Direct Detection of Trace Levels of Uranium by Laser-Induced Kinetic Phosphorimetry

Rossella Brina and Allan G. Miller*

Chemchek Instruments, Inc., 1845 Terminal Drive, Richland, Washington 99352

The kinetic phosphorimetric determination of uranyl ion in aqueous solutions at room temperature yielded a detection limit for UO_2^{2+} of 1 ng/L. The response to uranium is linear from the detection limit up to 5 mg/L. The method is fast and accurate, with no separative pretreatment needed for most of the real samples investigated. In the analysis of biological samples, wet-ashing with HNO_3/H_2O_2 is required for measurements near the detection limit. Samples with uranium concentrations higher than 0.1 μg/L gave relative standard deviations typically below 5%. Factors affecting the quantum yield of the uranyl ion phosphorescence, e.g. quenching from species present in the matrix, are accounted for in the kinetic analysis of the uranyl phosphorescence.

INTRODUCTION

The need for a sensitive, fast, and accurate method for the determination of uranium is particularly felt in the environmental, geological, and bioassay fields.[1,2] Some analytical methods used for uranium detection require extensive pretreatment of samples such as surface and ground water, sea water, ores, and urine, thus limiting the application of these techniques as routine methods.[3] Phosphorimetry is a sensitive and selective analytical technique, with low detection limits and a large linear dynamic range for many phosphors.[4,5] Under excitation by ultraviolet and visible radiation, many uranium compounds phosphoresce with emission of a characteristic green light.[6-9] The hexavalent uranium present as the uranyl ion UO_2^{2+} is believed to be responsible for the long-lived (10^{-3}-s) luminescence at room temperature, with uranium in other valences being essentially nonluminescent.[10] In solution, however, the uranyl ion must be protected from quenching in order to observe the long lifetimes.[6] This can be accomplished by complexing UO_2^{2+} with a substance such as phosphoric acid,[11] which yields phosphorescence lifetimes for UO_2^{2+} of a few hundred microseconds.

The photoluminescent emission of the uranyl ion has long been used for the determination of trace quantities of uranium.[6,10] The conventional fluorometric method of uranium analysis consists of obtaining a pellet from the uranium sample by fusion with sodium fluoride in a platinum crucible.[12,13] The chemical separation required before performing the analysis of certain samples, and the strictly regulated conditions for sample preparation make this method marginal for routine quality analysis. Two major factors limit the precision and accuracy of quantitative photoluminescence measurements of UO_2^{2+} in solutions of real samples. First, the fluorescence from organic components in the samples, with typical lifetimes of 10^{-9} s, may be superimposed on the long-lived uranyl phosphorescence, thus interfering with the uranium determination.[7] Secondly, species present in the real samples can quench the uranyl luminescence by deactivating the excited state through several possible nonradiative paths.[14-16] Pulsed-source phosphorimetry has the potential to circumvent these problems, because of the advantages that this technique has over conventional phosphorimetry.[17-19] First, the greater selectivity between short- and long-lived phosphors possible with time-resolved luminescence techniques can eliminate the problem of interference from fluorescing species present in the aqueous sample. Secondly, the higher signal-to-noise ratio in the pulsed-source time-resolved measurements allows for large dilutions of the original sample to reduce matrix effects (e.g. color, quenching).

This paper describes the application of kinetic phosphorimetry, as a practical, routine analytical method, to the detection of uranium in several real-world samples of environmental and biological interest. Kinetic phosphorimetry is based on laser excitation followed by temporal resolution of the phosphorescence signal. The dye laser source employed in this work is ideal for this type of spectroscopic measurement because of its high intensity, monochromatic radiation and the possibility of varying the excitation wavelength. Time-resolved photon counting has been shown to be particularly effective for the detection of uranium at trace levels.[20] Kinetic phosphorimetry combines multichannel scaler photon counting for discrimination against short-lived emitting species and scattered light with kinetic analysis of the uranyl phosphorescence for correction of quenching effects.[20-23] This correction was found accurate for up to 80% quenching, even

* To whom correspondence should be addressed.

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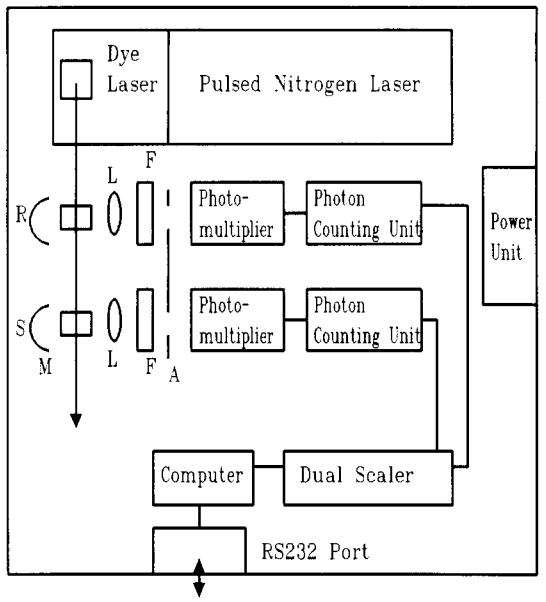

Figure 1. Schematic diagram of the kinetic phosphorescence analyzer KPA-11: (R) reference cell; (S) sample cell; (L) focusing lens; (F) interference filter; (A) apertures to the detectors; (M) mirrors.

at sub-part-per-billion levels of uranium.[20] The kinetic analysis of the uranyl phosphorescence provides highly precise and accurate measurements, thus eliminating the need for internal standards. One advantage of the kinetic phosphorimetry technique is the extremely low detection limit, which often permits analysis with dilution as the only required pretreatment to reduce matrix effects. The response to UO_2^{2+} is linear in the range of concentrations from the detection limit of 1 ng/L up to 5 mg/L, with results that are automatically correct for quenching effects.

EXPERIMENTAL SECTION

Reagents and Apparatus. Uranium standards were prepared from U_3O_8 99.968% (National Institute of Standards and Technology) by dissolution in warm HNO_3. Dilutions were carried out in 1 M HNO_3. Deionized water was used for all solutions. A 0.1 M phosphate-based solution was used as the complexing reagent for uranium in all the measurements. Lifetimes between 250 and 300 μs were typically obtained from the kinetic phosphorimetric analysis of the uranyl solutions with this complexing agent.

Steady-state excitation and emission spectra were recorded with a System 3 scanning spectrofluorometer (Optical Technology Devices; Elmsford, NY), equipped with a 150-W xenon arc lamp and a S20 response photomultiplier tube (190–900 nm, Optical Technology Devices). Silica cuvettes, 10 mm × 10 mm × 50 mm (NSG Precision Cells), were used in all of the luminescence experiments. The fused-pellet fluorometry and α spectrometry measurements were performed by U.S. Testing Co. (Richland, WA).

Kinetic Phosphorimetry Principles and Instrumentation. The kinetic phosphorimetry measurements were preformed using the kinetic phosphorescence analyzer KPA-11 (Chemchek, Richland, WA). The KPA-11 uses pulsed laser excitation and gated detection for the determination of organic compounds such as polyaromatic hydrocarbons, nitrogen and sulfur heterocyclics, and several lanthanide elements and uranium. A schematic diagram of the KPA-11 is shown in Figure 1. A nitrogen-pumped dye laser, with average power in the 0.1–0.5-mW range, provides the wavelength necessary for the excitation of the sample. The pulse duration is 3 ns at a repetition rate of 20 pulses/s. The laser simultaneously excites the reference cell (R in Figure 1) and the sample cell (S). The emitted light passes through interference filters (F) and is detected, at right angles to the laser excitation, by photomultiplier tubes operated in the photon-counting mode. The pulse of light which excites the uranyl complex occurs at time zero, and ensuing luminescence intensity measurements are taken at fixed time intervals (called time gates) after excitation. Each laser pulse triggers a multichannel scaler (MCS) photon-counting sweep of 1.65-ms duration. During this sweep, the signal from the detector is fed into a counting circuit, which is read and reset by the microprocessor. Each successive reading of the counter occurs after a constant interval of time and forms a time gate. A dwell time of 13 μs per time gate is used, which corresponds to 127 time gates per MCS sweep. The luminescence intensities recorded at each time gate are summed over the number of laser pulses used in the measurement. The data are collected, background-subtracted, and analyzed by a computer, which controls the operation of the KPA-11. The first four time gates (elapsed time 52 μs) are always discarded from the calculations so that the emission from short-lived luminescence sources does not affect the data.

The following summarizes the principles of the kinetic analysis performed on the luminescence intensity data. When secondary processes are absent, the equation that describes the first-order kinetic decay of the excited uranyl complex can be written as

$$\ln U^*_i = \ln U^*_0 - (k_p + k_q)t \quad (1)$$

where U^*_i represents the population of excited uranyl complex at time i, k_p is the rate constant for phosphorescent decay, and k_q is the rate constant for all other relaxation processes. The intensity, I, of the phosphorescence signal is proportional to the concentration of the emitting species, therefore (1) can be rewritten as

$$\ln I_t = \ln I_0 - (k_p + k_q)t \quad (2)$$

The number of detected photons at any time, t, is proportional to the number of excited ions. Thus, a linear fit of the luminescence intensities data in eq 2 gives an intercept at time $t = 0$, $\ln I_0$, proportional to the number of excited uranyl ions, independent of quenching effects.[17,20-23] The instrument plots the results as the natural logarithm of the photon count, I, versus elapsed time. The luminescence from the analyte is related to its concentration using the intercept I_0 from eq 2 in the calibration equation obtained with known uranium standards. The decay lifetime, τ, is the reciprocal of $(k_p + k_q)$, which is the negative reciprocal of the slope in eq 2. As a result, the linear fit of eq 2 allows the calculation of the concentration of the analyte and its lifetime. It should be noted at this time that the experimental variable the instrument actually determines is the photon count, rather than the luminescence intensity. Since the photon count is linearly related to the luminescence intensity over the time period of interest, luminescence intensity and photon count are sometimes used interchangeably in this paper, although photon count is more appropriate.

In the KPA-11, the time resolution parameters are computer-controlled and can be varied in order to obtain the set most suitable for the species to be determined. The KPA-11 has two ranges available for measurements (low and high range), which are due to two different-size emission apertures to the sample photomultiplier. This extends the analytical range of the instrument, allowing analysis of concentrated samples that would cause saturation of the detector in the low range. The digital electronics provide linear photon-counting response up to about 40 MHz. Higher level measurements are protected from counter saturation errors by shifting the time window to where the intensities fall within the limits of the electronics. This increases the delay time and extends the analytical range, although the accuracy of the measurements may be reduced. The dye solution was 1.8×10^{-3} M stilbene-420 (Exciton) in methanol. The 515-nm interference filters (Optometrics Corporation) have a 10-nm band-pass. The reference cell contained a 200 μg/L U solution. The reference measurement functions as an external standard, normalizing the sample measurements to correct for internal fluctuations such as laser brightness, temperature drifts, electrical line surges, and high-voltage drifts. The number of laser pulses

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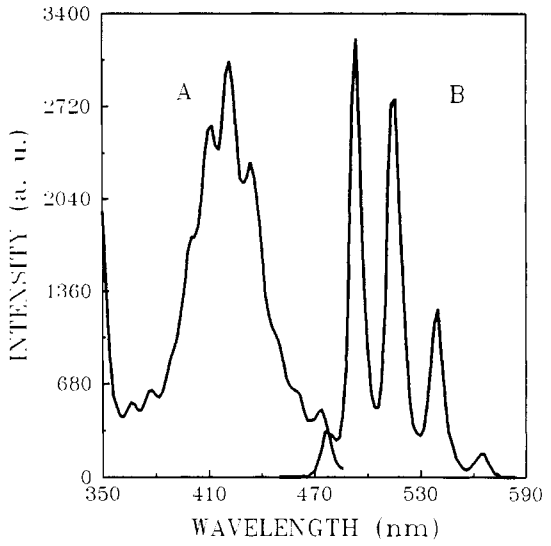

Figure 2. (A) Excitation spectrum of a 100 μg/L uranyl aqueous solution:emission wavelength, 515 nm; band-pass, 2.5 nm. (B) Emission spectrum of the uranium solution in (A): Excitation wavelength, 425 nm; band-pass, 2.5 nm. The spectra are background-subtracted.

was set at 200, unless otherwise specified. With this number of laser pulses, the analysis of one sample requires less than 1 min to be completed. Sample solutions were prepared by mixing 1 mL of the analyte solution with 1.5 mL of the complexing reagent described earlier.

RESULTS AND DISCUSSION

Steady-State Photoluminescence Spectra. Parts A and B of Figure 2 show the excitation and emission spectra, respectively, of a 100 μg/L uranium solution in water. The uranyl ion spectra are background-subtracted, but they are not otherwise corrected. The band-pass used for both spectra was 2.5 nm. The characteristic uranyl emission peaks at 494, 515, 540, and 565 nm are visible in Figure 2B. The excitation and emission wavelengths for the kinetic phosphorimetric analysis were determined on the basis of these spectra. The dye selected for the excitation wavelength was stilbene-420, at a concentration of 1.8×10^{-3} M in methanol. At this concentration, the lasing maximum is at about 425 nm. The interference filter used for the photoluminescence detection matches the emission maximum of UO_2^{2+} at 515 nm, with a 10-nm band-pass.

Detection Limit for Uranium by Kinetic Phosphorimetry. A solution containing 5 ng/L of U, a concentration near the detection limit of the kinetic phosphorimetry technique, was analyzed 10 times. The results are shown in Table I. The background count was 212 at the fifth time gate (elapsed time is 52 μs). The detection limit of 1 ng/L was calculated as 3 times the standard deviation of the measurements reported in Table I. The relative standard deviation (RSD) values obtained from measurements on uranium solutions at concentrations at or near the detection limit varied between 4 and 7%. With concentrations in the midrange and lifetimes longer than 200 μs, precisions of 1–3% relative standard deviation were commonly obtained.

Linearity of the Response to Uranium. Several standard solutions containing uranium were analyzed, ranging in concentration from the detection limit up to 10 mg/L. The values of the intercept of the ln I vs t plots (eq 2) for every concentration were then plotted as a function of the uranium concentration in solution, for both ranges (low and high), to assess the linearity of response. In the low range, these plots show that the response to uranium is linear (correlation coefficient of 0.999, with eight points) from the detection limit up to 20 μg/L. At concentrations higher than 20 μg/L, the counting units of the instruments are saturated; therefore some of the initial time gates have intensities out of range. At these high count rates, coincidence losses cause convex curvature of the ln I vs t plot in the initial time gates, lower values of the intercepts than those expected for these solutions, and a deviation from linearity of the intercept vs uranium concentration plots. In this situation, the intercept of the ln I_t vs t plots is calculated using the time gates having longer delay times than those originally preset (see Experimental Section). The response in the high range was linear from 10 μg/L to 5 mg/L, with a correlation coefficient of 0.998 with 11 points. At concentrations higher than 5 mg/L, saturation of the counting units occurs again and lower values of the intercept are obtained, as seen for the low range. In conclusion, the response to uranium over both ranges is linear from the detection limit of 1 ng/L up to 5 mg/L.

Table I. Detection Limit and Lifetime for a 5 ng/L Uranium Solution

U found (ng/L)	rel error (%)	photon count[a]	detn limit (ng/L)	lifetimes (μs)
4.81	3.8	293	1.00	285
4.88	2.4	310		
4.75	5	279		
4.79	4.2	290		
4.72	5.6	283		
4.41	11.8	307		
4.69	6.2	269		
5.25	5	312		
4.77	4.6	276		
4.70	6	225		

[a] Net photon count at fifth time gate (delay time is 52 μs). The background count at the fifth time gate was 212.

Analysis of Real Matrices by Kinetic Phosphorimetry. The major problem in the analysis of real matrices is spectral interferences. Four major types of interferences have been encountered. First, the inner filter effect was observed with yellow solutions, e.g. chromate, which absorbs the 420-nm exciting radiation. Second, other luminophors, such as some organic substances (e.g. humic acids and organic degradation products from incomplete ashing of soil or vegetation samples) emit intense fluorescence that excites the optics, causing curvature of the ln I vs time plots. Third, the quenching of uranyl luminescence by organic and inorganic species resulted in a shortening of the triplet-state lifetime and a reduction of the phosphorescence intensities of the excited uranyl complex. Reducing agents such as alcohols, halides (except fluoride), and oxidizable metals with electronic energy levels overlapping those of the uranyl ion are strong quenching agents.[14-16,19] Examples are silver, lead, iron(II), manganese(II), and thallium. Reliable results cannot be obtained by kinetic phosphorimetry when quenching exceeds 80%. The accuracy of the kinetic analysis of the uranyl phosphorescence has been demonstrated for up to 80% quenching by chloride.[20] We have found this to be the case for cationic quenchers, such as silver and thallium, as well as real-world samples. Fourth, the presence of a substance that may complex the uranyl ion differently than the phosphate complexing reagent, or may prevent the phosphate from complexing the uranyl ion, is also a cause of interference. Several different procedures have been adopted when the above mentioned interferences have occurred. The simplest pretreatment was dilution, which is effective when the uranium concentration in the samples is well above the detection limit of the technique. Taking the sample to dryness with an oxidizing acid (e.g. nitric acid) was in some cases effective in eliminating quenching agents and fluorescers. Samples of urine, vegetation, soil, or water containing decayed vegetation

Table II. Analysis of Water Samples by Different Analytical Techniques

sample description	radiochemical analysis (μg/L)	KPA[a] (μg/L)	fluorometry (μg/L)
well A	37.6 ± 4.0	36.8 ± 0.5	
well B	39.3 ± 5.0	35.8 ± 0.5	
well C	37.7 ± 4.3	37.7 ± 0.5	
"E" water			
analysis 1		33.4 ± 0.9	
analysis 2		33.5 ± 0.9	
		33.4 ± 0.9	
soft water			
analysis 1		28.0 ± 0.4	
analysis 2		27.8 ± 0.4	
		27.9 ± 0.4	
IQAP-2		85.4 ± 1.2	
IE019 (12.0 ± 10.4)	12.5 ± 1.0	12.6 ± 0.5	12.6 ± 1.5
QAP-8 (64.0 ± 4.5)	74 ± 7	65 ± 6	58 ± 7
EPA I1314 (29.0 ± 9)	30.5 ± 3	31.3 ± 1.0	

[a] Kinetic phosphorimetry analysis. Data were collected using a U.S. Testing Co. (Richland, WA) kinetic phosphorimeter. Laser pulses, 2000.

and other samples of biological origin had to be thoroughly wet-ashed to eliminate substances that could either strongly fluoresce or quench. In the following sections, the results from several real matrix analyses are reported. The pretreatment used, if any, for each different class of samples is specified in the appropriate section.

Water. Surface waters which were free of suspended material did not need sample preparation, and the analysis was done directly on the sample. For samples containing large amounts of suspended material, filtration was sometimes necessary, otherwise the sediments were allowed to settle for a few hours, and then the clear water was carefully sampled. Drinking water may usually be analyzed without pretreatment. The presence of interfering organic species in solution is detected through nonlinearities in the decay curve. Natural water may contain substantial amounts of salts, especially chloride, or HCl for preservation, which may cause severe quenching. In these cases, the sample was either diluted or, for severe effects, boiled to dryness with ca. 10% HNO_3; the residue was redissolved with ca. 2 M HNO_3 and then diluted to a final volume. Table II contains the results of the analysis of various water samples from different sources using three analytical techniques. The radiochemical and fused-pellet fluorometric data are compared with the kinetic phosphorimetry response. The number of laser pulses was set at 2000 for these measurements. The comparison of the kinetic phosphorimetry results with the traced, α isotopic analysis is very good (better than 2% in most cases), although the kinetic phosphorimetry data have substantially better precision. The "E" and "soft water" analyses were in duplicate, with one dilution of each sample analyzed twice. The level of agreement shown in Table II between repeated measurements is typical of the determination of the U with this technique. Since the IQAP-2 sample was preserved with HCl, seven aliquots were boiled to dryness with nitric acid. The residue obtained was redissolved in 1 M HNO_3 and then analyzed to obtain a relative standard deviation of 1.4%. The four samples at the bottom of Table II were interlaboratory exchange samples, and the exchange values are given in parentheses. In comparison with the radiochemical and fused-pellet fluorometry methods, kinetic phosphorimetry provided the best accuracy and precision.

Urine. Raw urine cannot be analyzed without pretreatment except at levels of U well above 20 μg/L. A large dilution (>1000) is necessary to reduce the matrix effects. Interferences are due to the presence of chloride and of organic constituents which may fluoresce, complex uranium, or quench uranyl phosphorescence. For low detection limits, wet-ashing of the urine sample to destroy proteinaceous compounds was performed. Typically, to wet-ash a urine sample, 2–3 mL of concentrated HNO_3 and 0.5 mL of 30% hydrogen peroxide were added to a 5–10-mL aliquot of the sample in a vial. The vial was soaked in hot 4 M nitric acid, to eliminate leachable U in the glass, prior to use in wet-ashing of the urine sample. The vial containing the U/HNO_3/H_2O_2 mixture was placed on a hot plate and slowly boiled to dryness. The oxidant can be replenished one to two times if the solid residue is yellow, until a white residue is obtained. When the wet-ashing was completed, the vial was placed in a muffle furnace at 500–550 °C for at least 0.5 h. After cooling, the residue was redissolved in 0.5–1 mL of 2 M HNO_3 with warming and then diluted to the original volume. Various wet-ashed urine samples were analyzed, both from people not exposed to uranium (background urines) and from uranium workers, each in five replicates. The number of laser pulses was 2000 in all these measurements. Background urines showed uranium content between 0.015 and 0.045 μg/L, with values of RSD in the range between 2 and 12%. Samples from uranium workers had up to 9.38 μg/L of U, while RSD values from 2.2 to 8.4% were observed in this case. The larger RSD values obtained in some of the results was likely caused by spattering during the wet-ashing procedure. Some urine samples were spiked with known amounts of uranium, to determine the recovery of U. The concentration of uranium in the urine samples after these additions varied from 0.056 to 107.96 μg/L. Seven replicate measurements were taken for each of the eight samples analyzed to calculate the RSD. The percent recoveries and RSD values are listed in Table III. The recoveries are generally within the RSD of 100%.

Table III. Recovery of Uranium from Spiked Urine Samples by Kinetic Phosphorimetry[a]

U present (μg/L)	U found (μg/L)	recovery (%)	RSD[b] (%)
107.96	99.8	92	3
10.56	11.2	106	7
2.089	1.88	90	9
1.223	1.235	101	
0.517	0.507	98	
0.154	0.159	103	
0.075	0.072	95	8
0.056	0.056	100	5

[a] Data were collected using a U.S. Testing Co. (Richland, WA) kinetic phosphorimeter. Laser pulses, 2000. [b] RSD values were calculated from seven repeated mesaurements.

Table IV. Comparison of Air Filter Uranium Data by Kinetic Phosphorimetry and by Fluorometry

sample	fluorometry ($\times 10^{-5}$ pCi/m^3)	kinetic phosphorimetry[a] ($\times 10^{-5}$ pCi/m^3)
L1190	3.07 ± 0.80	2.96 ± 0.13
L1191	3.07 ± 0.80	3.28 ± 0.16
L1204	4.89 ± 0.98	5.09 ± 0.26
L1207	2.26 ± 0.85	3.33 ± 0.20

[a] Data were collected with a U.S. Testing Co. (Richland, WA) kinetic phosphorimeter. Laser pulses, 2000.

Air Filters. Uranium collected on air filters can be determined by leaching the filters with warm 8 M nitric acid and then analyzing the leachate. Table IV shows the results of the analysis of dissolved cellulose filters using 2000 laser pulses. Aliquots of the solutions were wet-ashed to destroy the organics present due to the filter decomposition. A solution of the wet-ashed residue was then analyzed by kinetic phosphorimetry and also by the fused-pellet fluorometric method, which followed a chemical separation. The results

Table V. U Content in Zr Metal[a]

U present (μg/L)	U found (μg/L)	rel error (%)	lifetime (μs)	corr coeff[b]
5.5	5.6	1.8	145	0.998
7.5	7.7	2.7	213	0.999
9.7	8.0	18	151	0.997
9.7[c]	9.1	6	186	0.998
10.5	10.0	5	205	0.999
25.7	24.4	5	215	0.999

[a] Analyses were performed on solutions obtained following a 10-fold dilution of the original samples. [b] Correlation coefficient of the least squares fit of ln I vs t plot. [c] The original sample solution was diluted by a factor of 20 before performing the analysis.

from the two methods agree within the stated uncertainty. Uranium recovery measurements from three spiked filter solutions gave recoveries of 101%.

Soil. Leachable uranium in soil can be extracted from the solid matrix by boiling with 8 M nitric acid. At the end of the leaching process, the soil solution is concentrated and treated with 30% hydrogen peroxide to decompose any vegetation residues. The solution is then diluted to about 1 M nitric acid and analyzed. Although some solutions were yellowish, probably from dissolved iron, no serious interference was encountered in the measurements. Two soil samples from different locations were analyzed following this leaching procedure. The first contained 1.15 μg of U/g of soil, while the second contained 1.27 μg/g of U. These values are in the expected range for soil in this area.

Uranium in Zirconium Metal. The zirconium solutions were supplied by Teledyne Wah Chang (Albany, OR). Each sample was prepared by dissolving 1 g of zirconium metal in 100 mL of an acid mixture of 4.7% HF and 2.3% HNO_3. The original solutions prepared by Teledyne were diluted 1:10 with deionized water for the uranium analysis, to reduce the effect of the matrix. Table V summarizes the results obtained using 500 laser pulses. The results agree well (relative errors of less than 5%) with the reported value of U concentration, except for the solution containing 9.7 μg/L of U. A longer lifetime and better agreement with the nominal U concentration for this solution were obtained when a dilution factor of 20 was used, suggesting that matrix effects are responsible for the initial discrepancy.

Stack Scrubber Samples. The spent scrubber solutions for the kinetic phosphorimetric analysis were supplied by Martin Marietta Energy Systems (Paducah, KY). The original 0.3 M KOH solution accumulates typically unknown concentrations of fluoride, chloride, and uranium from the stack gases. Various stack scrubber samples containing 0–110 μg/L of uranium were analyzed. The chloride present in the samples represents the major interference for the analysis of uranium, since it quenches the uranyl ion luminescence. Two different treatments were adopted in order to reduce the effect of the matrix for these samples. In the first case, the samples were diluted in 1 M HNO_3 to reduce chloride to tolerable concentrations. For the second treatment, the sample was boiled to dryness with nitric acid to remove the chloride present, and the dry residue was redissolved in 1 M HNO_3 for the analysis. The results obtained by simple dilution (1:100 and 1:200) of eight of the samples in 1 M nitric acid showed good agreement with the data obtained by boiling aliquots of the same samples to dryness. The luminescence lifetimes for all of the diluted samples are around 100 μs, with slightly longer lifetimes at the higher dilution. The correlation coefficients for the ln I vs time plots are all above 0.99, and these plots do not show curvature. The kinetic phosphorimetry results are in good agreement (relative error of less than 5%) with the value of U concentration obtained for these samples by fused-pellet fluorometry performed by the supplier.

Table VI. Kinetic Phosphorimetry[a] Results for Synthetic Nuclear Fuel Reprocessing Samples

matrix	dilution factor[b]	lifetime (μs)	U expected (μg/g)	U found (μg/g)
A[c]	100	269	0.16	0.136
A	100	250	24	28.9
A	1000	265	3.9	4.24
A	100	144	0	0.012
	10	169	0	0.013
B[d]	100	134	4.0	2.94
C[e]	5000		18.3	19.3
C	2500		4.1	4.55

[a] Data were collected using a U.S. Testing Co. (Richland, WA) kinetic phosphorimeter. Laser pulses, 2000. [b] Dilutions were carried out in 0.5 M HNO_3. [c] Composition of the matrix: 0.6 M Zr, 4.8 M F, 0.4 M B, 0.4 M Al, 0.15 M Cd, >4 M H^+, 1.8 M NO_3^-, 0.1 M SO_4^{2-}. [d] Composition (A) + 0.001 M Cr(VI), and 0.001 M Fe(III). [e] Composition of the matrix: 0.8 M aluminum nitrate, 0.04 M ferrous sulfamate, 0.04 M sulfamic acid, and 0.4 M ammonia.

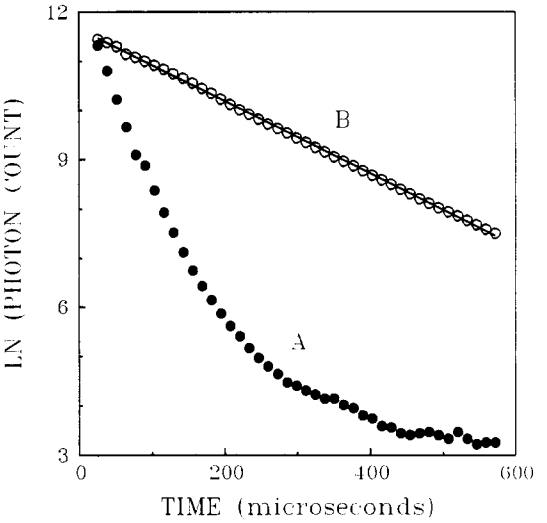

Figure 3. Logarithm of photon count vs time plot for a sample of simulated lung fluid containing uranium: (A) original sample diluted 1:5 in 1 M NHO_3; (B) original sample diluted 1:20 in 1 M HNO_3.

Process Samples. Kinetic phosphorimetry allows for the analysis of complex solutions without chemical separations. Some synthetic nuclear fuel reprocessing samples supplied by Idaho National Engineering Laboratory (Idaho Falls, ID) were analyzed, preceded only by a dilution. The compositions of the samples and the results are shown in Table VI. The number of laser pulses was set at 2000 for all the samples analyzed. The first four measurements are relative to the same matrix, but with different amounts of U. In some cases, replicate measurements are shown in Table VI. The lifetimes are an indication of the quality of the measurements. The sample with 4.0 μg/g of U also contained Cr(VI), which absorbed the blue excitation light, and caused the low result. Only a 10-fold dilution was required to analyze such a matrix for trace uranium. The strong quenching effect of the sulfamic acid is the reason the large dilution was required for matrix C in Table VI.

Synthetic Lung Fluid. Samples of simulated lung fluid containing uranium were supplied by Battelle Pacific Northwest Laboratory (Richland, WA). Chemical components of synthetic lung fluid include magnesium chloride (0.203 g/L), sodium chloride (6.019 g/L), potassium chloride (0.298 g/L), sodium phosphate (0.268 g/L), sodium sulfate (0.071 g/L), calcium chloride (0.368 g/L), sodium acetate (0.952 g/L), sodium bicarbonate (2.604 g/L), and sodium citrate (0.097

g/L). The major interferant in these samples is the chloride, which quenches the uranyl phosphorescence. The effect of the matrix on the luminescent response is seen in the decay curves in Figure 3. Figure 3A represents the response of a simulated lung fluid sample which was diluted by a factor of 5 before the analysis. The plot is quite curved, and the lifetime is short (85 μs) compared to the response from the same sample diluted 20 times (Figure 3B). Using a dilution factor of 20, the lifetime of uranyl increased to 197 μs. Figure 3 also shows the line obtained from the regression calculations for the 1:20 dilution. The uranium concentration in the sample was 177 μg/L.

CONCLUSIONS

Kinetic phosphorimetry provides a fast, sensitive, and accurate method for the direct determination of uranium in aqueous solutions from the ng/L to mg/L levels. This technique corrects phosphorescence data for matrix quenching, thereby most real-world samples can be analyzed either directly or with limited sample preparation. Chemical separations are only required for very low levels of uranium in samples with a substantially complex matrix. Routine analysis of environmental, geological, and biological samples can be easily and effectively accomplished, with accuracy and precision greater than with other techniques conventionally employed in uranium determinations and without the need for internal standards.

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