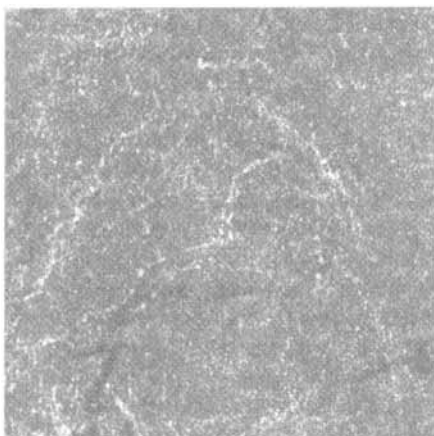


Determination of Uranium and Lanthanides in Real-World Samples by Kinetic Phosphorescence Analysis

Kinetic phosphorimetry provides a fast, sensitive, and accurate method for the direct detection of uranium and several lanthanide elements in aqueous solutions from part-per-trillion to part-per-million levels. This pulsed-source technique provides time-resolution and lifetime information, allowing for a more accurate analysis of complex matrices than that by conventional phosphorimetry. Kinetic phosphorimetry corrects luminescence data for matrix quenching, allowing real-world samples to be analyzed either directly or with reduced sample preparation. Chemical separations are only required for the determination of 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 performed.



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Phosphorescence, a time-delayed emission of light from excited species, provides the basis for many sensitive and selective analytical techniques (1,2). Recently, the development of pulsed-source time-resolved phosphorimetry (3) has allowed for the detection of trace amounts of metals including uranium (4,5) and several lanthanides (6,7). This technique significantly simplifies the measurement of phosphorescence (3,5,8) by addressing two critical issues with which analysts must be concerned when dealing with luminescence measurements in solution: the possibility of spectral interference from other compounds and the possibility of quenching the excited state by nonradiative pathways (for example, quenching by solvent molecules).

Pulsed-source time-resolved phosphorimetry involves measurement of the luminescence after a specific time delay following excitation. This reduces the effect of spectral interference when analyzing long-lived luminescent species because the emission is monitored after the short-lived luminescence has decayed to zero (5,9,10). Kinetic phosphorimetric analysis, a pulsed-source time-resolved technique, measures the rate of decay of the phosphorescence signal (10–13). This technique assumes that the phosphor decays through a first-order process, in which the concentration of the species of interest is related to the rate of change of the phosphorescence signal.

The conventional spectroscopic method for uranium determinations, *fused-pellet fluorimetry*, measures the emission from U(VI) present as the uranyl ion UO_2^{2+} , which has a luminescence lifetime in the millisecond range at room temperature (14). Uranium in other valences is essentially nonluminescent. The fused-pellet fluorimetric method involves the formation of a pellet by fusion of the sample with NaF in a platinum crucible (15,16), followed by measurement of the phosphorescence at the appropriate emission wavelength using the steady-state fluorimetric method.

Quenching is reduced in the solid state; however, the procedure is quite tedious, and the sensitivity is lower than in kinetic phosphorescence analysis. On the other hand, kinetic phosphorimetry analysis corrects for quenching effects (see next section).

The characteristic fluorescence of organic chelates of trivalent lanthanide ions has attracted considerable attention because of high quantum yields, large Stokes shifts, and very long decay times in solution (14). These properties have attracted researchers to use trivalent lanthanide ions as photoluminescent probes in a variety of areas, from the study of the nature of metal binding sites, to trace analysis of organic compounds, to immunoassays (17–19). Time-resolved measurements are commonly used in fluorescence immunoassays with terbium and europium as tags (7,20). These assays are frequently used in place of radioimmunoassays because the tag is stable and the problem of disposal associated with radioimmunoassay procedures is absent.

This work demonstrates how kinetic phosphorescence analysis is a sensitive, fast, and accurate technique for the determination of trace levels of uranium and lanthanide elements in a variety of samples of environmental, geological, and biological interest. As we discuss below, the technique provides quantitative analyses in the submicrogram-per-liter concentration range. These assays require considerably simpler sample pretreatment and are more precise than those obtained through the conventional phosphorescence technique mentioned earlier.

FUNDAMENTALS

Kinetic phosphorescence analysis (KPA) uses a pulsed source to excite the sample. Luminescence intensity measurements are taken at fixed time intervals (called *time gates*) after the excitation. For uranium, a time-gate duration of 13 μs is selected. The onset of the measurement period is dependent on the lifetime of the ion to be analyzed. The lifetime is the

time required for the intensity to fall to 1/e of its original value.

Nonradiative processes such as intermolecular quenching compete with phosphorescence. Quenching shortens the excited-state lifetime and reduces the luminescence intensity. One quenching mechanism for KPA measurements in an aqueous medium involves the admission of water molecules into the analyte ion coordination sphere. In this case, the analyte ion must be protected from quenching to observe the long lifetimes in solution. In KPA, the complexing agent Urplex (Chemchek Instruments, Richland, WA) is added to the uranium samples to minimize quenching by solvent molecules, while the lanthanides are complexed with ethylenediaminetetraacetate (EDTA) for the same purpose. The reduction of solvent quenching after complexation by Urplex is demonstrated by the increase in lifetime of a 5-ng/L uranium solution from unmeasurable levels (below 10 μ s) to 285 μ s. The longer lifetimes allow for increased sensitivity due to the larger signal-to-noise ratio (S/N) obtained in the time interval studied. Further correction of quenching effects is accomplished using the kinetic analysis of luminescence described below.

The principle of kinetic phosphorescence analysis is described in Equation 1, which represents a first-order kinetic decay.

$$\ln X_t^* = \ln X_0^* - (k_p + k_q) t \quad [1]$$

where X_t^* is the population of excited ions at time t (or $t = 0$), k_p is the rate constant for phosphorescence decay, and k_q is the rate constant for nonradiative decay processes.

The intensity (number of photons) of the phosphorescence signal (I) is proportional to the concentration of the emitting ions, thus Equation 1 can be replaced by Equation 2.

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

Equation 2 indicates that the number of detected photons at a given time is directly proportional to the concentration of excited ions. If a plot of $\ln I_t$ versus t is generated, the lifetime τ can be calculated from the slope ($\tau = -1/\text{slope}$), while the intercept gives $\ln I_0$, where I_0 is the luminescence intensity at the onset of the decay ($t = 0$). I_0 is directly proportional to the concentration of the phosphor and is independent of quenching effects (10–13). The measured luminescence is related to the analyte concentration in the sample using I_0 from known uranium standards. In KPA, the presence of a complexing agent and the kinetic analysis of luminescence combine to minimize quenching effects. This allows for highly sensitive and accurate measurements of very low levels of uranium and lanthanides in aqueous solutions. We will discuss later the effects of other types of interferences and possible corrective actions.

EXPERIMENTAL

Steady-state luminescence characteristics of the ions. The steady-state luminescence characteristics of uranium and the lan-

thanides described in this study are indicated in Table I, and the background-subtracted excitation and emission spectra of UO_2^{2+} in aqueous solution are shown in Figure 1. The lanthanide/EDTA luminescence spectra have a similar degree of complexity. For example, the emission spectrum of Sm(III) includes peaks at 561, 595, and 644 nm. The luminescence peaks are narrow (~ 10 – 20 nm half-width), as expected for Dy(III), Eu(III), Sm(III), and Tb(III) because the transitions involve the 4f electrons of the metals (14).

A kinetic phosphorescence analyzer.

The design of a kinetic phosphorescence analyzer (model KPA-11, Chemchek Instruments) is presented in Figure 2. A pulsed laser (3-ns pulse duration, 20-pulse/s repetition rate) is used in conjunction with a dye laser to excite the sample and reference cell. The desired emission wavelength is selected with an interference filter, and a photon-counting photomultiplier is used for detection. The onset of the measurement period is selectable, allowing the analyst to choose the appropriate time regime for analysis. This value depends on the lifetime of the species of interest. The first four time gates are always discarded from the calculations to eliminate the contribution from short-lived luminescent sources. In addition, the aperture size for the detector can be changed to select the appropriate concentration range (high or low) for the sample.

The excitation source for uranium determinations is a pulsed nitrogen laser coupled to a dye laser (stilbene-420, Exciton, Dayton, OH). This provides an excitation wavelength of 420 nm, very close to the uranyl absorption maximum of 415 nm. A 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (BPBD) dye solution (lasing range 360–390 nm) was used for Dy, Tb, and Tm, while a 2-(4'-biphenyl)-6-phenylbenzoxazole (PBBO) dye solution (lasing range 378–440 nm) was used for Eu and Sm. A timing scheme was used that provided a dwell time of 13 μ s per time gate for uranium; different values were used for the lanthanides. The number of laser pulses used for each measurement can be selected according to the accuracy needed and the time allowed for the experiment. For each measurement, the luminescence intensity recorded for each time gate is summed over the number of laser pulses selected to obtain a decay curve. In this work, the number of laser pulses for each measurement was set to 1000 (unless otherwise specified) for a sample-analysis time of 50 s.

The overall performance of the instrument used here for uranium determinations was discussed in a recent paper (21). The sensitivity of the system was determined by analyzing a uranium solution (5 ng/L) 10 times. The raw

Table I. Steady-state phosphorescence characteristics.

Element	Excitation peaks (nm)	Emission peaks (nm)
Dy	354*	482*
	368	574
	392	
	452†	
Eu	378	591
	392*	615
Sm	377	561
	405*	595*
	480	644†
Tb	352	490
	372	544*
	486†	582†
Tm	338†	451
	346	
	362*	
U	408	494
	430*	515
	435	540

* Most intense peak observed.

† Least intense peak observed.

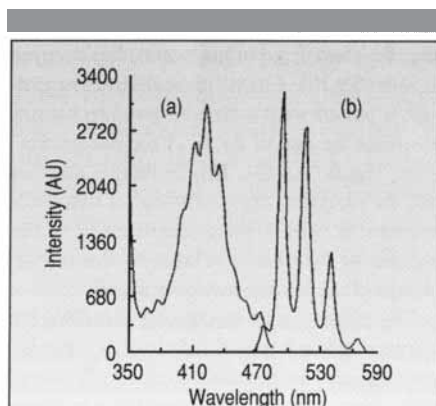


Figure 1. (a) Excitation spectrum of a 100- μ g/L UO_2^{2+} aqueous solution. Emission wavelength, 515 nm; bandpass, 2.5 nm. (b) Emission spectrum of the uranium solution in (a). Excitation wavelength, 425 nm; bandpass, 2.5 nm. (Reprinted with permission from Reference 21. Copyright 1992, American Chemical Society.)

data for the fifth time gate (elapsed time after excitation was 52 μ s) are displayed in Table II. The background photon count at the fifth gate was 212. The detection limit, calculated by using three times the standard deviation of the data, is 1 ng/L. The relative standard deviation (RSD) for the analysis of uranium solutions near the detection limit was 4%–7%; at higher concentrations, a more typical RSD of 1%–3% was obtained.

The linearity of the response to uranium was determined by preparing a series of eight solutions ranging from the detection limit to 10 mg/L. The response in the low range was found to be linear up to 20 μ g/L. At concentrations above that level, the counting unit of the detector is saturated, and some of the initial time-gate intensities may be out of range. This phenomenon may lead to a convex curvature of the decay plot, a lower value of the intercept than expected, and a nonlinear intercept–concentration plot.

To counteract this problem, the fit to Equation 2 is obtained using intensities at time delays longer than the one normally used, so that the intensities fall within the instrumental lim-

itations. Although this shift extends the analytical range, it reduces the accuracy of the measurements for these samples in the low range because of the longer extrapolation needed to obtain I_0 . The high range is used for samples with concentrations from 10 μ g/L to 5 mg/L. Above 5 mg/L, the counting unit of the detector is saturated once again, and a shifting in the time window used for the calculations may be observed. This shift extends the analytical range of the instrument, at the expense of accuracy, as discussed for the low range. In conclusion, the overall linear range of the KPA instrument extends from 1 ng/L to 5 mg/L.

INTERFERENCES

The development of assays for uranium and the lanthanides in real-world samples through kinetic phosphorescence analysis demands the consideration of several issues to maximize sensitivity and selectivity. These include the following:

- materials other than the analyte may absorb at the excitation wavelength selected (inner filter effect) and diminish the amount of light striking the analyte

- intense fluorescence from other species such as humic acids present in soil and ground water might cause distortions in the decay plot
- the excited state might interact with other species present in the sample to provide competitive nonradiative decay pathways (that is, quenching)
- compounds that absorb and emit at wavelengths similar to the species of interest will interfere with the analysis.

Typically, the presence of spectral interferences can be determined by examining the decay curve obtained from Equation 2. If the observed luminescence comes from two or more compounds, a nonlinear decay curve will be observed. On the other hand, quenching determines a shortening of the excited state lifetime and a reduction of the luminescence intensities. For uranyl luminescence, reducing agents such as alcohols, halides (except fluoride), and oxidizable metals (for example, silver, lead, iron[II], manganese[II], and thallium) are strong quenching agents.

These potential problems can be overcome using a variety of sample pretreatment processes. In some cases such as drinking water, the interferences are not an issue, and sample preparation is not required. However, natural water may contain a significant amount of salts, requiring pretreatment. The appropriate sample pretreatment process will be discussed as the analytical conditions are described.

URANIUM DETERMINATIONS

The concentration of uranium in a wide variety of matrices has been determined using the

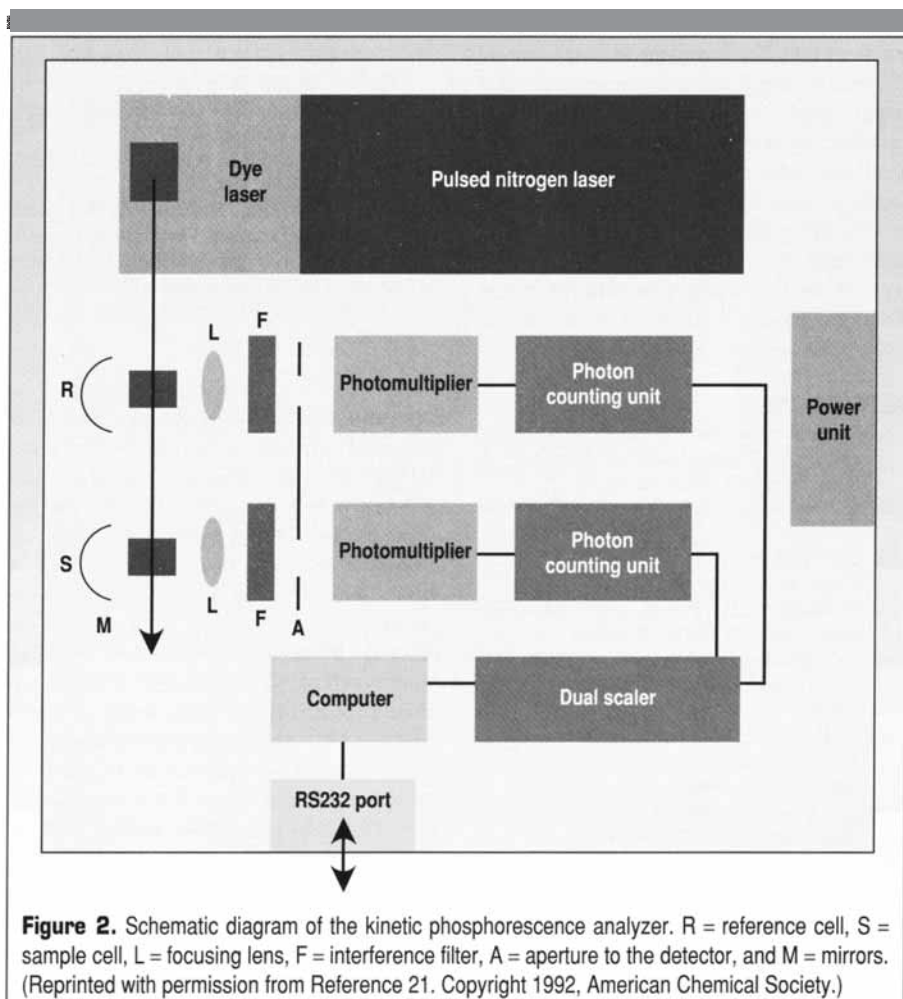


Figure 2. Schematic diagram of the kinetic phosphorescence analyzer. R = reference cell, S = sample cell, L = focusing lens, F = interference filter, A = aperture to the detector, and M = mirrors. (Reprinted with permission from Reference 21. Copyright 1992, American Chemical Society.)

Table II. Detection limit and lifetime for a 5-ng/L uranium solution. (Reprinted with permission from Reference 21. Copyright 1992, American Chemical Society.)

U found (ng/L)	Relative error (%)	Photon count*
4.81	3.8	293
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

Detection limit = 1.00 ng/L
Lifetime = 285 μ s

* Net photon count at fifth time gate.

KPA method. Typical samples include water, urine, air filters, soils, stack scrubber samples, and zirconium metal (21–27). In all analyses for uranium, the complexing agent Uraplex was added to the sample immediately before the measurement. For samples not containing interferences of the types described above, no sample preparation is needed. In most cases in which interferences exist, the common sample pretreatment is dilution. In extreme cases when treatment is necessary, the procedures are quite simple and will be described below.

Analysis of water. The analytical protocol for the analysis of water samples depends on the composition of the sample (21). Surface water can be readily analyzed without any pretreatment. Samples containing large amounts of suspended materials should be filtered before analysis.

In the analysis of water, the presence of quenching agents and interfering agents is typically the most significant issue. In the presence of quenchers such as chloride, the sample can be diluted or boiled to dryness with 10% HNO₃ and reconstituted with 1 N HNO₃. The accuracy of the kinetic analysis of phosphorescence has been demonstrated (10) in situations in which 80% of the uranyl phosphorescence was quenched by Cl⁻ or cationic quenchers such as silver and thallium.

To determine the accuracy and precision of the KPA technique for uranium measurements, water samples were analyzed by radiochemical analysis, fused-pellet fluorimetry, and KPA. The data in Table III clearly show that the KPA method provides better precision and a very good correlation to the radiochemical method. The last four samples in the table

were interlaboratory exchange samples (with the exchange value shown in parentheses). It is clear that KPA provided the best accuracy and precision of the three methods.

The American Society for Testing and Materials (ASTM) has recently released a standard test method for uranium in water using pulsed-laser phosphorimetric analysis (22). In this procedure (useful down to 0.05 µg/L), the sample is evaporated to dryness with concentrated HNO₃ and H₂O₂. This procedure is repeated until a white, translucent residue remains. This residue is reconstituted with water and analyzed.

Techniques for removal of dissolved uranium from a variety of contaminated waters are required for an increasing number of environmental applications. Surface and ground waters may contain high concentrations of dissolved uranium from natural processes or from contamination caused by mining activities, irrigation of agricultural lands, or disposal of nuclear waste. Microbially based processes may provide cost-effective mechanisms for metal removal, and several biological methods for extracting dissolved uranium have been developed, such as biosorption. Lovely and co-workers (23–25) have reported on the use of various microorganisms to reduce U(VI), which is soluble in water, to U(IV), which is insoluble, thereby suggesting an alternative enzymatic process for removal of dissolved uranium. The microbial reduction of dissolved uranium converts U(VI) to an extracellular precipitate of U(IV). The extent of U(VI) microbial reduction in groundwater samples was determined by KPA. U(VI) concentrations were measured directly, while U(IV) concen-

trations were determined after oxidation of the U(IV) in the sample to U(VI). The difference between the U(VI) concentration in the sample before and after oxidation gives the amount of U(VI) microbially reduced. The loss of U(VI) measured by KPA could be accounted for by the production of U(IV) in samples analyzed also by directly coupled plasma spectrometry after chemical separation of U(VI) and U(IV).

Analysis of urine. Radiological and environmental health laboratories frequently analyze urine (a more complex matrix than water) at the nanogram level to determine internal deposition of uranium. If internal deposition of uranium has occurred, the analysis will be used to detect and quantify the dosimetric consequences to exposed workers. In a recent study, Moore and Williams (26) described the development of a protocol for the analysis of uranium in urine using KPA. The sample is first digested with concentrated HCl, concentrated HNO₃, and 30% H₂O₂ to ensure that all the uranium is in the ionic form. An aliquot of the digested sample is mixed with concentrated HNO₃ and HClO₄ and heated to 270 °C until a residue remains. This residue is diluted to 5 mL and the solution is centrifuged, filtered, and then analyzed.

In this study, the effect of potential interferences was determined for K, Na, Mg, Ca, and transition metals Cr, Mn, Fe, Co, Ni, and Cu. These elements are commonly found in milk, urine, and soil. Moore and Williams reported that at high concentrations of the alkali ions, the observed uranium concentration was higher than expected (Figure 3). The effect of the transition metals was somewhat larger (fortunately, the typical levels are much lower). These results indicate that it may be necessary to separate the alkali ions or the transition metal ions if they are present at objectionable levels. In normal samples the con-

Table III. Analysis of water samples by radiochemical analysis, KPA, and fluorimetry. (Reprinted with permission from Reference 21. Copyright 1992, American Chemical Society.)

Sample description	Radiochemical analysis (µg/L)	KPA (µg/L)	Fluorimetry (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 11314 (29.0 ± 9)	30.5 ± 3	31.3 ± 1.0	—

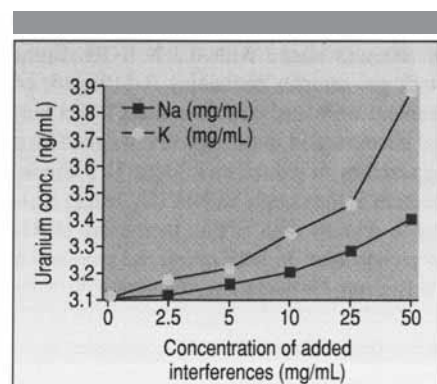


Figure 3. Effect of added alkali metals on the observed concentration of uranium. (Reprinted with permission from Reference 26. Copyright 1992, Elsevier Sequoia.)

centration of these interferants is not a problem; however, this may not be the case in the analysis of soil. The urine data indicated that the KPA method provided a good level of precision. Near the detection limit, the RSD was 20%, while at the 1- $\mu\text{g/L}$ level the RSD was 5%. In addition, the authors took part in an interlaboratory test procedure conducted by the U.S. Department of Energy Environmental Measurements Laboratory. This test indicated that the KPA method compared very well with the results of the other laboratories and provided data with better precision than the fused-pellet fluorimetric method (Table IV).

In a related series of experiments, Medley and co-workers (27) studied the diurnal variation of uranium levels in urine samples from workers at the Hanford UO_3 plant in Washington state using the kinetic phosphorescence analyzer. In these experiments, wet ashing, digestion, and ion-exchange processing were used to prepare the sample for analysis to ensure the highest precision. It was determined that mean background levels of uranium in urine were 0.015–0.03 $\mu\text{g/L}$ (with a lower limit of detection of 0.01 $\mu\text{g/L}$).

Analysis of soil. Soil is a very complex matrix containing a broad range of metal ions and humic acids. To analyze soil, leachable uranium is extracted by boiling with 8 N HNO_3 . The solution is concentrated and then treated with 30% H_2O_2 to decompose any organic (that is, vegetation) residues. No serious interferences were found and the results on two samples from different locations were within the expected range for uranium in the area. The first sample contained 1.15 $\mu\text{g/g}$ of U, while the second contained 1.27 $\mu\text{g/g}$ of U.

Analysis of stack gas streams. Conformance with federal regulation requires accurate monitoring of gaseous contamination. An on-line uranium emission monitoring system based on KPA can be used to determine the concentration of uranium in the particulate matter from a stack gas stream. The particulate matter was eluted with 0.3 N KOH. Eight stack gas samples containing 0–110 $\mu\text{g/L}$ of uranium were analyzed. Because Cl^- is a major interferant in these samples, we tried two approaches to reduce its effects: 1) a simple dilution of the sample with HNO_3 , and 2) boiling to dryness with HNO_3 , then using HNO_3 to reconstitute. In both cases, the correlation coefficients for the $\ln I$ versus time plots were greater than 0.99, showing no curvature in the decay plots. The luminescence lifetimes were $\sim 100 \mu\text{s}$, with slightly longer lifetimes at the higher dilution used (1:200). The results by KPA were in good agreement ($<5\%$ relative error) with those obtained by fused-pellet fluorimetry performed by the sample supplier (Martin Marietta Energy Systems, Paducah, KY).

LANTHANIDES DETERMINATIONS

Organic chelates of trivalent lanthanide ions, including Tb, Eu, Dy, Sm, and Tm, exhibit luminescence with long decay times (up to 1000 μs) and large Stokes shifts (typically 200–300 nm) (14). These properties allow for reduction of the optical background, and sensitive analyses can be obtained using KPA because much of the short-lived fluorescence is eliminated.

The basic KPA instrumentation described above can be used for the detection of the lanthanides. The lasing dye and the filters need to be changed because the excitation and emission wavelengths are different than that for uranium (Table I). The kinetic phosphorimetry parameters used for the analysis of the five lanthanides elements are listed in Table V.

The EDTA ligand is used to exclude solvent molecules from the coordination sphere, thereby reducing quenching. For example, the lifetime of a solution containing Tb alone (3.8 $\mu\text{g/L}$) was 389 μs , while the complexed ion had a lifetime of 1159 μs . Similarly, the complexed ion exhibited a fluorescence intensity 80% larger than the uncomplexed ion.

The detection limits and linear ranges for the lanthanide ions are presented in Table V.

At concentrations in the midrange, the RSD was found to be $\sim 3\%$. The ranging facility of the KPA-11 was used to obtain the very broad dynamic range (four decades for Sm and as many as seven for Tb). The sensitivity of KPA determinations of lanthanides appears to be a function of the complexant. Preliminary experiments indicate that the use of a β -diketone with a synergic agent (for example, triocetylphosphine oxide) provides a significant increase in sensitivity compared to the use of EDTA as a chelating agent.

In lanthanides determinations the presence of one element should not create an interference in the analysis of another. Eu and Sm have similar excitation wavelengths, so when using an excitation wavelength of 589 nm, the luminescence from one might be expected to interfere in the analysis of the other. However, the lifetimes of the two ions are quite different — 8 μs for Sm and 350 μs for Eu. A judicious selection of the observation time and gate width leads to noninterference.

In addition, the effect of adding Tb, Eu, Sm, or Dy to a solution of each of the lanthanides at a concentration near the detection limit was investigated. The relative error in the

Table IV. Results of an interlaboratory comparison conducted by EML. (Reprinted with permission from Reference 26. Copyright 1992, Elsevier Sequoia.)

Added by EML	Nanograms of total U/mL				
	RESL*	EML†	Lab 2‡	Lab 3§	Lab 4
0	0.12 \pm 0.02	0.14 \pm 0.11	0.04 \pm 0.04	1 \pm 1	8
0	0.09 \pm 0.02	-0.01 \pm 0.16	0.03 \pm 0.03	0 \pm 0	<5
3.3	3.3 \pm 0.2	3.3 \pm 0.3	2.8 \pm 0.5	3 \pm 1	<5
6.1	5.8 \pm 0.3	5.7 \pm 0.4	5.9 \pm 0.9	7 \pm 0	8
11.1	10.4 \pm 0.5	11.3 \pm 0.5	9.3 \pm 1.4	13 \pm 2	14
17.6	16.5 \pm 0.8	16.8 \pm 0.6	15.6 \pm 2.4	21 \pm 3	14

* KPA method.

† Separation, alpha spectrometry method (5600-min count).

‡ Separation, fused-pellet fluorometric method.

§ Fused-pellet fluorometric method.

Table V. Parameters, detection limits*, lifetimes, and linear ranges for lanthanide ions by KPA†.

Element	Excitation (nm)	Emission (nm)	Detection limits ($\mu\text{g/L}$)	Lifetimes (μs)	Linear range ($\mu\text{g/L}$)
Dy	368	580	0.2	15	0.2–200,000
Eu	392	620	0.05	350	0.05–25,000
Sm	405	589	2	8	2–50,000
Tb	375	550	0.01	1200	0.01–100,000
Tm	362	450	1	20	1–100,000

* The detection limit was calculated as three times the standard deviation from a set of 10 measurements on a lanthanide ion solution at a concentration near the detection limit.

† The complexing agent used for all of the measurements was 1×10^{-3} M EDTA in a 1 M sodium acetate buffer solution at pH ~ 4.5 .

concentration of the ion of interest, the lifetime of the excited state, and the correlation of the $\ln I$ versus time plot were used to determine the effect of the added ion. The results are summarized in Table VI. The interference of uranium, thorium, and iron was also investigated. Uranium showed essentially no interference up to 2.5 g/L, and below 2.5 g/L the RSD was less than 3%. Similarly, data for iron showed the RSD as <3% up to 100 mg/L in Tb and Eu, and 50 mg/L in the case of Dy, Sm, and Tm. For thorium the RSD was <3% for 500 mg/L Th in Tb, Eu, and Dy or 50 mg/L for Sm and Tm.

CONCLUSIONS

Kinetic phosphorescence analysis can provide rapid, sensitive, selective, and convenient analytical measurements for uranium and several lanthanides in simple as well as complex matrices. The sensitivity and precision of uranium determinations are considerably better than analyses involving the commonly performed fused-pellet fluorimetric technique. The high sensitivity and selectivity of KPA for Tb and Eu point to applications of this technique in fields such as clinical chemistry (for example, time-resolved fluoroimmunoassays) or in lanthanide ion probe spectroscopy.

KPA is very specific because the user can select excitation and emission wavelengths, gating time, and detector time-gate width. KPA provides the ability to measure an exceptionally broad dynamic range of the element of interest because the time window for the analysis is readily selected.

In uranium and lanthanides determinations in real-world matrices, KPA is capable of providing high levels of sensitivity. KPA of luminescence corrects results for matrix quenching, therefore most real-world samples are analyzed directly or with limited sample treatment compared with the fused-pellet fluorimetric method, which requires preparation for every sample. The technique is fast, requiring <1 min to complete each measurement. This speed, coupled with the selectivity provided by KPA, significantly reduces the amount of work and time in preparing and analyzing samples, suggesting that the technique should be very useful for routine analytical work. The KPA instrument can be easily converted for work in the field and can be used for on-line determinations of uranium in media such as stack gases and waste streams.

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Table VI. Summary of interference data.

Element	Interferant	A*	B
Dy	Eu	0.5	100
	Sm	1	200
	Tb	1	200
	Tm	1	200
	Fe	50	10,000
	Th	500	100,000
Eu	U	2500	500,000
	Dy	100	100,000
	Sm	100	100,000
	Tb	100	100,000
	Tm	200	200,000
	Fe	100	100,000
Sm	Th	500	500,000
	U	2500	2,500,000
	Eu	0.05	2.5
	Dy	0.05	2.5
	Tb	5	250
	Tm	100	5000
Tb	Fe	50	2500
	Th	50	2500
	U	2500	125,000
	Eu	10	10,000
	Sm	5	5000
	Dy	50	50,000
Tm	Tm	200	200,000
	Fe	100	100,000
	Th	500	500,000
	U	2500	2,500,000
	Eu	1	20
	Dy	100	2000
U	Sm	500	10,000
	Tb	1	20
	Fe	50	1000
	Th	50	1000
	U	2500	50,000

* The relative error is >5%, and the lifetime of the studied species starts decreasing above this value of the ratio of interferant concentration to the element concentration. A = maximum concentration of interferant ($\mu\text{g/L}$), B = maximum ratio of interferant to element.