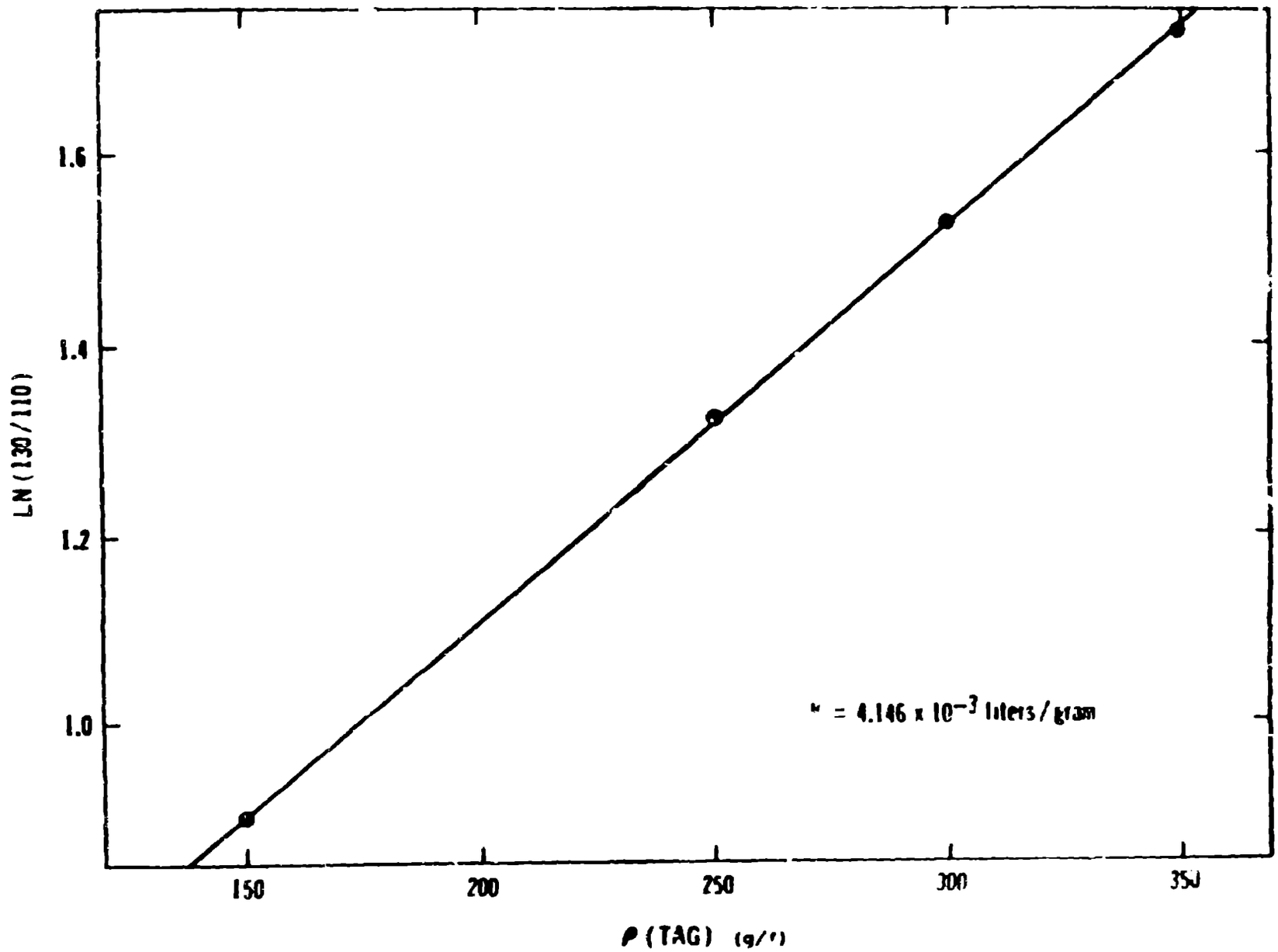
$$\rho_u = \frac{-\ln R}{K} .$$

The calibration constant K is determined using a set of standards that are representative of the type 3 samples. The results of a UNAS material type 3 calibration is shown in Fig. 6. Each point corresponds to an average of nine assays. The standard deviation in each of the four averages is 0.1% or less. The solid line is a fit to the four data points of the function $\ln R = -K\rho_u$ and yields a K value of $4.146 \cdot 10^{-3}$ l/g, with a standard deviation of 0.5%.

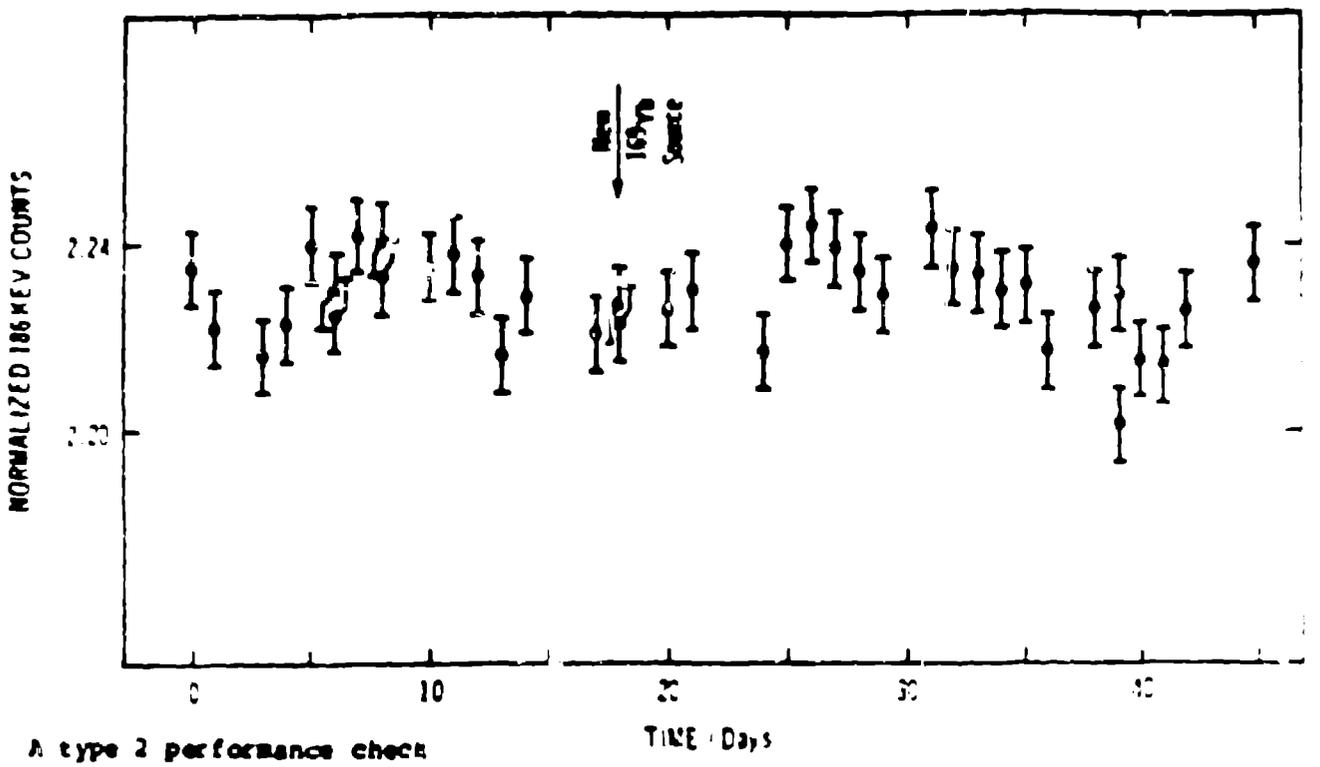
Although the UNAS is extremely stable, its performance is checked daily to ensure accurate assay results. The standards used for this purpose consist of a reference plastic standard for type 2 measurements, a 0.0025-cm-thick 93.15% enriched uranium foil (FOIL-2) to check type 1 and type 2 performance, and a 0.0025-cm-thick depleted uranium foil (FOIL-3) to monitor type 3 performance. Both foils are encased in plastic. Secondary standards are used rather than solution standards because experience has shown that the plastic sample containers are inadequate for long-term storage of the solutions.

The daily performance check routine consists of measuring these three standards and monitoring certain parameters. The intensity of the ^{169}Yb source is verified so sufficiently accurate assays can be obtained with the normal count times, the transmissions through the foils must fall within predefined limits, and the FOIL-2 186-keV peak area is checked against predefined limits. If these tests are passed, assays are allowed for the remainder of the day and if any test is failed, an appropriate alarm message is printed at the terminals.

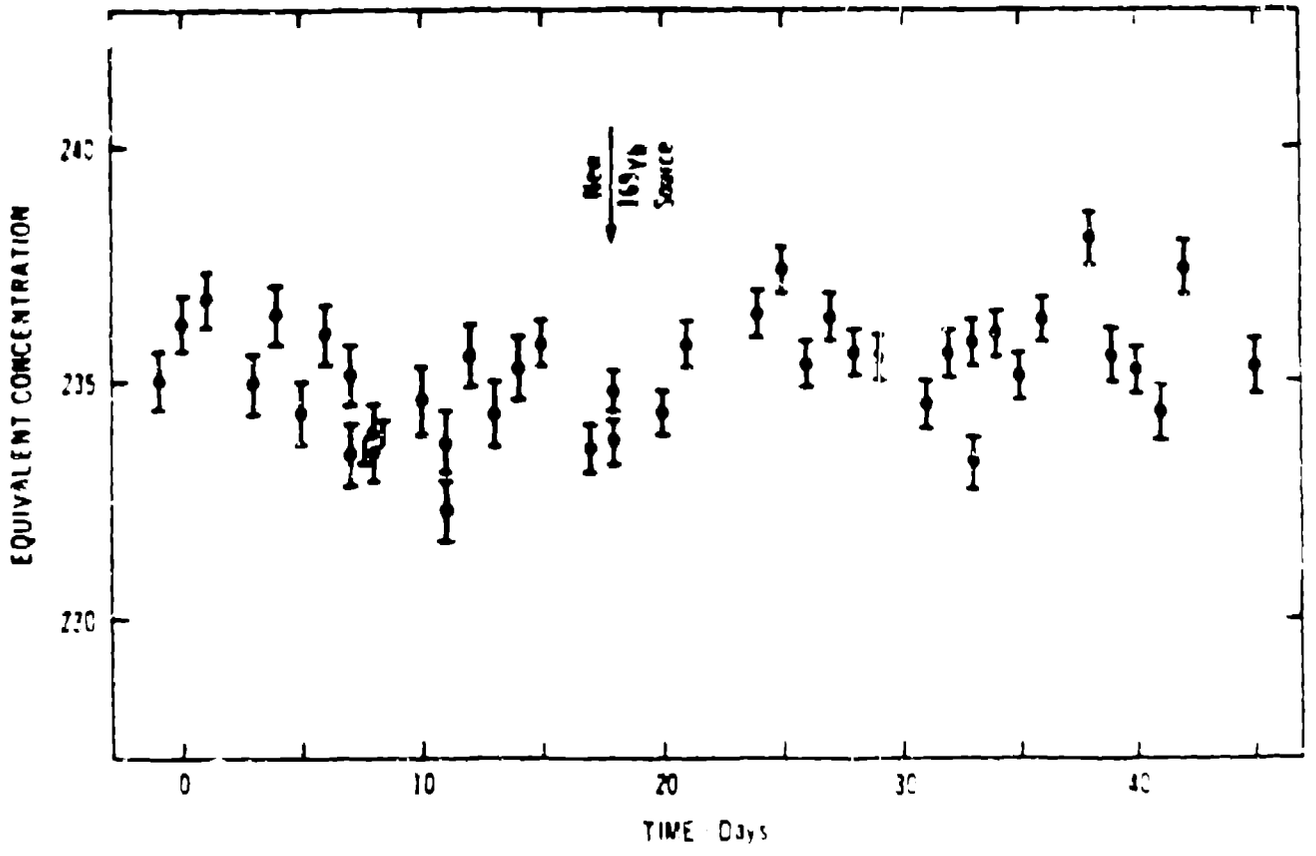
Figure 7 shows a recent 45-day series of FOIL-2 results. The normalized 186-keV peak area is plotted as a function of time. The standard deviation in these data is 0.65%, a typical value for a monthly average. Figure 8 shows the performance check results from FOIL-3 in the form of the equivalent concentration as a function of time. The standard deviation in the FOIL-3 data is 0.5%. The performance checks should be source independent and the ^{169}Yb source change indicated on July 3, 1979 (the 18th day in Figs. 7 and 8) had no effect on the performance check parameters. These two figures demonstrate the short-term stability of the UNAS. The long-term performance check results show a similar pattern and are also verified with primary solution standards. In its current mode of operation, the UNAS calibration is checked against fresh primary solution standards every six months. Calibration shifts as large as 0.5% have been discovered. Typically they are approximately 0.2%.



6. A type 3 calibration



7. A type 2 performance check



8. A type 3 performance check

The ^{169}Yb source has a 32-day half-life and consequently it must be replaced about three times a year. It can be irradiated and reused but only after a four-to six-week cooling time to allow the intensity of the shorter half-life contaminants to die away. The only other maintenance the system requires is that required by standard computer and commercial nuclear instrumentation.

MEASUREMENT ACCURACY AND PRECISION

The type 1 measurements are the basis for determining whether or not a distillate, raffinate, or other solutions can be discarded. High accuracy is not required for these particular measurements. These solutions are nearly always 0.010 g/l ^{235}U and it is extremely difficult to chemically analyze solutions that are this dilute. Consequently a comparison with chemistry was not repeated during this analysis. The type 2 comparison verified the system's capability to measure the 186-keV gamma ray from ^{235}U, and the type 1 measurement merely needs to determine whether the 186-keV radiation emitted from the sample is negligibly low.

Figure 9 shows the results of chemical analyses on type 2 solution standards. The ordinate is the fractional difference between the tag value and the chemical analysis. The abscissa is the tag value for the uranium concentration. Two types of chemistry were used, colorimetric and volumetric. Table I lists the biases and standard deviations for the data in Figs. 9 and 10. A large negative bias and a large standard deviation for volumetric chemistry on type 2 standards would arise from the one outlier data point obtained for a 30 g/l standard. This poor result could arise from one of two sources, a pipetting error, discussed below, or a misapplication of the chemical technique. The type 2 standards are made to resemble

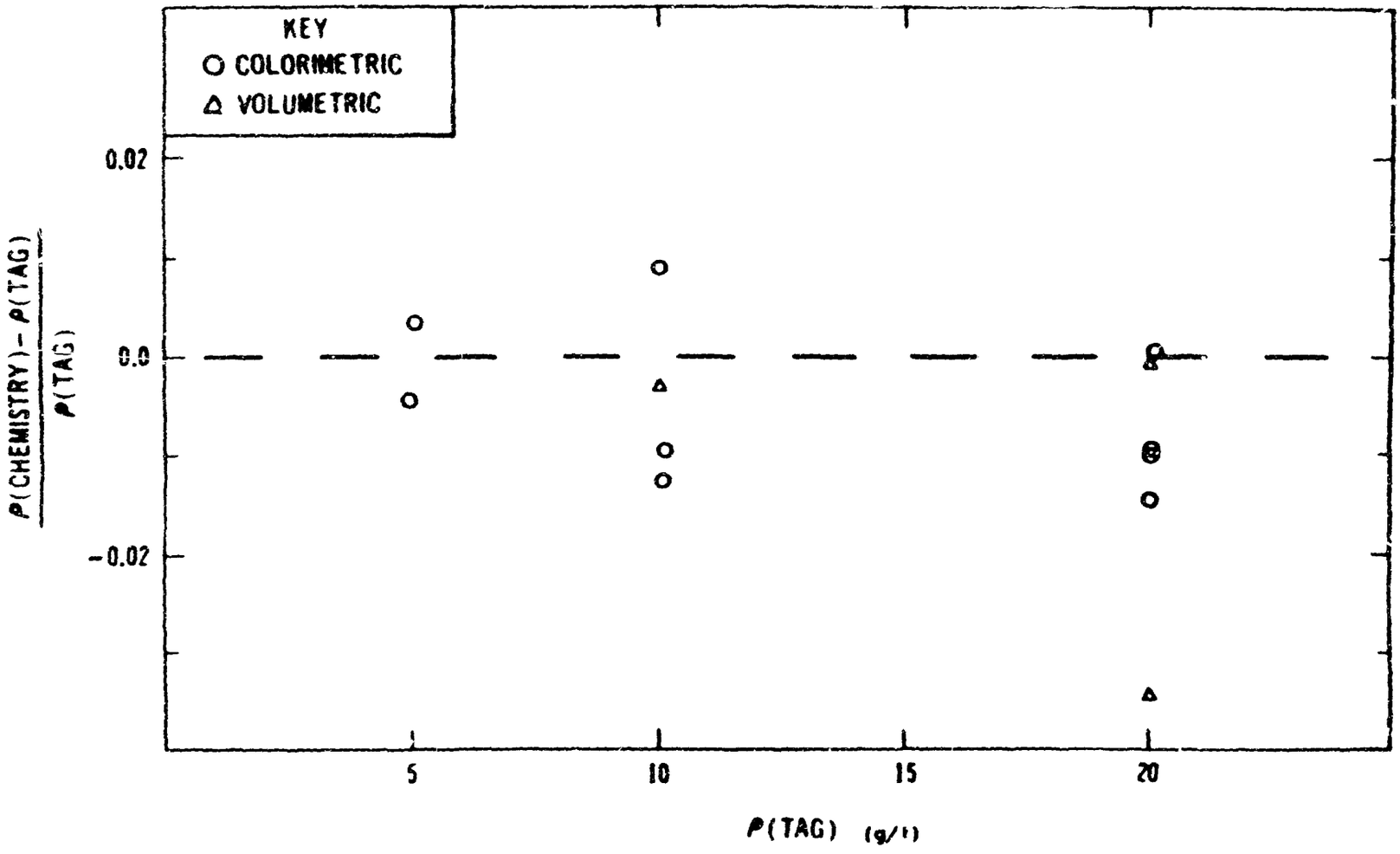
TABLE I. ANALYTICAL CHEMISTRY RESULTS ON SOLUTION STANDARDS

Material Type	Chemistry Technique	Bias	Standard Deviation
2	Colorimetric	-0.53%	±0.80%
	Volumetric	Insufficient data	
	Both	-0.72%	±1.11%
3	Colorimetric	-1.51%	±0.51%
	Volumetric	-0.24%	±0.30%
	Both	-0.84%	±0.76%

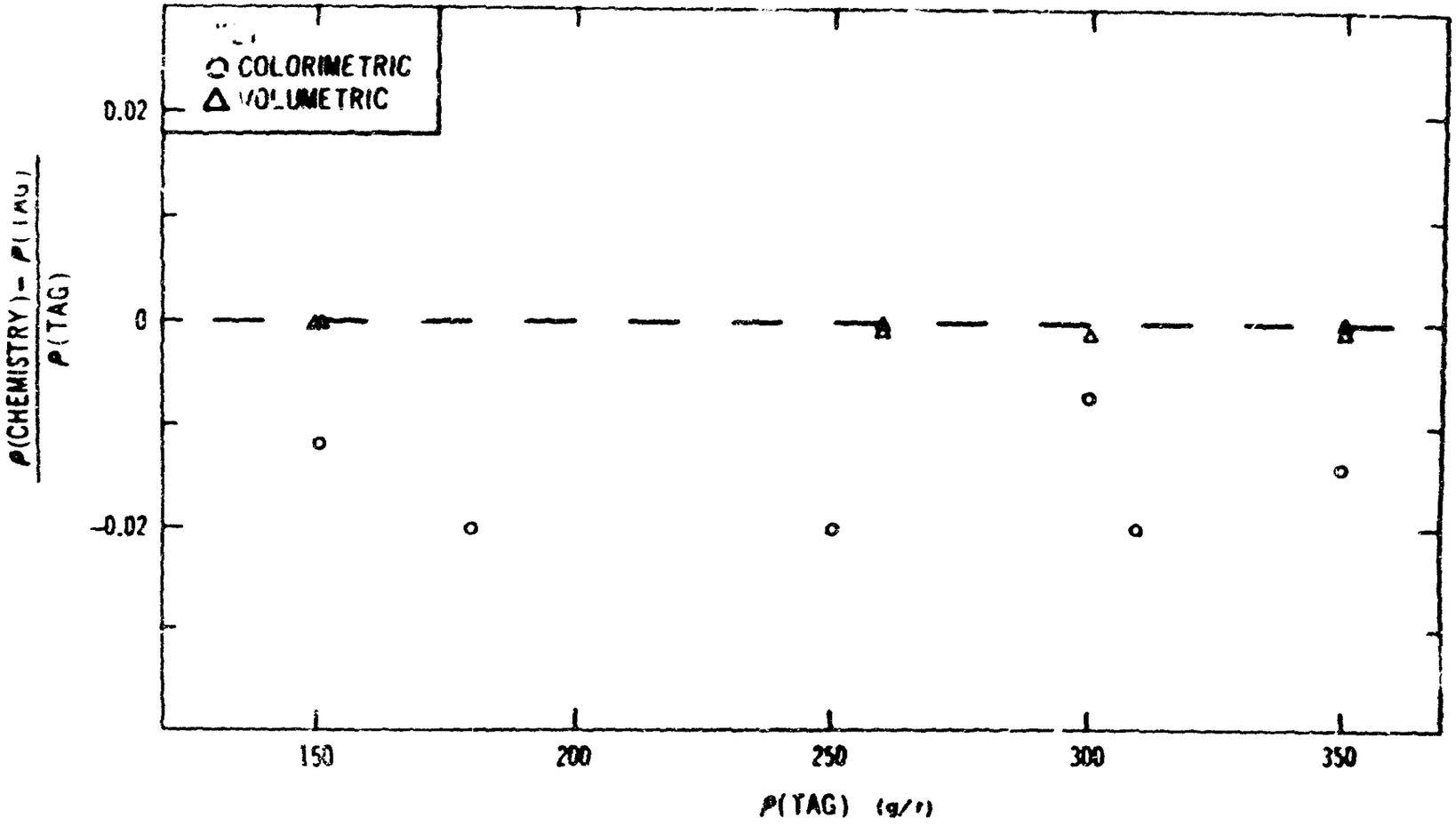
the plant solutions; consequently, they contain some amounts of interfering ions. The USAS is insensitive to these contaminants but the the chemical techniques are not. Figure 10 shows the chemical analysis results for the type 3 standards. The large negative bias displayed for the colorimetric analysis is probably not due to pipetting errors but more likely to an incorrect calibration in the chemical technique. Five of the six colorimetric values were obtained with the same chemical setup.

There is a certain amount of pipetting involved in drawing the samples and in the chemical analysis. Therefore, an independent analysis of the reproducibility of the pipetting was carried out.[5] Three operators using two uncalibrated pipettes drew a total of nine samples. The standard deviation of the nine values was 0.5%, and there were no significant differences between the averages of the values obtained by the different operators or the values obtained with the two pipettes. In another test, one operator drew eight samples with one pipette and obtained a standard deviation of 0.3%. This was not statistically different from the 0.5% obtained in the three-operator test.

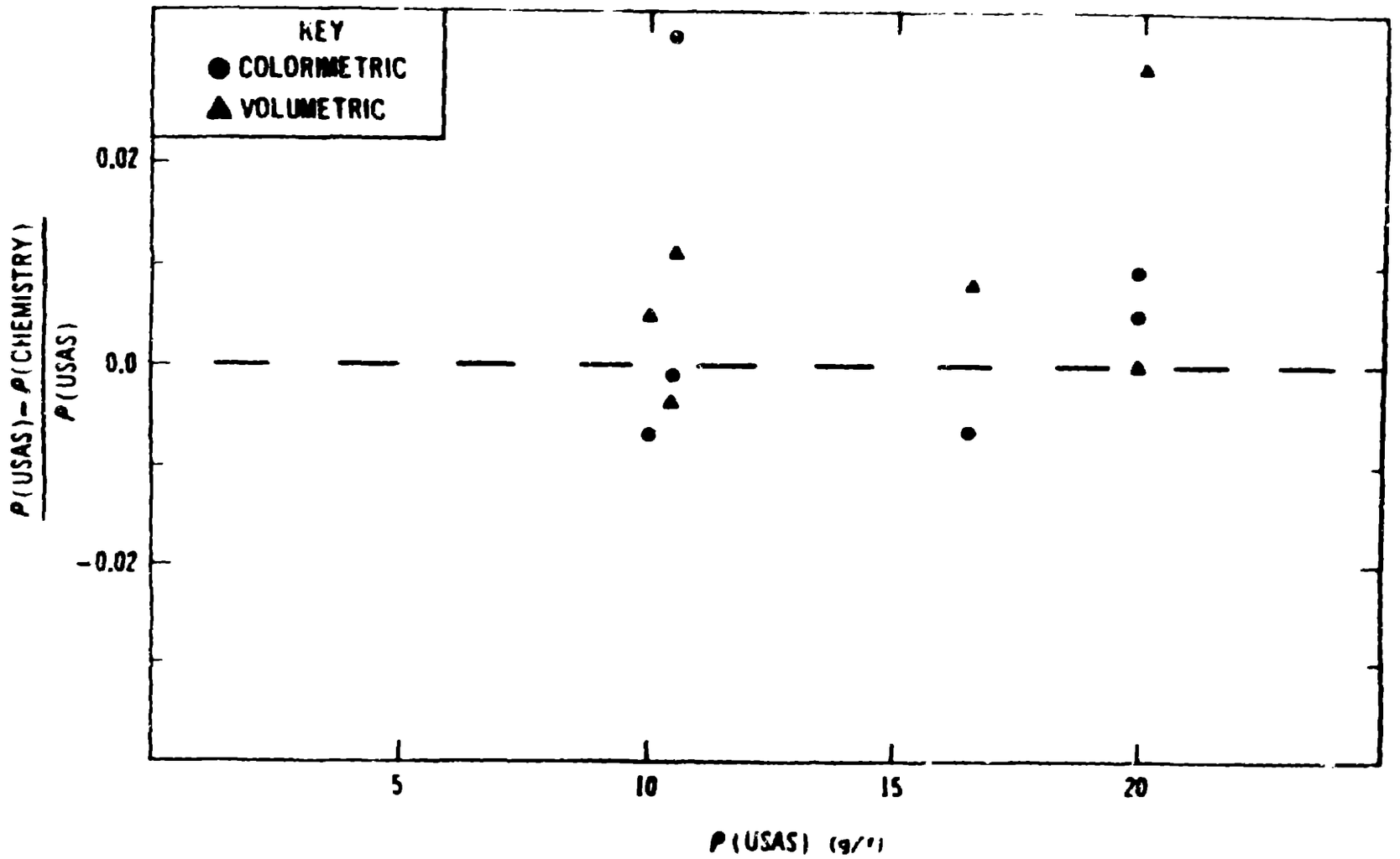
Figures 11 and 12 show the results of a comparison between analytical chemistry and the USAS assays of several unknowns. The type 2 and type 3 assays were 400 and 1000 seconds respectively and had a calculated uncertainty of 0.7% to 0.4%. In both figures, the ordinate is the fractional difference between the chemistry and the USAS results, while the abscissa is the USAS value for the concentration. Table II lists the biases and standard deviations for these comparisons.



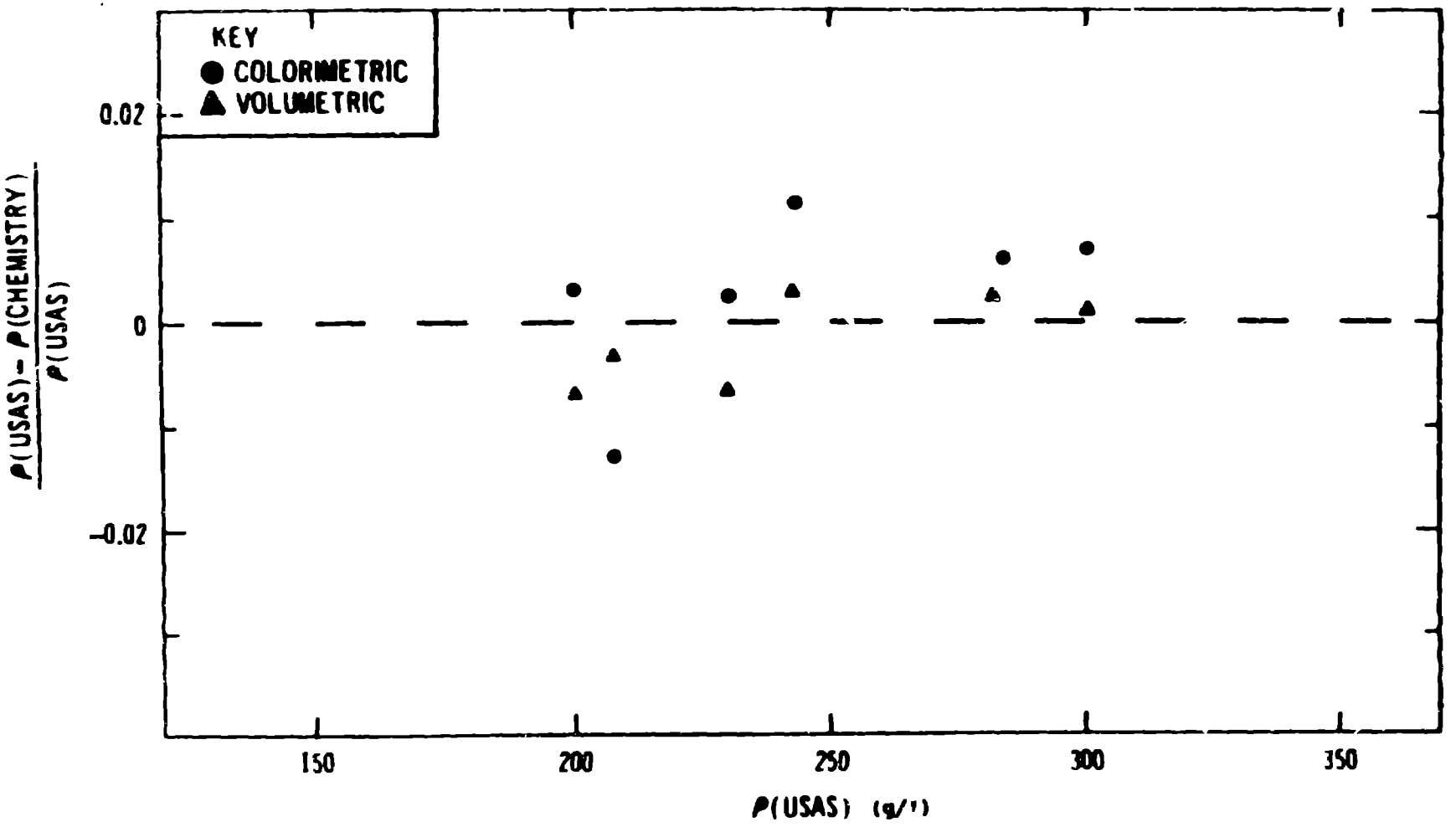
9. Chemical analyses of type 2 solution standards



10. Chemical analyses of type 3 solution standards



11. Chemical analyses of type 2 unknowns



12. Chemical analyses of type 3 unknowns

TABLE II. ANALYTICAL CHEMISTRY RESULTS COMPARED TO UBAS ASSAYS

Material Type	Chemistry Technique	Bias	Standard Deviation
2	Colorimetric	-0.5%	±1.40%
	Volumetric	-0.96%	±1.0%
	Both	-0.74%	±1.21%
3	Colorimetric	-0.29%	±0.84%
	Volumetric	+0.17%	±0.45%
	Both	-0.06%	±0.68%

For the type 2 [illegible] comparison, the chemistry results showed the same negative bias that was obtained with solution standards. For both the colorimetric and the combined results, the standard deviation is larger than that obtained with standard solutions, but this is expected since two additional sources of fluctuations are included in this comparison. These are the ±0.5% caused by the UBAS precision and the ±0.5% caused by pipetting the UBAS sample. When the three errors are combined in quadrature, the result is consistent with the value in Table II. The standard deviation exceeds the bias in all three cases, as it did for the chemistry results on the solution standards. In the comparison of the type 3 [illegible], the bias is less than that obtained with the standards. Once again the three precisions are consistent with the combined uncertainties. These data indicate that the UBAS is performing as well as the two chemical techniques.

A measure of the [illegible]'s long-term accuracy can be obtained from the semiannual verification with solution standards. Using the six-month-old calibration, the results in Table III were obtained with eight freshly made standards. The UBAS average in each case is the average of 30 assays made over a period of six days. These data show that the UBAS bias is less than 0.96% for the range 5-250 g/l. They also support the conclusion that the UBAS can do as well as the chemical techniques for the range 10-250 g/l.

TABLE III. UBAS ACCURACY COMPARISON

Tag Value	UBAS Average	UBAS Precision	UBAS-Tag Bias
2.002 g/l	2.036 g/l	±0.018 g/l	+1.70%
5.003	5.051	±0.034	+0.96%
10.000	10.085	±0.054	+0.85%
20.000	20.079	±0.071	+0.40%
150.001	151.193	±1.16	+0.83%
249.994	250.349	±1.66	+0.14%
299.994	298.500	±1.72	-0.50%
350.006	350.028	±1.77	+0.01%

CONCLUSION

The UBAS was designed around this recovery plant's requirements. The three assay techniques span five orders of magnitude in concentration. They are optimized to achieve the best results on these process solutions, which clump around three concentrations in the middle of each assay technique.

The UBAS has been in operation for almost four years in this process plant environment. During this time it has reliably provided approximately six assays daily, five days a week. It supplies at least two assays every workday and has supplied as many as twenty. It provides the process control/criticality function and the final numbers for accountability purposes. It is considerably more accurate than the previous NaI system was, largely through its ability to distinguish U from various other radionuclides, and it is just as timely. It is at least as accurate as the colorimetric chemical analyses used previously

and it has considerably faster response times. In terms of actual process plant man hours, it requires one to two orders of magnitude less time to prepare the samples than the chemical analysis requires. In addition, an answer is returned in 400-2000 seconds compared to an average two-week turnaround time for the chemistry.

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