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EVALUATION OF KINETIC PHOSPHORESCENCE ANALYSIS FOR THE DETERMINATION OF URANIUM

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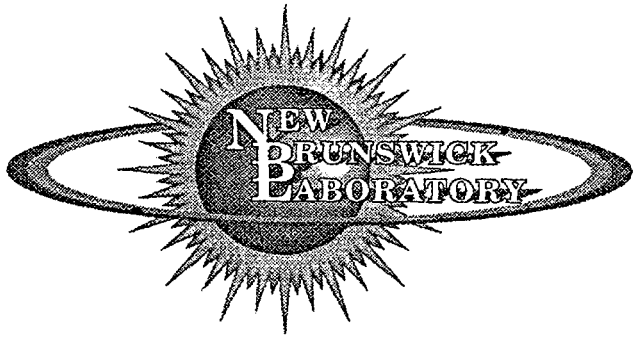

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ABSTRACT

In the past, New Brunswick Laboratory (NBL) has used a fluorometric method for the determination of sub-microgram quantities of uranium. In its continuing effort to upgrade and improve measurement technology, NBL has evaluated the commercially-available KPA-11 kinetic phosphorescence analyzer (Chemchek, Richland, WA). The Chemchek KPA-11 is a bench-top instrument which performs single-measurement, quench-corrected analyses for trace uranium. It incorporates patented kinetic phosphorimetry techniques to measure and analyze sample phosphorescence as a function of time. With laser excitation and time-corrected photon counting, the KPA-11 has a lower detection limit than conventional fluorometric methods. Operated with a personal computer, the state-of-the-art KPA-11 offers extensive time resolution and phosphorescence lifetime capabilities for additional specificity. Interferences are thereby avoided while obtaining precise measurements.

Routine analyses can be easily and effectively accomplished, with the accuracy and precision equivalent to the pulsed-laser fluorometric method presently performed at NBL, without the need for internal standards. Applications of kinetic phosphorimetry at NBL include the measurement of trace level uranium in retention tank, waste samples, and low-level samples. It has also been used to support other experimental activities at NBL by the measuring of nanogram amounts of uranium contamination (in blanks) in isotopic sample preparations, and the determining of elution curves of different ion exchange resins used for uranium purification. In many cases, no pretreatment of samples was necessary except to fume them with nitric acid, and then to redissolve and dilute them to an appropriate concentration with 1 *M* HNO_3 before measurement. Concentrations were determined on a mass basis (μg U/g of solution), but no density corrections were needed since all the samples (including the samples used for calibration) were in the same density matrix (1 *M* HNO_3).

A statistical evaluation of the determination of uranium using kinetic phosphorimetry is described in this report, along with a discussion of the method, and an evaluation of the use of plastic versus quartz cuvettes. Measurement with a precision of ± 3-4 % relative standard deviation (RSD) and an accuracy of better than ± 2% relative difference (RD) are obtained in the 0.0006 to 5 μg U/g-solution range. The instrument detection limit is 0.04 ppb (4×10^{-5} μg U/g solution) using quartz cells, and 0.11 ppb (11×10^{-5} μg U/g solution) using disposable methacrylate cuvettes.

INTRODUCTION

Uranium fluorescence methods have been used since the early 1950's for the determination of trace quantities of uranium.[1] Conventional uranium fluorescence measurements have been made in liquid media such as sulfuric and phosphoric acids, or in disks or pellets prepared by fusing the sample with salts such as sodium fluoride or sodium carbonate.[2] Methods where the fluorescence measurements are made directly on solutions have a sensitivity of only about 1μg U/mL of solution. They are very sensitive to quenching effects by various ions, and to interferences from traces of organic matter. Strict control of media composition and temperature is required to obtain satisfactory results. For these reasons, few laboratories used this method. In comparison, the fusion methods have a sensitivity of about 0.1 ng U/mL of sample and were used extensively. However, many factors affect the fluorescence in fused pellets. The fusion requires strictly regulated conditions of flux composition, heating time, and temperature. The method is lengthy, usually involving separations and extractions to remove interfering elements. If, however, the many variables are identified and controlled, laboratories can obtain precisions of 8-12% using fusion methods.[3]

A significant breakthrough in the determination of uranium by fluorometry was achieved through the use of pulsed-laser ultraviolet light as the excitation mode. This method has been used at NBL since 1979 with the Scintrex UA-3 Uranium Analyzer.[4] Measurements with a 2-3% RSD and accurate to better than 1% RD have been obtained in the 0.008 to 4 μg U/g-solution range.[3] The instrument detection limit is 0.05 ppb uranium.[3] It is a direct method requiring no separations, extractions, or fusions and therefore is many times faster than conventional fluorometric methods; each analysis requires only about 6 minutes. A special feature of the method is the use of a standard addition technique to eliminate sample matrix effects. The disadvantage of this technique is that fluorescence is strongly dependent upon the temperature of the solution; studies show that a 1° C increase causes a 3.5% loss in fluorescence in the 20-25° C range.[5] Accurate results can only be achieved by carefully heating the sample solutions to a consistent temperature. In addition, the method requires the use of an internal standard and corrections for anionic enhancement from certain concentration of acids (PO_4^{-3}, SO_4^{-2}, and F^-) have to be made.

Recently, a pulsed-laser uranium analyzer that detects and quantifies the longer-lived phosphorescence of uranium species became commercially available. The Chemchek Kinetic Phosphorescence Analyzer Model KPA-11 is capable of performing direct determinations of uranium in solution.[6,7] Because of a number of inherent advantages in the technique and the analyzer itself, NBL decided to investigate the use of the KPA-11 as a replacement for the Scintrex UA-3.

Minimal sample preparations are necessary prior to measurement by the KPA-11. Chemical separations are only required for the determination of very low-levels of uranium in samples with a substantially complex matrix. A reference solution, which functions as an external standard, is measured simultaneously with the sample. This normalizes the sample measurement for internal fluctuations such as laser brightness, temperature drifts, electrical line surges, and high voltage drifts. No temperature control of the sample is needed as in the laser fluorometric method.

In order to qualify the performance of the KPA-11, the following performance elements were statistically evaluated over the optimal ranges: 1) analytical error (method error, repeatability), 2) variabilities from other sources and 3) long-term precision and bias. In addition, the use of disposable plastic (methacrylate) cuvettes was evaluated and shown to be both economical, practical, and acceptable for concentrations above 6×10^{-4} μg U/g of solution. The results of these investigations are reported herein.

EXPERIMENTAL

Instrumentation, Apparatus, and Reagents

Instrumentation

A Chemchek Laser Kinetic Phosphorimeter/PC system, Model KPA-11, was used to perform phosphorimetry measurements.[8] The KPA instrument was modified by replacing the europium emission filter, which comes with the instrument, with a uranium emission filter (Oriel) that has a 515 nm central wavelength and a 10 nm bandpass. This allowed for the use of "in-house" uranium standard solutions which provided better normalization results than the europium solutions supplied with the instrument. The instrument uses a pulsed nitrogen/dye laser to supply monochromatic ultraviolet light to excite uranium atoms in the sample solution. The dye solution used was 1.8×10^{-3} *M* stilbene-420 (Exciton®) in methanol. The excited uranium atoms then emit a green phosphorescence which is filtered, amplified, and measured. To protect the uranyl ion from quenching, a phosphate-based complexing reagent is added which yields phosphorescence lifetimes for UO_2^{2+} of a few hundred microseconds. The KPA-11 is a fully integrated computerized system for data collection and analysis which allows for two separate calibrations covering two different calibration ranges. The system takes phosphorescence measurements during multiple time gates, analyzes the kinetics of the phosphorescence decay, and calculates the result in terms of selected units. The KPA performs a background correction and automatically corrects for most sample quenching from sample matrix effects thus eliminating the need for the internal standards required in the laser fluorometric method.

Instrument conditions were set so that 1000 laser pulses occurred for a sample analysis time of 50 seconds. The timing scheme used provided a dwell time of 13 μs per time gate. The first four time gates were discarded from the calculations so that the emission from short-lived luminescence sources did not affect the data. The maximum number of time gates was set at 49 to cover several excited state lifetimes. This also allowed for an accurate calculation of the intercept. For each measurement, the emission intensity recorded for each time gate was summed over the number of laser pulses to obtain a decay curve. Figure 1 is an example of a phosphorescence decay line (the logarithm of the light intensity sum for each time gate versus time) for uranyl ions. A linear fit of the intensities data gives an intercept at time t = 0, ln I_0, where I_0 is proportional to the number of excited uranyl ions independent of quenching effects.[6,7] This is related to analyte concentration in the sample using I_0 values from known uranium standards. The lifetime can be calculated as the negative reciprocal of the slope.

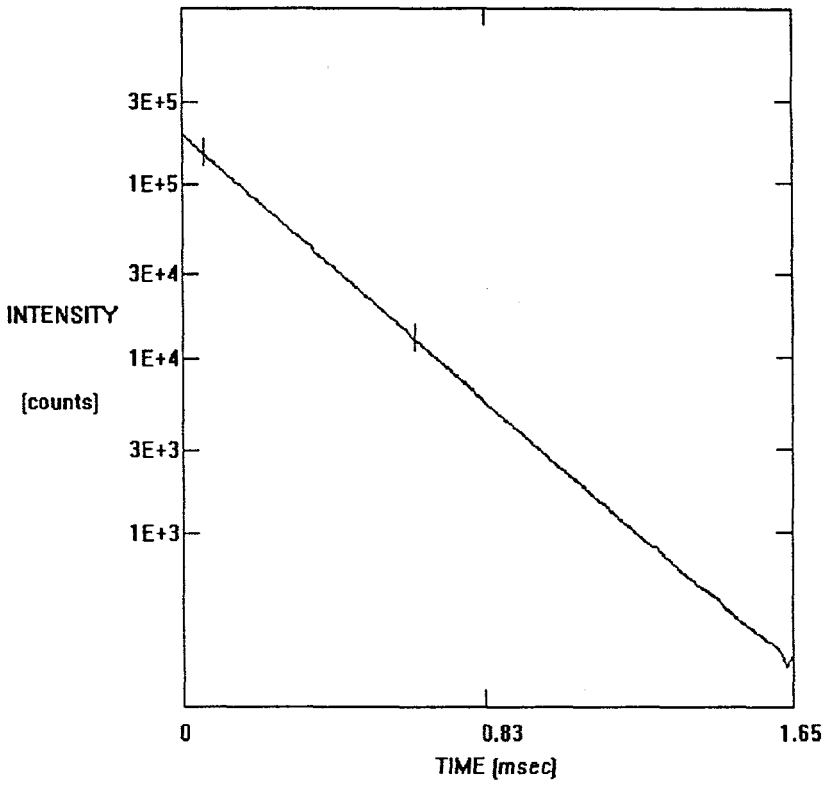


FIGURE 1 Decay Plot For Uranyl Ions

Apparatus

Two types of sample cells were used in the experiments. The performance of disposable methacrylate cells, 10 mm pathlength, 12.5 mm x 12.5 mm x 45 mm outside dimensions with polyethylene caps (Fisher Scientific) was evaluated versus the performance of quartz cells, 10 mm x 10 mm x 50 mm inside dimensions (NSG Precision Cells) normally used with the instrument. A 2-place top-loader scale and a 4-place analytical balance were used, as appropriate, for preparing weight dilutions of solutions or for preparing sample or standard weight aliquants. Disposable plastic transfer pipets (Samco No. 204, 232 types) were used to transfer acid and uranium solutions to the sample cells. A Whatman Jet-pipet® dispenser was used to dispense the complexant solution. A variable-speed vortex shaker was used to mix the solution in the sample cells.

Reagents

All reagents used were ACS reagent grade unless otherwise specified. Uranium standard stock solutions were prepared from CRM 112-A, Uranium Metal Assay Standard, a NBL Certified Reference Material. The uranium metal standard stock solutions were prepared by dissolving the uranium metal standard in nitric acid with heat. Calibration standards and test samples were prepared from 1 *M* HNO_3 dilutions of the uranium standard stock solutions. Deionized distilled water was used to prepare all reagents. Uraplex®, a phosphate based solution commercially available from Chemchek[6,7], was used as a complexing agent to enhance the phosphorescence

of the uranyl ions in solution. Hydrogen peroxide, 30%, was used to destroy any organic materials present in samples.

Procedure

General Description of Procedure

The detailed procedure is provided in Appendix A. Sample or standard solutions to be measured in the KPA-11 were prepared by weighing 1.00 g ± 0.02 g of the uranium solution and 1.50 g ± 0.02 g of the complexing reagent into a cuvette using an electronic balance with push button tare capability and readable to 0.1 mg. The prepared solutions were then mixed using a vortex shaker. All concentrations for calibration and measurement were in units of μg U/g solution. In addition, all solutions were in the same density matrix as the calibration solutions, eliminating the need to correct for density.

The KPA allows for two separate calibrations covering two calibration ranges. Standard solutions containing uranium, ranging in concentration from the instrument detection limit of 4×10^{-5} μg U/g of solution up to 50 μg U/g of solution, were analyzed to determine the method detection limits and linearity for each calibration range. The optimal ranges of response were determined to be from 0.0006 to 0.02 μg U/g of solution for the low range (larger aperture) and from 0.1 to 5 μg U/g of solution for the high range (smaller aperture). Based on these results, the instrument was calibrated to cover the concentration range of 0.001 to 0.02 μg U/g of solution for the low-level and from 0.1 to 5 μg U/g of solution for the high-level.

A uranium solution was used for the reference solution instead of an europium solution because crystalline deposits formed in the europium reference solution and caused lower than expected reference responses for normalization purposes. A 0.200 μg U/g of solution with complexant (1.00 ± 0.02 g of 0.500 μg U/g of solution plus 1.50 ± 0.02 g of the complexing reagent) was used as the reference solution. This reference solution functioned as an external standard, normalizing the sample measurements to correct for internal instrument fluctuations and temperature drift. Once an instrument calibration was performed, there was seldom need to recalibrate as long as the concentration of reference stock solution used for all measurements remained constant. It was found that uranium reference solutions stored in a Teflon® bottle were stable for a year.[3] A complete (7-point) recalibration was performed once a year with a newly prepared reference solution. A daily instrumental background was measured and stored for subtraction from the intensities obtained in subsequent measurements. The background was determined with 1.00 ± 0.02 g of 1.00 *M* HNO_3 and 1.50 ± 0.02 g of complexant to simulate a measurement on an analyte-free sample. This provided a correction for low-level signals produced by sources other than the analyte such as electronic noise, impurities in the reagent, and stray ambient light. The instrument calibration was updated for background during the daily background measurement using the fixed (stable) concentration reference solution.

For ease of use and to minimize cross-contamination, disposable methacrylate cuvettes were used. In addition, disposable plastic pipets were used to transfer the 1 *M* HNO_3 and the uranium solutions. A Whatman Jet-pipet® dispenser was used to dispense the complexant solution. All glass beakers used were acid cleaned to leach uranium from the walls. The glass beakers were soaked in warm 4 *M* HNO_3 for several hours, rinsed with deionized, distilled water and allowed to air dry.

Preparation of Uranium Samples

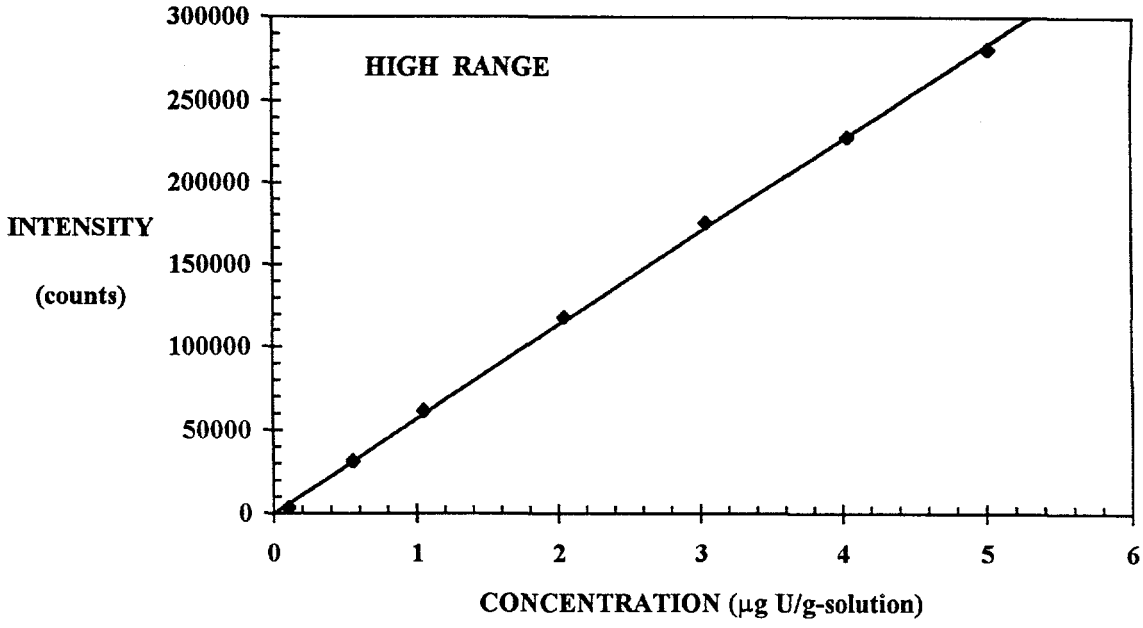
Four uranium sample types were prepared: standards for instrument calibration, knowns for system checks, QCs to determine if the measurement system is in statistical control, and blinds for method qualification studies. (NOTE: QCs are blinds for which the results obtained by the analyst are reported to a computerized measurement control system which then informs the analyst if the measurement system is in control. Quality assurance requirements at NBL dictate that reportable measurements cannot be made unless the measurement system is in control.) Two uranium stock solutions, 50 μg U/g of solution and 0.5 μg U/g of solution in 1 *M* HNO_3, were prepared for each of the four sample types from CRM 112-A, the NBL Certified Uranium Metal Assay Standard. For the high-level (associated with the high-range calibration curve) for each sample type, aliquants of the solution containing 50 μg U/g of solution were weighed into 50 mL beakers to prepare samples containing between 40 and 400 μg uranium. For the low-level (associated with the low-range calibration curve), aliquants of the solution containing 0.5 μg U/g of solution were weighed into 50 mL beakers to prepare samples containing between 0.08 and 1.6 μg uranium. The stock solutions and aliquants were verified (checked for proper preparation and aliquanting) by randomly sampling four to six samples for each solution or aliquant series and measuring them by phosphorimetry.

Prior to analysis, the aliquants were evaporated to dryness on a steam bath. They were diluted by a fixed amount by dissolving the dried sample aliquant in 8 g of 1 *M* HNO_3, taking a 0.1 g aliquant and diluting to 1.00 ± 0.02 g in the cuvette, followed by the addition of 1.50 ± 0.02 g of complexant. By following this dilution scheme, all samples were within the optimal measurement ranges and no further dilutions were necessary. This method of diluting samples by this fixed amount was also used with samples when no approximate concentration of the sample was known beforehand (see Applications section). Adjustments, if necessary, to this dilution ratio were made after the initial measurement so that the new sample preparation would fall within the optimal ranges of the KPA.

Developing Instrument Calibration Curves

The KPA was calibrated using seven calibration points for each range by measuring solutions of appropriate concentrations within the linearity limits of each range. A linear fit with zero intercept was used for the regression to fit the analytical response as a function of concentration. The calibration was verified by measuring dilutions of a 1000 ± 3 μg U/g of solution over the optimal ranges. The results of eight measurements in each range produced an average and standard deviation of 991 ± 13 μg U/g of solution for the high-level and 1001 ± 18 μg U/g of solution for the low-level. It should be noted that the daily background measurements and all sample measurements were performed using a stock reference solution of the same concentration as used with this original calibration.

A complete recalibration of the system, using new calibration solutions, was performed annually and after a new laser tube had been installed. Quality Control (QC) result trends will be used to determine when it is necessary to recalibrate the system. Figure 2 shows the calibration curves used for the low and high ranges.



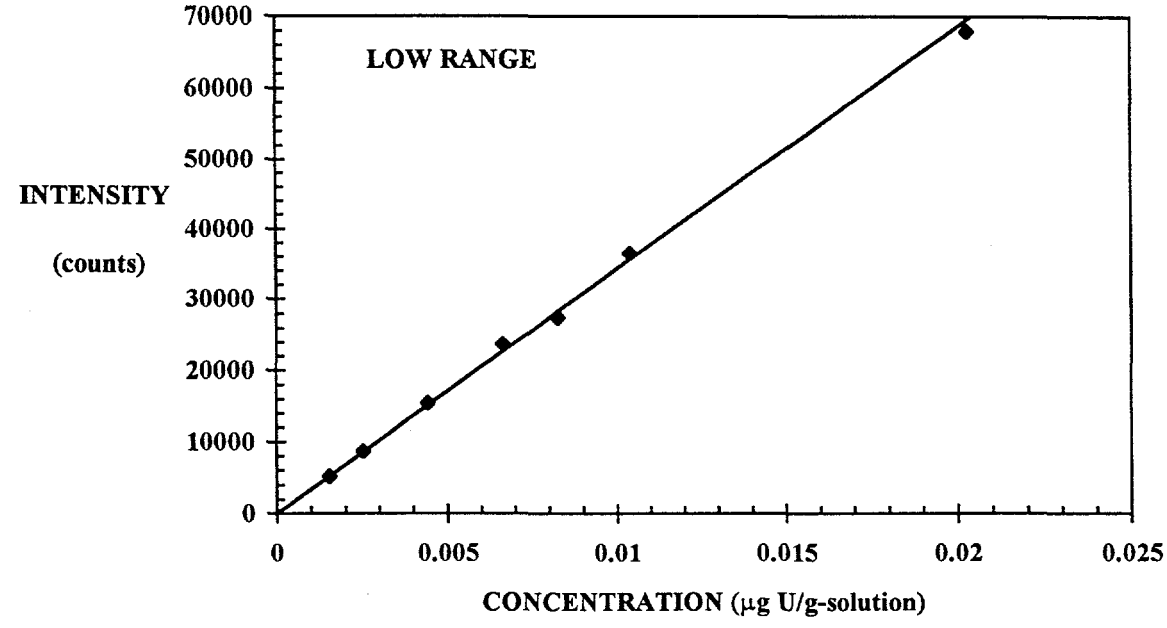


FIGURE 2 Calibration Curves

Determining Limits, Linearity, and Optimal Ranges

Kinetic phosphorimetry provides for the direct detection of uranium from the part-per-million to the sub-part-per-billion level. Optimal ranges for the best precision were determined. These ranges were subsequently used during the statistical evaluation of the method during qualification testing.

Because of the difficulty of cleaning the quartz cuvettes after each use, disposable methacrylate plastic cuvettes were used to eliminate contamination from previously measured samples and to maintain a reproducible background. These high quality plastic cuvettes have better transmission characteristics than polystyrene plastic cuvettes, but give higher background values than quartz cuvettes. To determine the loss in sensitivity using the methacrylate plastic cuvettes instead of the quartz cuvettes, the instrument detection limit (IDL) was determined for each type of cuvette. The IDL[9] is defined as the minimum concentration that can be determined by the instrument with 99% confidence that the analyte concentration in the matrix is greater than zero. The IDL for the methacrylate plastic cuvettes was determined by measuring the same blank solution in ten different cuvettes, calculating the standard deviation (S_{bkgd}) of the background measurements in terms of concentration in μg U/g of solution, and finally, calculating the IDL at the 99% confidence level using the formula of IDL = 2.8(S_{bkgd}). The IDL for the quartz cuvette was determined by making ten measurements on the same solution in a single quartz cuvette. The background measurements were performed for both the low and high calibration curve ranges. The results of these experiments are shown in Table 1.

TABLE 1 Instrument Detection Limits (IDL) Determined Using Methacrylate and Quartz Cuvettes

Cuvette Type	Low Range		High Range	
	S_{bkgd} (μg U/g-sol'n)	IDL = 2.8(S_{bkgd}) (μg U/g-sol'n)	S_{bkgd} (μg U/g-sol'n)	IDL = 2.8(S_{bkgd}) (μg U/g-sol'n)
Methacrylate	3.9×10^{-5}	11×10^{-5}	3.4×10^{-5}	10×10^{-5}
Quartz	1.4×10^{-5}	3.9×10^{-5}	2.1×10^{-5}	5.9×10^{-5}

A small loss in sensitivity is seen in using methacrylate cuvettes instead of quartz cuvettes. This is due to the larger background measurement variations caused by slight manufacturing variations in the methacrylate cuvettes. The detection limit (using quartz cuvettes) is at least three times better than conventional fluorometric methods and is equivalent to that of the Scintrex UA-3 Uranium Analyzer.

The method detection limit[9] (MDL) is the minimum concentration that can be measured by the procedure with 99% confidence that the analyte concentration in the matrix is greater than zero. Method detection limits were determined by measuring 10 times each, a 0.0005 μg U/g of solution for the low-level and a 0.5 μg U/g of solution for the high-level. The MDL for the methacrylate plastic cuvettes was determined by measuring the same solution in ten different cuvettes and the MDL for the quartz cuvette was determined by making ten measurements on the same solution in a single quartz cuvette. The standard deviations (S_{method}) for the low-level solution were 4.8×10^{-5} μg U/g of solution for the methacrylate and 1.8×10^{-5} μg U/g of solution for the quartz cells. The standard deviations for the high-level solution were 0.010 μg U/g of solution for the methacrylate and 0.003 μg U/g of solution for the quartz cuvettes. It should be noted that only one background is measured daily and its value is subtracted from subsequent measurements as a constant. The data used in the calculation of the standard deviations above did not include the variation in the background measurement. Therefore, to calculate method detection limits which include the background variation, the S_{bkg} data from

Table 1 must be included in the calculation by using the formula of MDL = $2.8((S^2_{bkg} + S^2_{method})^{1/2})$. The results of the calculation of the MDLs are shown in Table 2.

TABLE 2 Method Detection Limits (MDL) Corrected for the Background Variation

Cuvette Type	Low Range MDL = $2.8((S^2_{bkg} + S^2_{method})^{1/2})$ (μg U/g-sol'n)	High Range MDL = $2.8((S^2_{bkg} + S^2_{method})^{1/2})$ (μg U/g-sol'n)
Methacrylate	17×10^{-5}	0.03
Quartz	6×10^{-5}	0.01

The limit of quantitation[9] (LOQ) can be defined as ten times the standard deviation from the method detection limit and represents the minimum concentration that can be measured with a 99% probability that the measured value is within 50% of the true value. The results of the calculations are shown in Table 3. In the low range, a slightly higher LOQ results from using the methacrylate cuvettes instead of quartz cuvettes.

TABLE 3 Limits Of Quantitation (LOQ)

Cuvette Type	Low Range LOQ = $10(S^2_{bkg} + S^2_{method})^{1/2}$ (μg U/g-sol'n)	High Range LOQ = $10(S^2_{bkg} + S^2_{method})^{1/2}$ (μg U/g-sol'n)
Methacrylate	6×10^{-4}	0.1
Quartz	2×10^{-4}	0.03

The linearity of response was determined as 0.02 μg U/g of solution for the low-level and 5 μg U/g of solution for the high-level. At concentrations above these levels, convex curvature of the decay plot and a nonlinear intensity-concentration plot occur.

The optimal measurement ranges in terms of precision were selected based on the regions of linearity and the limits of quantitation determinations. The ranges selected were from 0.0006 to 0.02 μg U/g of solution for the low-level and from 0.1 to 5 μg U/g of solution for the high-level using the methacrylate cuvettes. The instrument was subsequently calibrated and the method statistically evaluated over these ranges.

The use of disposable methacrylate plastic cuvettes instead of quartz cuvettes saves time, prevents cross contamination problems, and provides acceptable results for concentrations above 6×10^{-4} μg U/g of solution. A small loss in sensitivity was found when using the methacrylate cuvettes instead of the quartz cuvettes in the low range.

QUALIFICATION OF THE METHOD

Statistical Plan of Analysis

A plan of analysis was prepared for the statistical analysis of the NBL procedure for the determination of uranium by laser phosphorimetry. The statistical plan allowed for the determination of the precision and bias which are required for the qualification of the method and for the establishment of laboratory limits.

The statistical plan called for three analysts (designated Analyst A, B, and C) performing measurements over a series of three days at the two concentration levels available as calibrated ranges on the instrument. On each day an analyst measured an initial blank (at both measurement levels of the instrument), two knowns (one at each level of the instrument), four QCs (two at each level of the instrument), and eight blind samples (blinds). A sufficient number of QCs was available to complete this study and for replacement of one out-of-control QC by two in-control QCs and for additional days of work. The analysts analyzed a total of 72 blinds (36 at each level), 18 knowns (9 at each level), and 36 QCs (18 at each level) for the entire study.

The knowns are used as system operation checks prior to the measurement of the QCs and the blinds. The QCs check the validity of the measurements of the laser phosphorimeter by checking the operation of the system during the day of measurement. Measurement control limits for knowns and QCs were set at 9% for high-level and 12% for low-level measurements based on previously measured data. Blinds are samples blinded to the analysts which are used to quantify the method. The analysts were informed of the range, high-level or low-level, in which the sample fell.

All samples were analyzed in duplicate. Determinations were to agree within 10.0% RD of each other. If they did not, an additional replicate was analyzed. The two measurements with the better agreement were accepted if $\leq$ 10.0% RD apart. The arithmetic mean of the two measurements was then determined and designated as the final assay value of the sample.

The choice of the samples and spares, as well as their order within the analysis schedule, was determined by a random number generator. The daily sample measurement schedule followed by all three analysts was as follows:

1. Blank (measured at both levels)
2. Known (High or Low)
3. Known (Low or High - opposite of #2)
4. QC (High or Low)
5. Blind
6. Blind
7. Blind
8. Blind
9. QC (Low or High - opposite of #4)
10. Blind
11. Blind
12. Blind
13. Blind
14. QC (High or Low)
15. QC (Low or High - opposite of #14)

The statistical analysis of the data investigated the following possible sources of variation: analytical error (method error, repeatability), analyst-to-analyst variability, day-to-day variability within analyst, and blind and QC-to-known variability. In addition, laboratory limits were established for the uranium laser phosphorimetry method.

Results and Discussion

QCs and Knowns

Each day, each analyst measured two knowns (one at each level for a total of six over the three days) and four QCs (two at each level for a total of twelve during the three days). The means and standard deviations of the knowns used by each analyst showed that day-to-day variation was not statistically significant for any of the analysts. The high-level and low-level knowns showed that none of the analyst-level combinations was significantly biased.

Table 4 shows the means and standard deviations of the %RDs for the QCs of each analyst for each analysis day. Day-to-day variation was not statistically significant for any of the analysts. Analyst-to-analyst variation was also not significant. However, the QCs of Analyst A exhibited a statistically significant bias. Analyst-to-analyst variation was not significant when the data were considered by uranium levels (high or low).

TABLE 4 Means And Standard Deviations of the %RDs for QCs by Analyst and Day

Day	Analyst A	Analyst B	Analyst C
Day 1			
Mean	- 1.2215	- 3.9529	- 2.0262
Std dev	± 2.0418	± 2.8948	± 2.2782
n	4	4	4
Day 2			
Mean	- 1.7199	+ 1.4647	- 0.0249
Std dev	± 0.7426	± 2.6438	± 2.6060
n	4	4	4
Day 3			
Mean	- 2.2355	- 0.4698	+ 2.8406
Std dev	± 2.0734	± 4.7539	± 2.6274
n	4	4	4
Total			
Mean	- 1.7256	- 0.9860	+ 0.2632
Std dev	± 1.6269	± 3.9800	± 3.0857
n	12	12	12

Table 5 shows that the high-level QCs of Analyst A were the cause of the significant bias in Analyst A's QC data. This was the only one of the six analyst-level groups that showed a statistically significant bias. All other sets of QCs were unbiased by level. However, it was observed that the mean value of the QCs is 2% to 3% lower than the mean value of the low-level QCs for all analysts. Individually, only Analyst A exhibited a significant difference in the high- vs low-level results.

TABLE 5 Analyst QCs Means (%RD) and Standard Deviations (%RSD) by Level

Level	Analyst A	Analyst B	Analyst C
High			
Mean	- 2.7946	- 2.5316	- 1.0645
Std dev	± 1.2154	± 3.4906	± 3.1323
n	6	6	6
Low			
Mean	- 0.6566	+ 0.5596	+ 1.5908
Std dev	± 1.2660	± 4.1138	± 2.6198
n	6	6	6

Blinds Data

Each analyst was required to analyze eight blinds each day for three days, a total of 24 blinds. Of the 24 blinds, 12 were high-level blinds and 12 were low-level blinds. The significant negative bias exhibited by Analyst A in the QC data required the blind sample data for Analyst A to be QC corrected to correct for sampling/procedural (non-instrumental) measured differences between the QCs and the blind samples. This correction brought the data of Analyst A in line with the data of Analyst B; however, the blind sample data of both Analysts A and B showed a negative bias. Daily and total blinds means (after correction) with standard deviations are illustrated in Table 6. Table 6 shows that the blinds results from Analysts A and B are similar but lower than those of Analyst C. Note that Analyst B exhibited a statistically significant negative bias (in the total data), and that Analyst A remained negatively biased even after the QC correction. The internal variation in data exhibited by each of the three analysts is similar (standard deviations are all a little more than 3%).

TABLE 6 Means (%RD) and Standard Deviations (%RSD) for Blinds by Analyst and Day

Day	Analyst A*	Analyst B	Analyst C
Day 1			
Mean	+ 0.4663	- 5.7067	- 1.2772
Std dev	± 2.3440	± 2.4955	± 2.4663
n	8	8	8
Day 2			
Mean	- 3.2064	+ 0.9526	- 3.2886
Std dev	± 2.4467	± 1.4121	± 1.9101
n	8	8	8
Day 3			
Mean	- 3.5478	- 3.8098	+ 1.5790
Std dev	± 3.5945	± 2.6606	± 2.8843
n	8	8	8
Total			
Mean	- 2.0960	- 2.8546	- 0.9956
Std dev	± 3.2973	± 3.5840	± 3.1073
95% CI	± 1.3926	± 1.5136	± 1.3123
n	24	24	24

* Analyst A blinds data QC corrected

Day-to-day variation was significant in the blinds data for all individual analysts. Note that day-to-day variation was not significant in the knowns and QCs. Although analyst-to-analyst variation was not significant in the QC data, analyst-to-analyst variation was statistically significant in the blinds data (even after the QC-correction of Analyst A data). Certain combination variations are significant here was because all data from both levels were combined. In fact, the low and high-level ranges are actually independent because of separate

calibrations. It was shown later, from long-term QC data, that while the low and high-levels have similar precision, the low-level results trend independently from the high-level results.

The results of the blinds data for all analysts are summarized by uranium level in Table 7. After QC correction of Analyst A data, analyst-to-analyst variation in the individual levels (high and low) was not significant. Analysts A and C continued the same trend seen in the QCs in that the mean value of the high-level measurements was 2% to 3% lower than the mean value of the low-level measurements. This difference was observed in the QCs of Analyst B, but not in the blinds of Analyst B.

TABLE 7 Analyst Blinds Means (%RD) and Standard Deviations (%RSD) by Level

Level	Analyst A	Analyst B	Analyst C
High			
Mean	- 3.3103	- 2.4118	- 2.1841
Std dev	± 2.6882	± 3.0438	± 2.7193
n	12	12	12
Low			
Mean	- 0.8816	- 3.2975	+ 0.1929
Std dev	± 3.5055	± 4.1431	± 3.1164
n	12	12	12

The high- *vs* low-level differences were not statistically significant for any of the analysts. The high-level data have a significant negative bias for all analysts; however, the lack of bias in the low-level data is primarily because of the greater amounts of variation in the low-level data by each analyst.

Combined Blind Sample Data

The combined data set of all blind samples showed the range of RDs to be from -8.31% to 2.23% for a range of 10.5% for the high-level blinds, and from -10.28% to 5.38% for a range of 15.7% for the low-level blinds. A summary of the blinds data for all analysts combined is shown, by level, in Table 8.

The negative bias for all measurement groups was evident by looking at the means ± the 95% confidence intervals of the mean. These sample measurements generally have a negative bias of about 2%. Neither the day-to-day variation nor the difference between high- and low-level samples was significant in the combined data set.

TABLE 8 Combined Blinds Data by Level

Level	n	Mean (%RD)	Std dev (%RSD)	95% CI
High	36	-2.6354	± 2.7839	± 0.9424
Low	36	-1.3287	± 3.8080	± 1.2890

An overall precision value of ± 3-4% RSD is comparable to the ± 2-3% RSD for the NBL laser fluorometric method and to the published ± 1-3% RSD midrange value for laser kinetic phosphorimetry by Chemchek.[6,7] By measuring samples over the optimal ranges as discussed above, cell and background variations do not contribute significantly to the random error. The KPA itself corrects for several variables in order to improve accuracy and precision. These include laser power, ambient temperature change, electrical line surges, and high voltage drift.

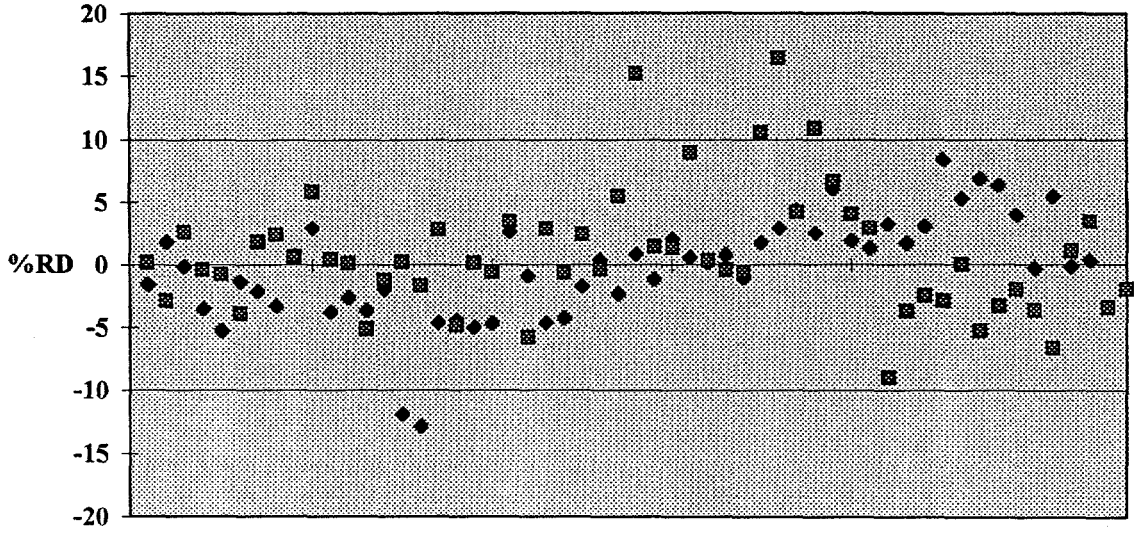
Weighing Errors

In the method used here, it was assumed that the weight of the sample was 1.00 g and the weight of the sample and complexant was 2.50 g. Weighing was performed quickly and accurately by placing the empty cell on a top-loading balance, taring the cell weight, and reading the net sample and total (sample plus complexant) aliquant weight after dispensing. Solutions were dispensed and weighed to within the range of ± 0.02 g. This error can be compensated for by making corrections for each measurement using the exact net weight of the sample and sample plus complexant using the correction factor of $0.4 \times (W_{sample + complexant})/W_{sample}$.

This equation equals 1.00 and assumes that W_{sample} = 1.00 g and $W_{sample+complexant}$= 2.50 g. For the weight range of ± 0.02 g, this correction factor ranges from 0.988 to 1.012 with a standard deviation of 0.5 %. Hence, not using the weight correction contributes 0.5% of the random error. With this correction, precisions of 2-3% RSD can be obtained for the method. Weighing errors due to evaporation were found to be negligible if the procedure is performed quickly.

Long Term QC Results

An evaluation of data obtained by four analysts who analyzed more than 100 uranium quality control standards over a two-year period from showed unbiased results over the optimal ranges. Over the low range, measurements gave a mean of -0.2% RD with precision of ± 3.6% RSD and over the high range, a mean of +0.2% RD with a precision of ± 3.4% RSD. Figure 3 shows the data over time for both the high and low ranges with the few outliers noted. While the overall statistics for both measurement levels are similar, it can be seen that the results for each level do not track each other. This is consistent with the fact that each analytical range is independent of the other in terms of calibration. This also verifies that the statistical evaluation of results should be done by level where variations in analyst, day, and level combinations were shown to not be significant.



CONTROL CHART 5/95 - 5/97

◆ HI RANGE ■ LOW RANGE

FIGURE 3 Long-Term QC Results

Determination of Measurement Limits

Several components of variation must be considered to determine the measurement control limits for the method. Components include analyst-to-analyst and the day-to-day variations in the sample measurements, measurement bias, and the measurement variation (the error term). They are listed below in Table 9.

TABLE 9 Measurement Control Limit Components

COMPONENT	HIGH-LEVEL	LOW-LEVEL
BIAS	-2.635%	-1.329%
ANALYST AND DAY	2.858%	3.486%
MEASUREMENT VARIATION	2.053%	2.718%
MEAN SQUARE ADDITION OF RANDOM COMPONENTS	3.520%	4.420%
95 % CONFIDENCE INTERVAL FOR RANDOM COMPONENTS	7.040%	8.840%
TOTAL	9.675%	10.169%

Measurement Control Limits for uranium assay measurements by laser phosphorimetry with the KPA were set at ± 10.0%, the same as in the NBL fluorometric method. As with all NBL control limits, these limits will be subject to annual review and revision.

APPLICATIONS

Applications of kinetic phosphorimetry at NBL have included: 1) the sorption and elution behavior of uranium on commercially available resins tested for the quantitative separation of uranium from elemental impurities, 2) the determination of the level of contamination present in the laboratory and in the reagents used to prepare uranium isotopic samples, and 3) the measurement of the uranium levels in retention tanks.

Determination of Elution Curves

Laser kinetic phosphorimetry has been used at NBL to determine sorption and elution curves and to estimate uranium losses at various stages in an ion exchange process study (topical report NBL-331)[10]. This investigation into a separation procedure with quantitative recovery of uranium was prompted by a need to meet waste reduction requirements and reference material characterization demands. At NBL, a major emphasis has been placed on developing uranium assay measurement methods that will avoid the generation of mixed wastes. The measurement methods under development at NBL, however, are not expected to be as free of matrix interferences as existing procedures and therefore will require prior removal of impurities. In addition, the necessity for a high degree of accuracy in the uranium assays performed at NBL demands a purification procedure providing essentially quantitative (>99.9%) recovery of uranium. Therefore, uranium separation procedures that provide large separation factors for a variety of impurities were selected and investigated for quantitative recovery of uranium.

The performances of four Bio-Rad resins, AG 1-X2, 1-X4, 1-X8 and MP-1, were initially tested with pure uranium. This allowed an initial comparison of the capabilities of the resins prior to method optimization. Experiments were done in triplicate and repeated to confirm the results. Samples containing 12 mg of uranium were dissolved in 15 mL of 8 *M* HCl, and the solutions were transferred to preconditioned columns. An additional 10 mL of acid was used to rinse the beaker, and the wash solutions were transferred to the column. The 25 mL of solution used to load the sample was collected. The columns were successively washed three times (20 mL, 10 mL, and 10 mL aliquots) with 8 *M* HCl and the wash fractions were collected separately. Uranium was then eluted with varying portions (initially with 2 mL and 3 mL aliquots, then five 5 mL aliquots, and finally two 5 mL aliquots were combined to give a 10 mL portion and thus a total of 40 mL of eluant) of 1 *M* HCl. These eluate fractions were individually collected. All the collected load, wash and eluate fractions were evaporated, fumed twice in concentrated nitric acid, redissolved in 1 *M* HNO_3 and assayed for uranium using the KPA technique.

Table 10 gives the sorption and elution behavior of the four resins. When the sample was transferred onto the resin, a pale yellow-colored region was observed at the top of the resin bed. With the AG 1-X2 resin, the KPA data indicated that uranium was lost in both the load and the wash fractions. This was visually observable as the broad, pale yellow band became diffuse and moved down the column. An average of over 30% of the uranium was lost in the load and wash solutions for this resin. The other three resins performed significantly better, with cumulative losses during the 25 mL load and 40 mL wash being less than 5 µg U. While the majority of the uranium was desorbed in the first 20 mL of eluant, there was some tailing evident in later eluate fractions. Based on these results, the AG 1-X2 resin was eliminated from the study.

The NBL Titrimetric Method results indicated that uranium recovery for both the AG 1-X8 and AG MP-1 resins averaged 100%. KPA analysis corroborated these results.

TABLE 10 Adsorption And Elution Behavior Of Uranium On Bio-Rad Resins

Volume (mL)	Effluent Fraction	Micrograms Uranium in Effluent Fraction When 12 mg of Uranium was Loaded to the Column			
		Bio-Rad Resin			
		1-X2	1-X4	1-X8	MP-1
25	Load	21.0	0.3	0.5	0.1
20	Wash 1	740.1	0.6	0.5	0.1
10	Wash 2	1131.6	1.4	0.3	0.7
10	Wash 3	1754.3	2.5	0.1	4.0
2	Eluate 1	7761.9	8.0	644.9	0.3
3	Eluate 2	81.6	9719.8	7646.7	9918.4
5	Eluate 3	7.2	1484.1	2152.7	890.9
5	Eluate 4	0.4	13.8	145.4	110.2
5	Eluate 5	0.1	2.5	17.7	14.7
5	Eluate 6	0.0	0.5	3.5	3.0
5	Eluate 7	0.0	0.1	0.8	1.5
10	Eluate 8	0.0	1.8	0.3	0.2

-Load and Washes done in 8 M HCl
-Elutions in 1 M HCl
-Data are averages of 3 runs with the exception of 1-X2 resin (2 runs)

The Bio-Rad AG 1-X8 and AG MP-1 resins were also tested for uranium breakthrough and uranium recovery on 5 mg, 10 mg, 15 mg, 20 mg and 25 mg size uranium samples by using laser phosphorimetry. For uranium breakthrough tests, samples were transferred with 25 mL of 8 *M* HCl and successively washed with 20 mL of 8 *M* HCl until at least 160 mL of the acid was added to the column. The overall results indicate that the losses (< 0.02%) are minimal for the amounts of acid (< 50 mL) used for the ion exchange of actual samples.

In addition to this initial testing of the variables affecting the sorption and elution of the various sorbed complexes, the recovery of uranium, including acid concentrations of the load and wash solutions and the degree of cross-linking of the ion exchange resin were investigated and are described in the report. Statistical testing of an optimized procedure using Bio-Rad AG 1-X8 and AG MP-1 resins was also discussed. The effect of impurities on the quantitative recovery of 12 mg uranium samples was tested over the range of 10% by weight of impurities (mole ratio of U to impurities of 2:1) to 40% by weight of impurities (mole ratio of U to impurities of approximately 1:1.7).

Using laser phosphorimetry for sorption and elution behavior, the NBL Titrimetric Method to evaluate the quantitative recovery of uranium, and X-ray fluorescence for impurity analysis, the study showed that both Bio-Rad AG 1-X8 and AG MP-1 resins were capable of quantitative recovery (>99.9%) while providing separation from commonly found impurities that could potentially interfere with uranium analysis.

Uranium Isotopic Blank Study

In conjunction with the work on a Uranium Isotopic Dilution Mass Spectrometry method, a study was performed to determine the level of contamination present in the laboratory and in the reagents used to prepare isotopic samples.[11] Presently, NBL is using the U/TEVA-Spec column separation method for isotopic sample purification because it provides more consistent uranium recoveries and a purer product than the ether extraction method. A comparison of preparation blanks performed before and after laboratory cleaning showed that by using good analytical technique and working in a clean environment, it is possible to prepare samples for isotopic analysis which contain less than 0.05 nanograms of uranium contaminant per milligram of uranium.

Retention Tank Samples

NBL routinely monitors the laboratory's retention tanks for uranium using phosphorimetry. The advantage over alpha spectrometry and nondestructive methods is the higher sensitivity (ng/g versus μg/g) and the measurement of total uranium content (all isotopes). The tanks contain mostly phosphates, carbonates, surfactants, and neutralized acids which cause quenching of uranyl luminescence. NBL dissolution methods were used to pretreat retention tank samples containing uranium to provide solutions for analysis. For retention tank measurements, samples were heated in nitric acid to dissolve uranium. For samples in which the matrix was significantly soluble in nitric acid, the entire sample is dissolved. For samples in which the matrix was not significantly soluble in nitric acid, the sample was then filtered and ashed. If necessary, further treatment included adding nitric and hydrofluoric acid to dissolve the residue. The filtrate and redissolved residue were combined. The sample or a portion of it was evaporated, fumed twice in concentrated nitric acid, redissolved in 1 *M* HNO_3 and assayed for uranium using the KPA technique. The KPA results from samples pretreated by this method have acceptable decay times (> 200 μs) and linearity (0.99+). The uranium content of the retention tank was then calculated from the KPA assay and the retention tank liquid volume.

CONCLUSION

Replacement of the Scintrex UA-3 Analyzer with a kinetic phosphorescence analyzer was effectively accomplished, with accuracy and precision equivalent to the NBL fluorometric determination and without the need for internal standards. In addition, the technique is fast and the phosphorescence lifetime determination capabilities of the KPA offer additional selectivity. The use of disposable cuvettes was found to be acceptable when uranium concentrations are greater than 6×10^{-4} μg U/g-solution. The accuracy of the method was ± 2% RD, with a precision of ± 3-4% RSD for the range of 6×10^{-4} to 5 μg U/g of solution. Statistical analysis showed that by level (high or low), no significant analyst-to-analyst or day-to-day variations were found. Long-term QC results were unbiased. Applications of the method include uranium contamination studies, testing uranium purification procedures, and the determination of uranium in retention tank samples.

term QC results were unbiased. Applications of the method include uranium contamination studies, testing uranium purification procedures, and the determination of uranium in retention tank samples.

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APPENDIX A

NBL PROCEDURE NBL-SA-U(E)-8: DETERMINATION OF MICRO- TO SUB-MICROGRAM QUANTITIES OF URANIUM USING LASER-INDUCED KINETIC PHOSPHORIMETRY

DETERMINATION OF MICRO- TO SUB-MICROGRAM QUANTITIES OF URANIUM USING LASER-INDUCED KINETIC PHOSPHORIMETRY

I. INTRODUCTION

A. Applicability

This method is used to measure uranium concentrations in effluent and other materials in which uranium is present at the micro- to sub-microgram level.

B. Summary of Method

The phosphorimeter employed is a commercially-available Kinetic Phosphorescence Analyzer, KPA-11 (Chemchek, Richland, WA).[1] This instrument uses a pulsed nitrogen/dye laser to supply monochromatic ultraviolet light to excite uranium atoms in the sample solution. These atoms then emit a green phosphorescence which is filtered, amplified, and measured. To protect the uranyl ion from quenching, a phosphate-based complexing reagent is added which provides phosphorescence lifetimes for UO_2^{2+} of a few hundred microseconds.

The KPA incorporates kinetic phosphorimetry techniques in a computerized system. The kinetic analysis of the uranyl phosphorescence provides highly precise and accurate measurements, thus eliminating the need for internal standards. The system takes phosphorescence measurements during multiple time gates, analyzes the kinetics of the phosphorescence decay, and calculates the result in terms of selected units. The KPA performs a background correction and automatically corrects for most sample quenching from sample matrix effects.

Samples and standards are dissolved and diluted to an appropriate volume with 1 *M* HNO_3 before measurement. Concentrations are determined on a weight basis. No density corrections are needed since all samples and standards are prepared in the same density matrix.

C. Method Performance

This method is capable of producing a relative standard deviation $\leq$ 3.0% with a bias of less than 2.0% relative difference for solutions containing 1.0 x 10^{-3} to 5.0 μg U/g solution. The optimized low operating range is 1.0 x 10^{-3} to 2.0 x 10^{-2} μg U/g solution. The optimized high operating range is 0.50 to 5.0 μg U/g solution. Time required per determination is six minutes.

The detection limit for uranium is 2 x 10^{-5} μg U/g solution. A solution near the detection limit was analyzed 10 times. The detection limit was calculated as three times the standard deviation of the measurements.

D. Interferences/Limitations

1. Because of the low level of uranium in the samples to be analyzed, care must always be taken that uranium is not introduced to the samples as an impurity by reagent additions or sample treatments.[1]

2. Several interfering species exist, which either enhance or quench the phosphorescence intensities:

   a. Materials other than uranium may absorb at the 425 nm excitation wavelength (inner filter effect) and diminish the amount of light striking the uranium. Visible excitation light (425 nm) may be absorbed by yellow solutions, for example, chromate. Reduced signals and low results may occur.[1,2,3,4]

   b. Many organic substances, such as humic acids present in soil and ground water, and organic degradation products from incomplete ashing, emit luminescence of varying lifetimes after excitation, causing distortions in the decay plot.[1,2,3,4,5]

   c. Shortened lifetime and reduced phosphorescence intensities of the excited uranyl complex result when quenching occurs by organic or inorganic species. Reliable results cannot be obtained when quenching exceeds 80 to 90%. Reducing agents such as alcohols, halides (except fluoride), and oxidizable metals [e.g., silver, lead, iron(II), manganese(II), and thallium], are strong quenching agents.[1,2,3,4,5]

   d. A chemical may interfere by complexing the uranyl ion differently than the phosphate complexing reagent, or may prevent the phosphate from complexing the uranyl ion. The effect will be noted by a different lifetime.[1,2,3,4]

   e. Suspended particles interfere by strongly reflecting the laser beam. The reflected light will disrupt the normal decay curve of uranium causing distortions in the decay plot.[1,5]

f. A substance that holds the uranium out of the photoluminescence process causes static quenching and low results. An example is a complexant that maintains uranium as U(IV).[1,2,3,4] (Photoluminescent uranium is the UO_2^{2+} ion.)

3. These potential problems can be overcome using a variety of sample pretreatment processes.

a. Evaporating the sample to dryness with an oxidizing acid (e.g., nitric acid) and with hydrogen peroxide (if organics are present) eliminates some quenching agents and fluorescers. Particles/colloids may also be coagulated or eliminated. Substantial amounts of organic materials will not be eliminated.[1,2,3,4,5]

b. If the concentration of uranium in the samples is high enough so that they can be diluted one hundredfold with 1 *M* HNO_3, then interferences can be minimized by diluting their effect.[1,2,3,4,5]

c. Samples of urine, vegetation, and soil or water-bearing decayed vegetation must be thoroughly wet-ashed to eliminate substances that may either strongly fluoresce or quench.[1,2,3]

d. Chemical separations are only required for very low levels of uranium with a substantially complex matrix.[1,3]

E. Traceability to Primary Standards

The KPA is calibrated using uranium reference solutions that are prepared from uranium standard solutions prepared according to NBL-CAL-U(E)-2 using CRM 112-A, a NBL certified reference material.

F. Safety Procedures

Review Material Safety Data Sheets (MSDS) and safety procedures in the NBL Safety Analysis Report (SAR) prior to performing the procedure.

The levels of uranium measured by the Chemchek KPA-11 Phosphorimeter are usually very low. Suitable precautions must be taken to avoid contamination. Wear safety glasses or goggles and lab coats when handling samples.

Nitric acid is very corrosive and can cause painful burns. Wear gloves, safety glasses or goggles, and labcoats when handling. If

acid contacts the skin, flush the affected area with water. If a burn results from acid contact, seek medical treatment.

If it is operated with the cover on and all interlock devices in place, the Chemchek KPA-11 Phosphorimeter is considered a Class I laser under requirements of 21 CFR 1040.1. No additional protective measures need to be taken by personnel operating the laser under normal conditions.

To minimize shock hazard, the instrument chassis and cabinet must be connected to an electrical ground. The power cable must be plugged into a three-contact outlet.

NOTE: **The instrument contains a potentially hazardous dye and laser. Do not open the instrument without obtaining instructions from and the prior approval of the Environmental Safety and Health Office (ESHO).**

II. INSTRUMENTS, APPARATUS, AND REAGENTS

A. Instruments

1. Balance, 80-g capacity, readable to 0.1 mg (4-place balance), with push button tare capability.

2. Balance, 1200-g capacity, readable to 0.01 g. (2-place balance).

3. Model KPA-11 Laser Kinetic Phoshorimeter/PC System including software, Chemchek Instruments, Inc.

B. Apparatus

1. Uranium emission filter, 25-mm diameter, central wavelength 515 nm, bandpass 10 nm, to replace KPA-11 europium-reference emission filter.[1]

2. Cuvettes, methacrylate, 10 mm pathlength, 12.5- x 12.5- x 45-mm outside dimensions, disposable.

3. Cuvette caps, polyethylene, disposable.

4. Cuvette racks, polypropylene.

5. Vortex shaker, variable-speed.

6. Pipets, plastic, transfer, disposable, Samco No. 204, 232 (order from Fisher Scientific).

7. Dispenser, Jet-pipet®, Whatman.

8. Beakers, polypropylene, disposable, 15-, 50-mL.

9. Beakers, glass, 50-mL, acid-cleaned. Soak in warm 4 *M* HNO_3 for several hours, rinse with distilled deionized water, and allow to dry.

10. Bottles, Teflon®, 125-, 1000-mL.

11. Parafilm®, Grade M.

C. Reagents

All reagents are ACS reagent grade unless otherwise specified. Solutions may be made up in multiples or fractions as required. Give consideration to waste minimization in determining the amounts of reagents prepared.

1. "Uraplex" uranium complexing reagent. Commercially available from Chemchek. Dilute per supplier instructions and store in Teflon® bottle in refrigerator for up to 3 months.

2. Water, deionized distilled.

3. Nitric acid, concentrated.

4. Nitric acid, 1 *M* HNO_3. Add 63 mL of concentrated nitric acid to about 700 mL distilled water. Dilute to 1 L. Store in a 1-L Teflon® bottle.

5. Hydrogen peroxide, 30%.

6. Uranium standard stock solutions, 50 μg U/g and 0.5 μg U/g solutions, to prepare knowns and blinds.

   a. Using a 4-place balance, weigh an appropriate amount of a uranium standard solution prepared according to procedure NBL-CAL-U(E)-2, then transfer it to a previously-weighed (2-place balance) suitably-sized Teflon® bottle.

   b. Calculate the final solution weight required to prepare a 50 μg U/g solution uranium standard stock solution (see step IV.A).

c. Add 1 *M* HNO_3 to the bottle to obtain the calculated solution weight. Weigh and mix thoroughly.

d. Calculate the concentration (factor, f) of the stock solution (see step IV.B). Label bottle with preparation date, preparer's initials, notebook reference where preparation is documented, and the solution concentration.

e. Using a 4-place balance, weigh an appropriate amount of the 50 μg U/g solution uranium standard stock solution, then transfer it to a previously-weighed (2-place balance) suitably-sized Teflon® bottle.

f. Calculate the final solution weight required to prepare a 0.5 μg U/g solution uranium standard stock solution (see step IV.C).

g. Add 1 *M* HNO_3 to the bottle to obtain the calculated solution weight. Weigh and mix thoroughly.

h. Calculate the concentration (factor, f_s) of the stock solution (see step IV.D). Label bottle with preparation date, preparer's initials, notebook reference where preparation is documented, and the solution concentration.

7. Uranium reference solution, 0.500 μg U/g solution.

a. Using a 4-place balance, weigh an appropriate amount of the 50 μg U/g solution uranium standard stock solution, then transfer it to a previously-weighed (2-place balance) 125-mL Teflon® bottle.

b. Calculate the final solution weight required to prepare a 0.500 μg U/g solution uranium reference solution (see section IV.E).

c. Add 1 *M* HNO_3 to the bottle to obtain the calculated solution weight. Weigh and mix thoroughly.

d. Calculate the concentration (factor, f_r) of the reference solution (see section IV.F). Label bottle with preparation date, preparer's initials, notebook reference where preparation is documented, and the solution concentration.

III. PROCEDURE

A. Sample Preparation

The uranium sample should be in aqueous solution near neutrality with little suspended matter and free of large amounts of organic materials.

1. Tare a clean 50-mL beaker. Weigh an aliquot of the sample to contain between 40 and 400 μg U, if possible, into the beaker using a disposable pipet (Samco No. 204). Record the weight, W_a, and the dilution (bottle) factor of the sample, f_b.

2. Add 2-3 mL of concentrated HNO_3 to the solution.

3. Add 0.5 mL of hydrogen peroxide if organics are present.

4. Heat the solution to dryness on a steam bath to obtain a pale yellow or white residue. Repeat steps 2, 3, and 4 as necessary.

5. If the sample is to be stored, cover the beaker with parafilm®.

B. Instrument Preparation

1. Turn on the KPA by pressing the power switch on the power strip. Assure that indicator lights on the instrument, computer and printer are on.

2. Assure that the Main Menu screen Time Gates reads 5,49 and the Laser Pulses read 1000-1000.

C. Instrument Calibration

1. On the Main Menu screen, select [F2] - Calibrate

2. On the Calibration Menu screen, select [F1] - Calibration.

3. Verify that all seven concentrations have a check mark placed before them. If not, use the space bar and the arrow down key [↓] to add a check.

4. Prepare reference:

   a. Tare a new cuvette. Weigh 1.0 ± 0.02 g of the uranium reference solution (see step II.C.7) into the cuvette using a disposable pipet (Samco No. 232).

   b. Tare the same cuvette. Weigh 1.5 ± 0.02 g of Uraplex solution into the cuvette using a dispenser or disposable

pipet (Samco No. 232). Cap and mix well using Vortex shaker.

c. Place the cuvette in the reference holder of the KPA door.

5. Prepare blank:

a. Tare a new cuvette. Weigh 1.0 ± 0.02 g of 1 *M* HNO_3 solution into the cuvette using a disposable pipet (Samco No. 232).

b. Tare the same cuvette. Weigh 1.5 ± 0.02 g of Uraplex solution into the cuvette using a dispenser or disposable pipet (Samco No. 232). Cap and mix well using Vortex shaker.

c. Place the cuvette in sample holder of the KPA door.

6. Close and lock the KPA door.

7. Select [F3] - Background.

8. Select [F1] - Measure Background.

9. Enter initials and chemist ID number. Press [Enter].

10. Press [Enter] and wait for the background to be measured. Note that the red laser indicator light of the KPA is on. If not, assure that the door is locked.

11. From the analytical report (printed or on-screen), review the diagnostic information for the validity of the result and take the appropriate action. For best results, the lifetime should be greater than 200 μs with a R^2 value greater than 0.99. Record the reference intensity, lifetime, R^2, and blank (sample) intensity in the log book.

a. The reference intensity should be between 10,000 - 70,000. An intensity value less than 10,000 for a properly prepared reference is indicative of problems with the laser tube or dye cell.[3]

b. The blank (sample) intensity for the high range should be a few counts and for the low range it should be up to several hundred counts. A high background is due to dirty cuvette windows or contamination. Prepare and measure a new blank with a new cuvette. If necessary, prepare a new 1 *M* HNO_3 solution.

c. The reference lifetime should be greater than 200 μs. A smaller value occurs when Uraplex decays after several months' storage; prepare and measure a new reference using freshly prepared Uraplex solution.

d. A R^2 value should be greater than 0.99. A smaller value is caused by contaminating sample phosphors or dirty cell windows; prepare and measure a new reference/Uraplex solution.

12. Select [F1] - Continuation Calibration.

13. When the Calibration Screen appears, verify that the bottom line contains a linear equation with a zero intercept. If not, press [F5] and select Linear, 0 Intercept.

14. Press [F4] - Plot Calibration. Inspect the plot to confirm a good fit of calibration results.

15. Press [ESC] to end.

16. Press [Page Up] to switch to the High range.

17. Repeat steps III.C.7-15 for the High range using the same reference and blank.

18. Press [ESC] two times.

19. Enter initials and chemist ID number then press [Enter]. Include a calibration comment if desired. Press [Enter].

20. Remove the "blank" cuvette from the sample holder of the KPA door.

D. Sample Measurement

NOTE 1: Use the same batch of 1 *M* HNO_3 that was used to prepare the blank for instrument calibration (see step III.C.5).

NOTE 2: Use a 4-place balance throughout this section.

1. Tare uncovered sample beaker (see step III.A.5). Weigh 8 g of 1 *M* HNO_3 into the beaker using a disposable pipet (Samco No. 204) and record weight, W_o. Swirl beaker to dissolve and mix.

2. Tare a 15-mL disposable beaker. Weigh 1 g of sample solution into the beaker using a disposable pipet (Samco No. 204) and record weight, W_i. Cover original sample beaker with parafilm.

3. Add 1 *M* HNO_3 into the disposable beaker using a disposable pipet (Samco No. 204) to reach a final weight of 10 g and record weight, W_f. Swirl to mix.

4. Tare a new cuvette. Weigh 1.0 ± 0.02 g of the diluted sample from the disposable beaker into the cuvette using a disposable pipet (Samco No. 232).

5. Tare the same cuvette. Weigh 1.5 ± 0.02 g of Uraplex solution into the cuvette using a dispenser or disposable pipet (Samco No. 232). Cap and mix well using Vortex shaker.

6. Place the cuvette in sample holder of the KPA door.

7. Close and lock the KPA door.

8. On the Main Menu screen, select [F1] - Analyze

9. On the Sample Analysis Menu screen, select [F1] - Analysis of Sample.

10. Enter initials and chemist ID number. Press [Enter].

11. On the Analysis of Sample Menu screen:

    a. Enter a filename in Sample ID. Press [Enter].

    b. Enter LIMS number in description. Press [Enter].

    c. Choose range (high/low) if known (defaults to low). Press [Enter].

    d. Assure that the dilution factors are set at 1 mL each.

    e. Press [F1] - Continue

12. Press [Enter] and wait for the sample to be measured.
    Note: The red laser indicator light of the KPA should be on. If not, assure that the door is locked.

13. Press [F4] - Plot. View the sample decay linearity. Results with a R^2 less than 0.96 will plot automatically.

14. Press [ESC].

15. Press [F6] - Sample relation to Std.

16. Press [ESC].

17. Remove the cuvette from the sample holder of the KPA door.

18. Verify that the result shown on the plot is within the chosen range: High range: 0.50 to 5.0 μg U/g solution; Low range: 1.0 x 10^{-3} to 2.0 x 10^{-2} μg U/g solution. If the results are within the chosen range, go to step III.D.19. If not, continue in this step:

    a. If the result is greater than 50 μg U/g solution or less than 1.0 x 10^{-3} μg U/g solution, repeat measurement using a different sample dilution (change W_i and/or W_f, see steps III.D.2-3).

        (1) Press [F1] - Analyze Next Sample.

        (2) Follow steps III.D.2-7, and steps III.D.11-18.

    b. If the result is between 5 and 50 μg U/g solution or between 2.0 x 10^{-2} and 0.5 μg U/g solution, repeat measurement using a second sample dilution done in a cuvette.

        (1) Press [F1] - Analyze Next Sample

        (2) Tare a new cuvette. Weigh an appropriate amount of the diluted sample from the disposable beaker into the cuvette using a disposable pipet (Samco No. 232) and record weight, W_i' ($0.05 \leq W_i' \leq 1.02$ g).

        (3) Add 1 *M* HNO_3 into the cuvette using a disposable pipet (Samco No. 232) to 1.0 $\pm$ 0.02 g and record weight, W_f'.

        (4) Follow steps III.D.5-7, and steps III.D.11-18.

19. Press [F1] - Analyze Next Sample, and repeat III.D.4-7, 11-18 for duplicate analysis.

20. To analyze another sample, press [F1] - Analyze Next Sample, and repeat III.D.1-7, 11-19.

21. When samples measurements are complete, press [ESC] three times. Data is saved.

22. Type Y to return to DOS.

23. Turn off the KPA by pressing the power switch on the power strip.

E. Validation of Result

From the analytical report (printed or on-screen), review the diagnostic information.

1. If the lifetime is greater than 200 μs with a R^2 value greater than 0.99, the result is valid.

2. If the results show any of the following conditions, take the appropriate action and repeat the measurement.

   a. If the lifetime is short, less than 100 μs and/or curved, with a R^2 value less than 0.96, then either

      (1) Increase the dilution as large as practical, or

      (2) Wet-ash the sample to destroy interfering organics.[1,2,3]

   b. If the lifetime is greater than 350 - 600 μs and the decay plot is curved, with a R^2 value less than 0.96, particulates and/or organic phosphors may be present or the cell is dirty, then either

      (1) Centrifuge or wet-ash the sample,[1,2,3] or

      (2) Prepare and measure the sample with a new cuvette.

   c. If the result is near the analytical detection limit with a curved decay plot, with a R^2 value less than 0.96, or a lifetime less than 100 μs, then

      (1) If the cell is contaminated or dirty, prepare and measure the sample with a new cuvette.

      (2) Check lifetimes with standard additions (e.g., 0.1 mL of uranium reference solution in the cell).[1,2,3] If the same result is obtained, the luminescence may be completely quenched. Either

         (a) Wet-ash the sample to destroy interfering organics,[1,2,3] or

         (b) Perform chemical separation of dissolved minerals, soils, or metals from the sample (ion exchange, ion chromatography and solvent-solvent extraction).

F. Data Handling

1. From the analytical report (printed or on-screen), record the KPA Result, μg U/g solution.

2. Calculate total uranium, in μg, for the aliquant (see section IV.G).

3. For known standards, calculate the %RD (see section IV.H).

4. For samples, calculate uranium concentration, μg U/g (see section IV.I).

G. DOCUMENTATION

Record all data and results on the KPA Results Form (see Attachment 1). All data collected, calculated and recorded on the KPA Results Form should be included in a NBL notebook. Include the date, number and issue date of this procedure, the balances used, the notebook reference which documents solution preparation, sample numbers and their dilution (bottle) factors.

IV. CALCULATIONS

A. Final solution weight to prepare 50 μg U/g solution uranium standard stock solution.

$$\text{final soln wt, g} = \frac{(\text{g std soln taken})(\text{conc std soln, } \mu\text{g U/g})}{50\ \mu\text{g U/g}}$$

B. Concentration of uranium standard stock solution, f.

$$f,\ \mu\text{g U/g} = \frac{(\text{g std soln taken})(\text{conc std soln, } \mu\text{g U/g})}{\text{final soln wt, g}}$$

C. Final solution weight to prepare 0.5 μg U/g solution uranium standard stock solution.

$$\text{final soln wt, g} = \frac{(\text{g stock soln taken})(f)}{0.5\ \mu\text{g U/g soln}}$$

where: f = result from IV.B in μg U/g solution.

D. Concentration of uranium standard stock solution, f_s.

$$f_s,\ \mu\text{g U/g} = \frac{(\text{g stock soln taken})(f)}{\text{soln wt, g}}$$

where: f = result from IV.B in μg U/g solution.

E. Final solution weight to prepare 0.500 μg U/g solution uranium reference solution.

$$final\ soln\ wt,\ g = \frac{(g\ stock\ soln\ taken)\,(f)}{0.500\ \mu g\ U/g\ soln}$$

where: f = result from IV.B in μg U/g solution.

F. Concentration of uranium reference solution, f_r.

$$f_r,\ \mu g\ U/g = \frac{(g\ stock\ soln\ taken)\,(f)}{soln\ wt,\ g}$$

where: f = result from IV.B in μg U/g solution.

G. Total uranium for the aliquant.

$$Total\ U,\ \mu g = W_0\ x\ \frac{W_f}{W_i}\ x\ \frac{W_f'}{W_i'}\ x\ KPA\ RESULT$$

where: W_0 = the dissolution weight in grams
W_f = the final sample weight of the first dilution in grams
W_i = the aliquant for the first dilution in grams
W_f' = the final sample weight of the second dilution in grams
W_i' = the aliquant from the second dilution in grams
KPA RESULT = the uranium assay in μg U/g solution

H. Percent relative difference, %RD.

$$\%RD = \frac{\mu g\ U\ measured - \mu g\ U\ known}{\mu g\ U\ known} \times 100$$

I. Uranium concentration for the sample.

$$U\ conc,\ \mu g\ U/g = \frac{Total\ U}{W_a\ x\ f_b}$$

where: f_b = the dilution (bottle) factor in (g sample)/(g solution)
W_a = the aliquant weight in grams
Total U = result from IV.G in μg U

V. QUALITY ASSURANCE

A. Known and Blind Standards Preparation

1. Weigh aliquants into acid-cleaned 50-mL beakers. For blind standards, submit beakers to QC Program project leader.

   a. High Range: Use the 50 μg U/g uranium standard stock solution (see step II.C.6) to prepare aliquants containing between 40 and 400 μg U.

b. Low Range: Use the 0.5 μg U/g uranium standard stock solution (see step II.C.6) to prepare aliquants containing between 0.08 and 1.6 μg U.

2. Evaporate to dryness on a steam bath.

3. Cover the beaker with parafilm®.

B. Measurement Control

At the beginning and end of each day of analysis, analyze a series of "known" and "blind" standards to determine the acceptability of the day's data as described in Figure 1 for each level used.

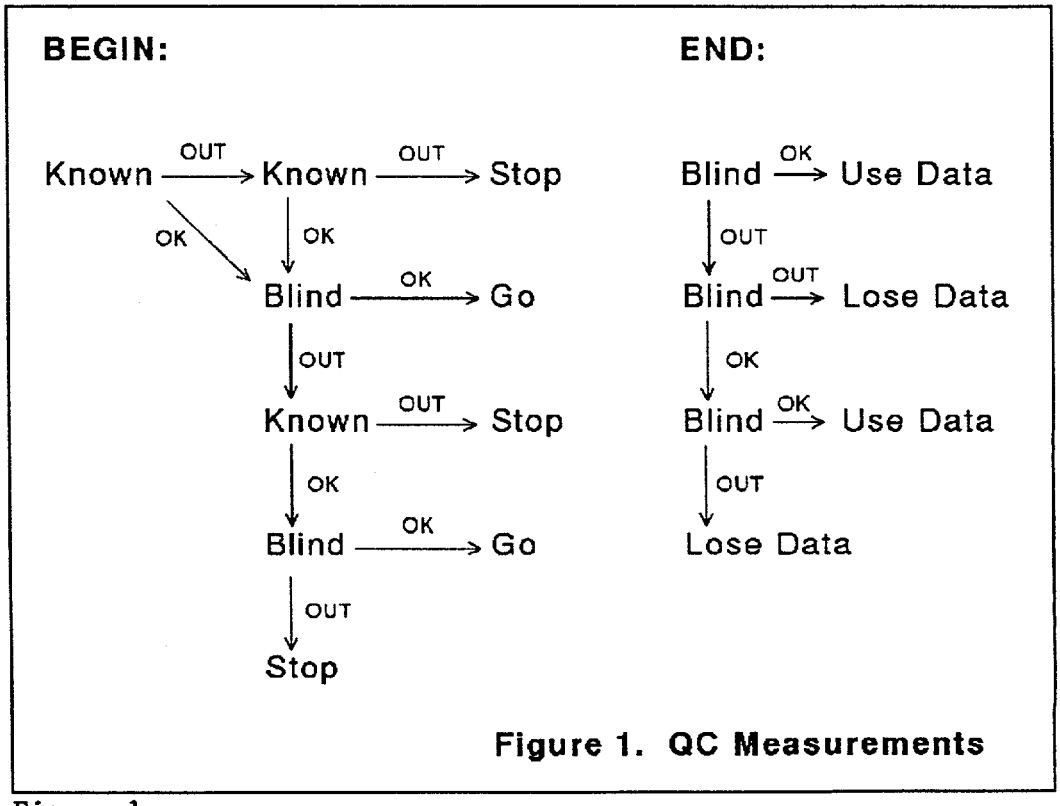

Figure 1. QC Measurements

Figure 1

"Blind" and "known" standards are prepared according to Section V.A.

If "known" standards are out-of-control, remeasure background and recalibrate according to section III.C. Prepare and measure another known.

Results of "blinds are monitored by the NBL computer-based QC program. The program indicates whether the obtained value is within predetermined control limits. Unless a specific problem is noted, this program is the sole criterion for accepting or rejecting assay data for this method. When out-of-control results are obtained, data may not be used. Stop analysis, correct the problem, and document its resolution before continuing.

C. Replicates

Analyze standards in duplicate. Determinations must agree within 5.0% of the lower result. If they do not, analyze an additional replicate. accept the two measurements with the better agreement if ≤ 5.0% apart. If they are > 5.0% apart, discard the three results and repeat the analysis.

VI. TRAINING

A. Training Plan

A new analyst shall be trained by a qualified analyst. This training includes all related safety concerns and precautions (see section I.F.). After reading and understanding the written procedure and the Chemchek KPA-11 Operation and Service Manual,[1] the new analyst observes a qualified analyst perform the procedure.

The qualified analyst provides the new analyst with "known" standards. The qualified analyst observes the new analyst's technique. The new analyst practices the procedure until able to complete a minimum of ten acceptable determinations in duplicate within one day with the mean of the results within ±3.0% of the reference (known) value, a relative standard deviation within 4.0%, and a maximum of two outliers.

B. Qualification Plan

The new analyst obtains at least twenty "blinds" prepared for the quality control (QC) program. Twenty acceptable determinations in duplicate (see section V.C) must be performed within a two-week period with five determinations performed on each of four days. The data is entered into the computer QC program. If the computer flags any entries as outliers, the new analyst should immediately discuss the information with a qualified analyst to determine the cause. An analyst is qualified if the mean of the results on 20 blinds is within ±3.0% of the reference (known) value with a relative standard deviation within 4.0%.

The new analyst must routinely consult a qualified analyst after qualification until sufficient experience, as determined by the qualified analyst, is gained to effectively determine when and how to use alternative procedures of preparing the sample for analysis or alternative options of quantification.[1,2,3]

The qualification information should be entered on the form "Blind standards Proficiency Testing Report," found in the NBL QA Manual.

C. Requalification Plan

If more than one year has elapsed since the analysis of "blind", the analyst must requalify by the determination of five "blinds" in duplicate (see section V.C) with no more than one outlier.

VII. SAMPLE STORAGE AND DISPOSAL

A. Storage

1. Uranium standard stock solutions of 50 μg U/g of solution may be stored in Teflon® bottles for up to two years.

2. Uranium standard stock and reference solutions of 0.5 μg U/g of solution may be stored in Teflon bottles for up to one year.

3. Sample, knowns, and blinds aliquanted into beakers and evaporated to dryness normally are not stored for longer than one year.

4. Liquid samples may be stored in plastic bottles; however, transpiration of water through the bottle can be expected. Bottles from which samples will be taken over long periods of time must be weighed after use and before reuse and sample dilution factor corrected correspondingly. The bottled solutions should be retained for at least 30 days after the analyses have been reported in case repeat analysis is requested by the submitter.

B. Disposal

Transfer unwanted uranium-containing solutions to recoverable uranium lots.

VIII. REFERENCES

A. Supporting

1. KPA-11 Operation and Service Manual, Kinetic Phosphorescence Analyzer, Chemchek Instruments, Inc., Richland, WA, June, 1992.

2. R. Brina and A. G. Miller, "Direct Detection of Trace Levels of Uranium by Laser-Induced Kinetic Phosphorimetry," Anal. Chem., Vol. 64, No. 13, 1992, pp. 1413-1418.

3. R. Brina and A. G. Miller, "Determination of Uranium and Lanthanides in Real-World Samples by Kinetic Phosphorescence Analysis," Spectroscopy, Vol. 8, 1993, pp. 25-31.

4. Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry, 1992 Book of ASTM Standards, Section 11, Vol. 11.02 Water (II), number D5174, pp. 442-444.

5. Argonne National Laboratory/Analytical Chemistry Laboratory Standard Operating Procedure: "Determination of Uranium in Waters by Kinetic Phosphorimetry," Analytical Methods Database, DOE Compendium, Method-ID 036B.

B. Suggested Reading

1. W. Campen and K. Bächmann, "Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water," Mikrochim. Acta [Wien], 1979 II, pp. 159-170.

2. A. C. Zook, L. H. Collins, and C. E. Pietri, "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorometry," Mikrochim. Acta [Wien], 1981 II, pp. 457-468.

3. A. C. Zook, and C. E. Pietri, "Application of an Accurate, Precise and Rapid Method for the Determination of Sub-Microgram Quantities of Uranium," 25th Conference on Analytical Chemistry in Energy Technology on October 6-8, 1981, published in Lyon, W. S. (ed.), "Analytical Chemistry in Nuclear Technology," Ann Arbor Science: Ann Arbor, Michigan, 1982, pp. 44-47.

4. A. C. Zook and L. H. Collins, "Application of a Direct Method for the Determination of Trace Uranium in Safeguards Samples by Pulsed Laser Fluorometry," American Nuclear Society Topical Meeting, Nov. 26-30, 1979, published in NBS Special Publication 582, June, 1980, pp. 147-153.

Attachment 1

KPA Results Form	Reference Values:
Analyst Name:	High Range Intensity:
Analysis performed for:	Low Range Intensity:
	High Range Background:
	Low Range Background:

									Checklist:		
	Initial Dissolution	1st dilution		2nd dilution		KPA Assay	Total U*	Conc U** of samp	R^2	Life time	In Range?
Sample ID, aliquot wt (W_a), bottle factor (f_b)	Wo (grams)	Wi (grams)	Wf (grams)	Wi' (grams)	Wf' (grams)	(μg U/g soln)	μg in aliquot	(μg U/g samp)	>0.99?	>200?	HI?*** LO?***

* Total U (μg): W_o x (W_f/W_i) x (W_f'/W_i') x KPA RESULT (μg U/g soln) ** U Conc (μg U/g) = Total U/(f_bxW_a) *** HI: 0.5 - 5 LO: 0.001 - 0.02 μg U/g soln

APPENDIX B

BACKGROUND AND MISSION

OWNERSHIP

New Brunswick Laboratory (NBL) is owned and operated by the U.S. Department of Energy (DOE). Although it is part of DOE's Chicago Operations Office system, its primary sponsor is the Office of Safeguards and Security in DOE's Office of Nonproliferation and National Security, Office of Security Affairs.

DOE MISSION

DOE is entrusted to contribute to the welfare of the nation by providing the scientific foundation, technology, policy, and institutional leadership necessary to achieve efficiency in energy use, diversity in energy sources, a more productive and competitive economy, improved environmental quality, and a secure national defense.

NBL MISSION

NBL serves as the U.S. government's central authority for nuclear materials measurements and measurement evaluation. It is also the U.S. government's certifying authority for nuclear reference materials. These functions assure that the United States maintains an accurate and reliable nuclear safeguards program, particularly in the area of nuclear materials accountability. NBL's program and technical capabilities not only enhance domestic nuclear security but also support international nonproliferation efforts. Its nuclear measurements and measurement evaluation roles allow the federal government to perform independent technical audits and validate nuclear material measurements made by contractors. NBL also has the technical capability for the independent resolution of measurement and safeguards anomalies that may arise from nuclear operations and the transfer of materials between sites.

NBL HISTORY

NBL was established by the Atomic Energy Commission in New Brunswick, New Jersey, in 1949. It was initially staffed by scientists from the National Bureau of Standards who had contributed to the science of measuring nuclear materials for the Manhattan Project. At first, NBL's mission was to provide the federal government with the capability to assay uranium-containing materials for the nations developing atomic energy program. Over the years, NBL expanded its capabilities, improving methods and procedures, developing new ones, and certifying additional reference materials for use around the world. It incorporated the capability to make plutonium measurements in 1959. During the period from 1975 through 1977, NBL was relocated from New Jersey to the current site at Argonne, Illinois.

Since its beginning, NBL has been a center of excellence in analytical chemistry and the science of measuring nuclear materials. In this role, NBL continues to make state-of-the-art measurements of elemental and isotopic composition for a wide range of nuclear materials.

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