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Author
Perry, Dale L.

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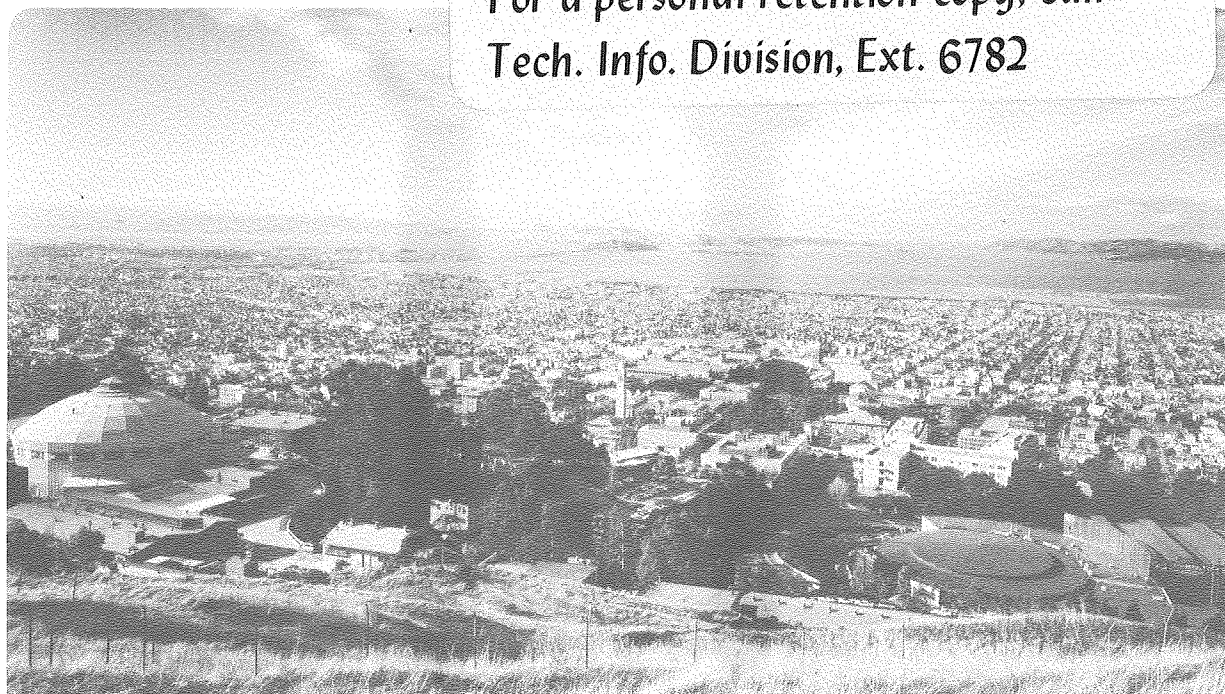
EARTH SCIENCES DIVISION

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SAMPLES BY LASER INDUCED FLUORESCENCE SPECTROMETRY

Dale L. Perry, Stanley M. Klainer, Harry R. Bowman,
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April 1981

DISCLAIMER

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AQUEOUS SAMPLES BY LASER INDUCED FLUORESCENCE SPECTROMETRY

Dale L. Perry, Stanley M. Klainer*, and Harry R. Bowman,

Earth Sciences Division, Lawrence

Berkeley Laboratory, University of

California, Berkeley, California 94720

and

Fred P. Milanovich, Tomas Hirschfeld, and Steven Miller

Chemistry and Environmental Science Divisions, Lawrence

Livermore Laboratory, University

of California, Livermore, California 94550

ABSTRACT

A new method of analysis for ultra-trace quantities of uranium in aqueous samples has been developed with a detection limit of 4×10^{-14} M (10^{-5}ppb, 0.01 pg/mL). This detection level is considerably less than the average concentration of 0.1 ppb uranium found in natural groundwaters. The procedure consists of an initial co-precipitation of the solution uranium with calcium fluoride, calcination at 800 °C, and monitoring the uranium content by laser-induced fluorescence excitation (LIFE). Analytical data using this technique are presented for previously analyzed groundwater samples containing 10^{-6}-10^{-7} M uranium. The fluorescence yield dependence on calcination time and temperature and on cation and anion interferences is discussed.

INTRODUCTION

The ability to rapidly and conveniently determine extremely small quantities of uranium in the geologic environment is desirable from several standpoints. The recent emphasis on a more complete understanding of the migration of actinide materials through soils and various types of mineral deposits (especially around nuclear waste repositories) requires rapid, high sensitive analytical techniques. Hydrogeochemical exploration for uranium also requires routine analysis at very high sensitivity of a large number of samples in order to detect the presence of uranium ores through the groundwater concentration gradients they induce. Finally, an accurate and precise determination of uranium trace levels in geologic surroundings is important for basic geophysical research in radiometric age dating and terrestrial heat-flow phenomena.

Several methods of analysis for uranium have been reported in the chemical literature (1), many of which involve initial separation or enrichment techniques. The technique reported here (2) has considerably lower detection limits for the determination of uranium but is still simple enough for routine laboratory use. It involves a coprecipitation of the UO_2^{2+} ion from solution in a CaF_2 matrix and subsequent sample preparation closely patterned after those used by Wright and co-workers (3-5) in their study of lanthanide ion substitution in a CaF_2 crystal. This is followed by air calcination of the precipitate at elevated temperatures. The co-precipitated uranium is then spectroscopically monitored by laser-induced fluorescence excitation (LIFE).

This report describes the technique used for the co-precipitation of uranium in calcium fluoride matrices, experimental parameters (such as

calcination temperature and time, initial uranium concentration in solution, and interfering cations and anions) that affect the concomitant fluorescent yield, spectra and intensity of the samples, and the instrumentation used to obtain the spectra. Detection limits, uranium co-precipitation efficiency, and selectivity are discussed, along with the results of the application of the technique to actual uranium-containing groundwater samples.

EXPERIMENTAL SECTION

Reagents

Reagent purity is crucial at these concentration levels, and a number of reagents were evaluated for background uranium content. The combination of reagent grade Matheson, Coleman & Bell NH_4F and Mallinckrodt $Ca(NO_3)_2 \cdot 4H_2O$ quartz distilled, de-ionized water was required to achieve 10^{-12} M background levels. Reagent grade $Mg(NO_3)_2 \cdot 6H_2O$ (Mallinckrodt), NaCl (Mallinckrodt), $Na_2HPO_4 \cdot H_2O$ (J.T. Baker), and $NaCO_3$ (Mallinckrodt) were also used. A stock solution of 5×10^{-3} M $UO_2(NO_3)_2 \cdot 6H_2O$ was prepared in distilled, de-ionized water and discarded whenever turbidity appeared.

Apparatus

All spectra were taken on a laser excited fluorescence spectrometer (Figure 1) employing a Spectra Physics Model 165 argon ion laser. The laser was coupled via a set of beam redirector mirrors to a Claissen filter to isolate the desired excitation wavelength and focused into a specially made Spex right-angle optical bench containing an f/1.2 collection lens. The lenses were aligned to generate a 100 μm diameter common focus in a sample holder inclined at 45°. The collected light was refocused at f/8 into a Spex No. 14018 0.75m focal length double monochromator equipped with holographic

4

gratings blazed at 500 nm. The monochromatized light was re-imaged at f/2 onto a cooled (-20 °C) RCA C31034A GaAs photomultiplier (PMT) in a Products for Research RF-TSA cooled housing. The PMT was operated at < 2000 volts using a Power Design 2K-15 adjustable filtered HV source. The photoelectron pulses were conditioned, windowed, and counted by a photon counting system consisting of Ortec Model 9301 and 9302 amplfiers and an Ortec Model 9349 ratemeter or a Princeton Applied Research Model 162 boxcar integrator. The output of the ratemeter or boxcar was fed to a Hewlett Packard Model 3456A electrometer having an HPIB interface and controlled by a Tektronix Model 184 Time Mark Generator. The electrometer was in turn coupled to a Tektronix Model 4051 graphics processor having a flexible disk attachment, a Tektronix Model 4631 hardcopy generator, and a Tektronix Model 4662 plotter. All the spectra used for analysis were taken using an excitation wavelength of 488 nm and an excitation power of 65 microwatts except where noted.

Uranium tracer studies were performed using a Packard Model A4606 Scintillation Counter.

Procedure

All glassware was pre-washed with dilute nitric acid followed by repeated rinsing with quartz-distilled water in order to remove any possible contaminant metal ions on the glass surfaces. One milliliter of a $UO_2(NO_3)_2 \cdot 6H_2O$ solution of appropriate concentration was added to a 250 mL beaker with 5 mL of 1 M $Ca(NO_3)_2 \cdot 4H_2O$ and 14 mL of distilled, de-ionized water. Thirty mL of a 0.3 M NH_4F solution was then added dropwise with stirring using a magnetic stirring bar over a period of 55-60 seconds, giving a final solution volume of 50 mL. For cation and anion interference studies, the appropriate volume of quartz triply distilled water

5

was replaced with an equal volume of cation or anion solution of known concentration holding the total volume constant at 50 mL. All solution concentrations of metal ions were expressed with respect to the final solution volume prior to precipitation. The above solutions were then covered with "Parafilm" and allowed to precipitate and settle for one day. The CaF_2 precipitates were centrifuged and dried in the centrifuge tubes at 105 °C for two hours. The precipitate was removed from the walls of the centrifuge tubes with a stainless steel spatula and crushed. The samples were fired in porcelain crucibles for three hours, usually at 800 °C (Lindberg Model 51333 box furnace accurate to $\pm$ 1 °C), allowed to cool to room temperature in the open air, and crushed again in a vibrating ball mill (a mortar and pestle were initially employed, but the vibrating ball mill produced a more homogeneous powdered sample and better reproducibility in the spectra). The CaF_2 samples were then pressed into 200 mg pellets 1 cm in diameter and 1 mm thick.

RESULTS AND DISCUSSION

A number of workers have studied the luminescence of uranium in CaF_2. Lupei and Lupei (6) reported a phosphorescent spectrum exhibiting a zero-phonon line centered at 521.25 nm (19184 cm^{-1}) with associated vibronic side structure. Their studies indicated that the luminescent species most probably has a distorted octahedral UO_6^{6-} structure. Nicholas (7) reported a concentration dependent luminescence. At low concentrations of uranium, a spectrum Nicholas called Type I was observed with a no-phonon line at 521.40 nm (19179 cm^{-1}) and an equally intense line at 520.02 nm (19230 cm^{-1}). At approximately 1% uranium concentrations, Nicholas reported a spectrum dominated by lines at 528.09 nm (18936 cm^{-1}) and 527.09 nm (18972 cm^{-1}).

6

According to Nicholas, these lines are due to uranium clustering and are called Type II spectra. Lines contained in the Type I and II spectra appear as pronounced bands in the fluorescence emission spectra obtained in this work (Figure 2).

In the present study, the fluorescence yield of coprecipitated and calcined uranium was measured at nine excitation wavelengths from 457.9 nm to 568.2 nm using a combination of krypton ion and argon ion lasers as the excitation source. The maximum fluorescence yield occured at 488.0 nm, which was therefore chosen as the excitation wavelength for this work.

Laboratory samples were prepared containing uranium as the uranyl ion in the 10^{-4} - 10^{-12} M concentration range. Precipitates taken from solutions of 10^{-5} M and lower uranium concentrations yielded white solids and gave excellent fluorescence spectra, whereas larger concentrations gave yellow precipitates which exhibited very poor fluorescence. CaF_2 samples that had undergone no high-temperature calcination gave only a minimal, diffuse fluorescence signal.

In the working concentration range of 10^{-5} - 10^{-12} M, several experimental parameters that could influence the intensity of the fluorescence were investigated. First, a log-log plot of fluorescence intensity vs. the molarity of the uranium contained in the initial, un-precipitated solution yielded a linear calibration from 10^{-6} to 10^{-12} M. Second, the intensity of the spectrum was independent of calcination temperature in the 500-800 °C range, with a slight increase at 1000 °C. Third, prolonged heating of samples (up to 48 hrs) at any one temperature had only a minimal effect on the intensity of the fluorescence emission.

The interference of other ions was investigated over a wide range of concentrations. Interference was observed for these ions at and above the following concentration levels: Fe^{3+}, 10^{-5} M; Mg^{2+}, 10^{-5} M; Al^{3+}, 10^{-5} M; Mn^{2+}, 10^{-3} M; Na^+, 1 M; SO_4^{2-}, 10^{-2} M.

The coprecipitation yields at various uranium concentrations were determined using tracer quantities of ^{233}U and standard scintillation counting techniques. The co-precipitation efficiency appeard to be linear over the uranium concentration range of 10^{-5} M (2.7 ppm) to 10^{-8} M (2.7 ppb). About 84% of the solution uranium was co-precipitated with the CaF_2 at 10^{-5} M and 88% at 10^{-8} M uranium. The chemical yield dropped off at higher concentrations, and the overall results of the measurements became less reproducible.

Figure 2 shows the fluorescence spectra of a CaF_2 sample precipitated from a 10^{-12} M uranium solution and a reagent blank sample compared with the spectrum of a CaF_2 sample precipitated from a 10^{-8} M uranium solution sample. These three spectra were obtained with continuous wave laser excitation using the apparatus of Figure 1. The spectra of the 10^{-12} M and reagent blank sample, while indicating features of the 10^{-8} M spectrum, were considerably distorted by contributions from other sources. The distortion was removed (Figure 3) by using delayed sampling techniques (chopped excitation and boxcar integration) indicating that it was due to prompt (< 50 μsec) processes such as scattering, Raman, and short lived fluorescence. Therefore the long lifetime of the uranium fluorescence (170 μsec at room temperature for samples used in this work) could be effectively used to discriminate against contributions from other processes which became competitive in measurements performed at ultra-trace concentrations.

The spectrum of 10^{-12} M uranium (Figure 3), which was obtained with a time constant of 0.3 sec, exhibits a signal/noise ratio of approximately 30. By using a 10 sec time constant and accepting a signal/noise ratio of 7, a detection limit of 4×10^{-14} M is achievable. This sensitivity is superior to that of radioactive counting. The relative sensitivity of these techniques can be shown by comparing excited state lifetimes which yield << 1 photon/ atom/year for even highly radioactive actinides versus > 1 photon/atom/ millisecond for their fluorescent species. This difference is further compounded by the greater ease with which an atom (or molecule) can be recycled through the excited state in fluorescence measurements.

The fluorescent technique, however, is extremely sensitive to contamination, which significantly reduces its utility in many applications. This liability is greatly diminished in the present method by the coprecipitation which concentrates the UO_2^{2+} 50-100 times from solution while rejecting most solution impurities. The calcination further enhances the sensitivity by destroying most organic contaminants and increasing the quantum efficiency of the uranium.

Three surface water samples from a natural slough were analyzed using the present technique. High uranium concentrations (320 $\pm$ 30, 162 $\pm$ 20, and 65 $\pm$ 6 ppb) had been detected in these filtered (0.45 micron filter) water samples in a previous study (8). Other elements determined in these samples and their concentration ranges (in mg/l) were: B, .08-.09; Li, .003-.005; Na, 9-15; Mg, 14-21; Al, $\sim$ .01; SiO_2, 6-10; P_2O_5, .2-3; SO^{2-}, 11-12; Cl, 5-6; K, 5.5-6.8; Ca, 50-70; Mn, .003-.160; Zn, $\sim$ .01; Sr, .23-.27; Mo, .04-.05; As, .14-.17; HCO_3, $\sim$ 240; Fe, .02-1.0.

The laser measurements in the present work indicated uranium levels of 350 $\pm$ 30, 200 $\pm$ 20, and 63 $\pm$ 5 ppb, respectively, in aliquots taken from the stored samples above. The agreement was quite good, considering the long

storage period (ten months) between the two sets of uranium determinations. The technique was also successfully applied to municipal water supplies that contained uranium at the 10^{-10} M level. These measurements were undertaken to see if any unknown interference problems would be encountered in the analysis of natural water samples.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the photon counting spectrofluorometer used in this work.

Figure 2. Fluorescence spectra of CaF_2 precipitated from a 10^{-12} M UO_2^{2+} solution, a 10^{-8} M UO_2^{2+} solution, and a reagent blank sample. The 10^{-12} M and reagent blank were taken with 1 mW laser power, 488 nm excitation, and 3 s time constant. The 10^{-8} M spectrum was taken with 65 μw laser power and .3 s time constant.

Figure 3. Fluorescence spectrum of a CaF_2 sample precipitated from a 10^{-12} M UO_2^{2+} solution taken with boxcar integration. The operating parameters were: laser power, 150 μW; laser pulse width, 500 ms; time constant, .3 s; boxcar delay, 50 μs; and boxcar integration width, 50 μs.
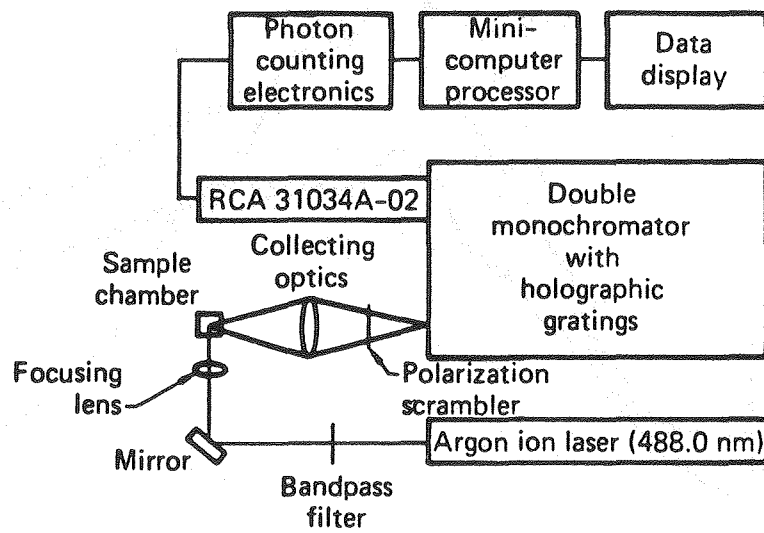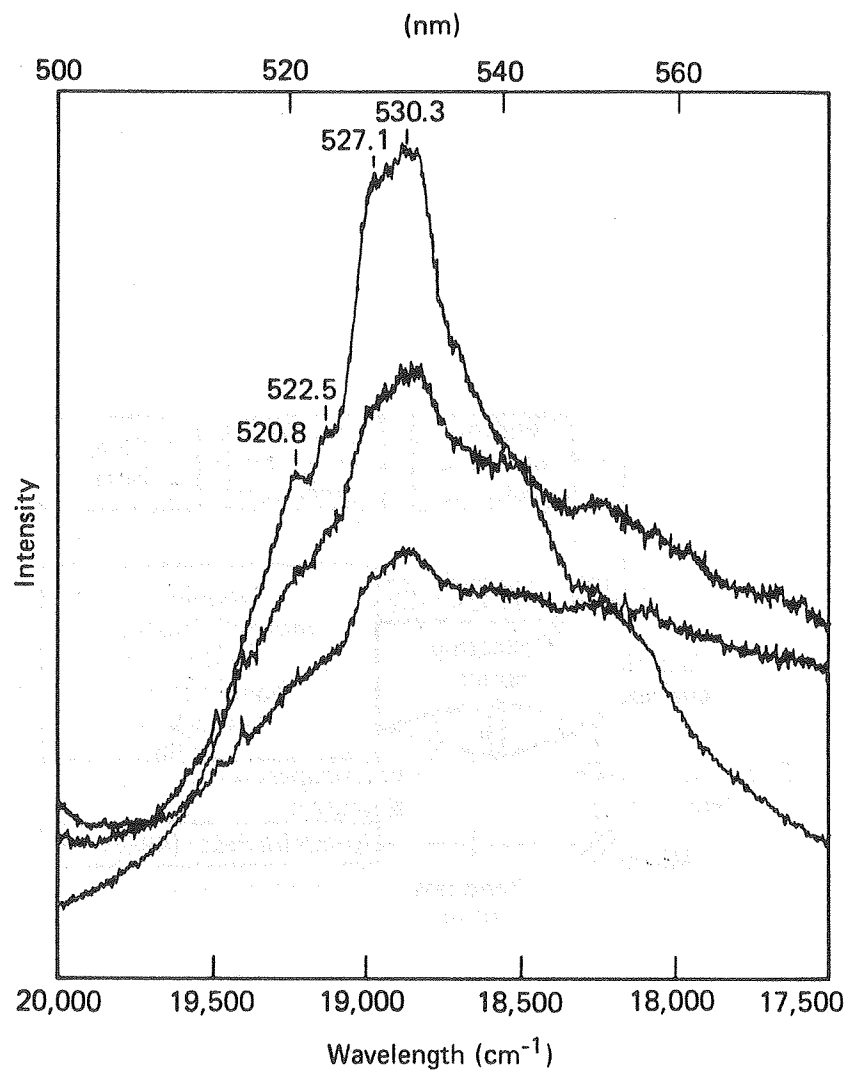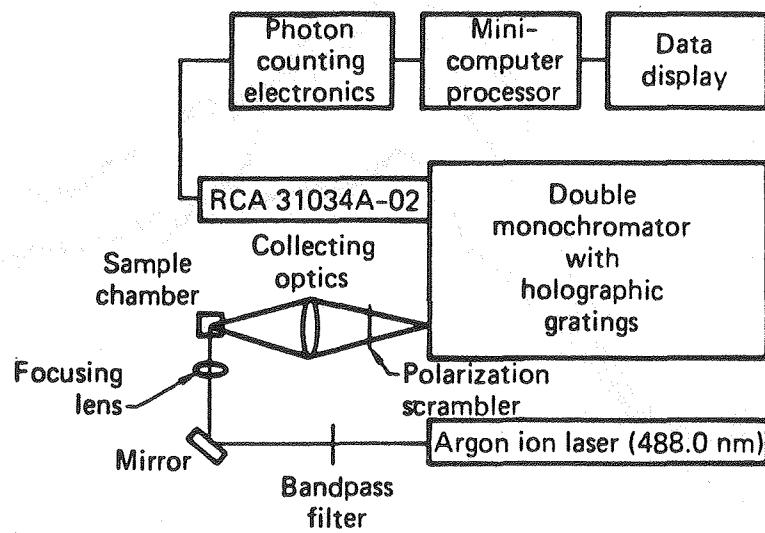
Figure 1.

Figure 2.

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