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The Fluorometric Determination of Uranium in Natural Waters

by

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THE FLUOROMETRIC DETERMINATION OF URANIUM IN NATURAL WATERS

by

A. D. Hues, A. L. Henicksman, W. H. Ashley, and D. Romero

ABSTRACT

Duplicate 200- μ l aliquots of the water samples, as received, are transferred by means of Eppendorf pipettors onto 0.4-g pellets of 2% LiF-98% NaF flux, contained in platinum dishes. The pellets are dried under heat lamps; then fused over special propane burners. The fused pellets are transferred to a Galvanek-Morrison fluorometer, where they are excited with ultraviolet radiation and the fluorescence is measured. The uranium is calculated by comparing the measured fluorescence with that of other pellets, carried through the same procedure, which contain aliquots of standard uranium solutions. The sensitivity of the method is about 0.2 ppb of uranium, and the precision is approximately 15 relative percent in the 0.2- to 10-ppb uranium concentration range.

I. INTRODUCTION

The reliable determination of uranium at concentrations in the low parts-per-billion (ppb) range in natural surface and ground waters is essential to the success of the Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) for the National Uranium Resources Evaluation. Because of the low uranium levels expected, a fluorometric method was chosen as being acceptably sensitive and precise for the purposes of the program.

The method used is substantially that developed by Centanni et al.¹ with modifications made at the Los Alamos Scientific Laboratory. In this method, aliquots of the sample are transferred, without separation of the uranium, onto pellets of 2% LiF-98% NaF flux which are then dried and fused. The fused pellets are excited with ultraviolet radiation and the fluorescence measured in a Galvanek-Morrison fluorometer.

The modifications to the method mostly involved equipment changes to facilitate operations and increase the sample analysis rate. A quick-opening valve, pilot light ignition, and a heat shield were added to the Fletcher burner used for the fusions; a twin shell blender was used for blending the flux materials;

and the fluorometer was improved by substituting a digital voltmeter for the microammeter and by modifying the amplifier circuit and the response linearity. The procedure was changed by using 200- μ l sample aliquots in place of 100- μ l aliquots for analysis. These modifications are discussed in more detail in subsequent sections.

II. PROCEDURE

Safety and Cleanliness

Extreme care must be taken in cleaning the work areas for the fluorometric determinations of low concentrations of uranium. A laminar air flow, "clean" room is recommended for this purpose. As this equipment was not immediately available, much care was taken in cleaning the laboratory before use. Walls, benches, fume hoods, and floors were thoroughly washed, and surfaces difficult to clean were sprayed with a clear plastic sealer. Thereafter, only new equipment and supplies, which had never been exposed to uranium contamination, were allowed in the laboratory. The laboratory floors are wet-mopped three times a week, protective clothing which has been worn in areas potentially contaminated with uranium is excluded from the laboratory, and access is restricted to the few necessary analysts. All glass and platinum ware is thoroughly cleaned in quartz-distilled nitric acid and rinsed with quartz-distilled water.

Pellets are fused in fume hoods to prevent the escape of combustion gases and heat into the room, and didymium glassblower's goggles are worn for eye protection during the fusions. The flux materials, primarily sodium fluoride, are potentially hazardous in milligram quantities,^{2,3} and exposures are kept to an absolute minimum. Rubber gloves are worn while pelleting the flux, and the analysts wash their hands after contact with the material. All operations which require the flux to be exposed, such as making the pellets and pipetting the sample aliquots, are done in open-front plastic boxes attached at the rear to a filtered exhaust, and a slight air flow is maintained through the box.

The published maximum allowable concentration of air-borne sodium fluoride is 2.5 mg/m³ of air,^{2,3} while the estimated lethal dose for man is 2.5 g. The total particulate matter found at the opening of the open-front boxes, using 0.5- μ m Millipore filters in an air sampler, varied from 0.005 mg/m³ to about 0.05 mg/m³ of air. Inspection of the filter paper under low-power magnification revealed that a substantial part of this small amount of material was "tramp" dust and organic fibers. As an added precaution, a 24-h air sample is taken once a week, and the air flow in the exhaust hoods is checked weekly.

Apparatus

Blender, Patterson-Kelly, Twin Shell, or equivalent, for blending the flux.

Burner, Fletcher, modified after Jarrell-Ash Manual No. 26-000, and according to directions by Centanni.¹ See Fig. 1. A quick-opening valve was added to open and close the propane and air lines simultaneously without disturbing the control valve settings, and a pilot light was added to ignite the propane-air mixture. In order to protect the rubber tubing connections, an asbestos-board heat shield was built around the barrel and connections of the burner.

Key to callouts in side view: 1) Weld, 2) 44-mm (1.75-in.) pipe, 3) 38-mm (1.5-in.) pipe, 4) 79-mm (3.125-in.) stainless steel rod, 5) 6-mm (0.25-in.) plate, 6) 0.38-mm (0.015-in.) sheet metal, 7) 101-mm (4-in.) weld cap, 8) 7.9-mm (0.3125-in.) stainless steel plate, 9) 5 mesh, 16 gauge, nichrome screen, 10) Perforated copper screen, 11) #36 drill, 5-40 N.C.2, 12) 4.2-mm (0.167-in.) plate. Courtesy of Phillips Petroleum, Grants, NM.

Fig. 1.

Modified Fletcher burner.

Dishes, platinum, 19-mm-diam, stamped from 0.25- or 0.37-mm sheet.

Fluorometer, Jarrell-Ash Model 26-000, or equivalent. The microammeter on the fluorometer was replaced with a digital voltmeter to facilitate reading, and the amplifier circuit was modified to minimize drift. Another modification was made to improve the linearity when going from one range multiplier switch to another.

Pellet maker, Jarrell-Ash Catalog No. 26110, or equivalent, adjusted to deliver pellets weighing 0.4 g.

Pipettor, Eppendorf, 200- μ l.

Pyrometer and thermocouple.

Screens, 5x5 mesh, 16 ga, nichrome wire. Circles are cut to fit easily in the burner top ring. These screens are easier to use if they are flattened with a heavy hammer to provide a smoother surface on which to set the platinum dishes.

Reagents

Lithium fluoride, reagent grade, tested for fluorometric suitability.

Mixed fusion flux, 98% NaF and 2% LiF. Mix for at least 8 h in the blender. Cover the ends of the shell with polyethylene sheet before attaching the covers to prevent contact of the flux with the gaskets.

Nitric acid, quartz-distilled.

Sodium fluoride, reagent grade, tested for fluorometric suitability. See INTERFERENCES.

Uranium standard solution, 100-ppb. Prepare a stock solution from NBS SRM 950 or 960 by dissolving an amount sufficient to contain 10 mg of uranium in 5 ml of quartz-distilled HNO_3 and diluting to 100 ml. Transfer a 100- μ l aliquot of this solution to a 100-ml volumetric flask, add 5 ml of quartz-distilled HNO_3 , and dilute to 100 ml with quartz-distilled water. This stock solution contains 100 ppb of uranium, and from it, working standards are prepared by dilution of appropriate aliquots with quartz-distilled water and adjusting the HNO_3 content to 5% with the quartz-distilled acid.

Uranium working standard solutions, 1-ppb and 5-ppb. Prepare by diluting 1-ml and 5-ml aliquots of the 100-ppb uranium standard solution to 100 ml.

Water, quartz-distilled.

Analysis of Samples

1. Place 20 clean platinum fusion dishes and a number strip on a nichrome screen in the arrangement shown in Fig. 2.
2. Place a pellet of flux in each dish, using the pellet maker.

Fig. 2.

Arrangement of platinum dishes on screen.

3. Turn on the fluorometer to warm up.
4. Using the Eppendorf pipettor, deliver an aliquot of the high standard (5 ppb) to each of the dishes identified as S5 and an aliquot of the low standard (1 ppb) to each S1 dish. Deliver equal aliquots of a blank solution, consisting of 5% HNO_3 in quartz-distilled water, to the pellets identified as B1.
5. Deliver duplicate aliquots of each sample onto pellets arranged as in Fig.2. Record the sample numbers and the screen number.
6. Dry the pellets under the heat lamp for 45 min.
7. Ignite the burner and adjust the flow of air and propane to give a temperature of 900 to 950°C. Measure the temperature with a tray of empty dishes in place and the thermocouple probe pressing down on a dish. The flame gets hotter as the burner heats up. A good flame has rather soft cones about 9 mm high. The air and propane lines are designed so that a single lever simultaneously activates a plug valve on each line, thus allowing the flame to be instantly turned on, using a pilot light, or turned off, with a 90° throw of the lever. If the adjustments are not changed, the burner flame will usually be satisfactory when ignited.
8. Put the tray of dishes in position and fuse for exactly 3 min. Turn off the flame.
9. When the melts have solidified, place the tray on a 13-mm-thick transite sheet and cover it at once with a Petrie dish. Allow the pellets to cool for at least 15 min, but not more than 1 h.
10. After the fluorometer has been on for at least 30 min, place a pellet containing the high standard in the slide, press the slide in, depress the 0.01-scale switch, and use the FINE VOLTS control to adjust the voltmeter to read approximately 15.
11. Pull the slide to load position and zero the meter with BACKGROUND control. Repeat these two steps until readings are stable.
12. Read and record the fluorescence of each pellet in millivolts as shown on the digital voltmeter.
13. Calculate a calibration line from the data obtained for the standard solutions and the blanks. Commonly, the equation is calculated from the data obtained for the blanks and the 5-ppb uranium standard solutions, and the 1-ppb standard solutions are used as controls. Calculate the uranium contents of the samples using this equation.

III. INVESTIGATIONS OF PROCEDURE PARAMETERS

The early sample analyses were made using 100- μl aliquots. Standard solutions were prepared to contain from 1 to 10 ppb of uranium. The relative standard deviation in analyzing these standards was approximately 45% at the 1-ppb level and 15% at the 5-ppb level. Substantial improvement in precision was obtained by increasing the aliquot size to 200 μl . The relative standard

deviations of the control standards were reduced to 20% at the 1-ppb level and to 12% at the 8- and 10-ppb levels. A 200- μ l aliquot is the maximum liquid volume that can be used without causing the pellet to collapse.

To avoid interference from the many elements likely to be present in natural waters, a modification of the extraction procedure described by Centanni¹ was investigated for possible use. In this extraction, a 1-ml sample of water is taken and 10 ml of saturated $\text{Al}(\text{NO}_3)_3$ solution, 200 μ l of HNO_3 , and 1 ml of ethyl acetate are added. The phases are mixed thoroughly to extract the uranium, and an aliquot is transferred from the organic phase to a flux pellet which is then dried, fused, and read as described under PROCEDURE. Although conditions were established for the quantitative recovery of the uranium, the analysis time was greatly increased, and the precision was poorer because of the extra manipulation. The extraction separation was not investigated further, and the application of the method in this program was restricted to relatively pure waters containing 10 ppb or less of uranium.

IV. EFFECTS OF DIVERSE IONS

The effect of certain foreign substances on the apparent fluorescence of uranium has been widely reported. Some interfere by decreasing the fluorescence, called "quenching," and a few metallic ions and many organic compounds may interfere by enhancing the fluorescence. Quenching has been reported in sodium fluoride matrices by thorium, iron, chromium, manganese, lead, calcium, and rare earths. Silicon, titanium, vanadium, copper, and nickel have also been mentioned as interfering. In the analysis of water, this list of elements was viewed with suspicion because the conditions were different, and the work was done at uranium concentrations several orders of magnitude higher. Michelson⁴ states that the quenching effect is dependent only upon the ratio of quenching agent to flux, is independent of uranium concentration, and can be avoided by using a large dilution factor. He also points out that certain ions, such as calcium, antimony, tellurium, and magnesium, in very low concentrations, may enhance the fluorescence, thus making extreme dilutions questionable.

Because the metal ion concentrations in naturally occurring waters is variable and usually unknown, a general assessment of their effects on the fluorescence of uranium is difficult. It is likely, however, that the metal ion concentrations are adequately low to ensure usable accuracy for survey work in all but highly mineralized areas.

Limited experimental work indicated that aluminum, titanium, magnesium, thorium, nickel, chromium, cobalt, manganese, zinc, calcium, and iron can be tolerated at ratios between 1000 and 10 000 to 1 part uranium. Vanadium, however, produced a significantly high bias at a 1000 to 1 ratio.

Initially, some difficulty was experienced with the flux mixture, and random high values were attributed to interference from minute dark particles dispersed through the flux mixture. The source of this contamination was found to be the cover gaskets on the V-shell blender. The problem was eliminated by covering the gaskets with polyethylene sheet. Abnormally low values obtained on standards were thought to result from attack on the platinum by moisture in insufficiently dried flux pellets. Several lots of NaF were investigated for suitability as a flux component. It was found that some were too granular,

some were too dense, and some were not cohesive enough to form pellets. Furthermore, blank readings varied by as much as a factor of 10 between several lots. A substantial supply of the best available material was obtained. Because of the relatively small amount of LiF in the flux mixture, a study was not made of the variability of this material, nor was a study made of possible alternate flux compositions.

V. RELIABILITY

Routine analyses of 200- μ l aliquots of standard solutions in sets of samples by four analysts over a period of one month, gave the values shown in Table I.

TABLE I
ROUTINE ANALYSES OF STANDARD SOLUTIONS

<u>No. of results</u>	<u>U, ppb^a</u>	<u>U Found, Av. ppb</u>	<u>Std. Dev., ppb</u>	<u>Rel. Std. Dev., %</u>
1832	1.0	1.12	0.24	21.4
226	8.0	7.86	0.96	12.2
260	10.0	9.68	1.22	12.6

^aNominal value.

A study was also made by analyzing blank pellets, containing 5% HNO₃ in quartz-distilled water, and standards containing 1- and 5-ppb uranium. Both 100- and 200- μ l aliquots were used, and the results are shown in Table II.

A comparison was made between the fluorometric method and the delayed neutron counting methods on a set of 12 Alaska water samples. Some of these samples contained appreciable amounts of sediment. The samples were analyzed as received; then they were filtered and the filtrates were analyzed by both methods (Table III).

Based on these studies, guidelines were established for determining acceptability of results for a sample or set of samples. Each tray of 20 flux pellets contains three blank pellets, three 1-ppb standards, three 5-ppb standards, one either of 8- or 10-ppb standard, and five samples in duplicate. If a blank or a 1- or 5-ppb standard value lies outside the following limits, the set is repeated.

Blanks	0 ± 0.6 ppb
1 ppb standards	± 0.6 ppb from long-term average
5 ppb standards	± 0.8 ppb from the actual value

The individual sample values must lie within the following limits, or the sample must be repeated.

TABLE II
ANALYSES OF BLANKS AND STANDARD SOLUTIONS

<u>No. of values</u>	<u>U, ppb ^a</u>	<u>Aliq. Size, μl</u>	<u>Std. Dev., ppb</u>	<u>Rel. Std. Dev., %</u>
69	0	100	0.44	-
14	0	200	0.10	-
240	1.0	100	0.54	50
497	1.0	200	0.30	28
81	5.0	100	0.70	14
14	5.0	200	0.26	5

^aNominal values.

TABLE III
FLUORESCENCE AND DELAYED NEUTRON COUNTING ANALYSES

<u>Sample No.</u>	<u>U found, ppb; unfiltered</u>		<u>U found, ppb; filtered</u>	
	<u>Fluorometry</u>	<u>DNC^a</u>	<u>Fluorometry</u>	<u>DNC</u>
400270	0.7	0.4	0.6	0.7
400272	0.7	0.6	0.9	0.5
400273	1.7	1.4	1.1	1.6
400279	0.1	0.0	0.2	0.2
400280	0.4	0.2	0.1	0.1
400261	0.4	0.3	0.4	0.3
400262	0.5	0.3	0.5	0.2
400255	0.4	0.1	0.3	0.0
400254	1.3	0.2	0.4	0.3
400228	0.6	0.3	0.9	0.2
400247	0.8	0.0	0.8	0.0
400285	1.0	0.2	0.9	0.2

^aDNC = delayed neutron counting.

0 - 3 ppb	average $\pm$ 0.6 ppb
3.1 - 7 ppb	average $\pm$ 0.8 ppb
7.1 - 10 ppb	average $\pm$ 1.2 ppb

Samples showing negative values not below -0.6 ppb are acceptable and are handled in the normal manner. If either value is more negative than -0.6 ppb, the analysis is repeated. Samples having apparent uranium contents greater than 10 ppb or less than -0.5 ppb are not reported. These samples are reanalyzed by delayed neutron counting.

Normally, about 25 ml of sample, contained in polyethylene bottles, are received. Most of these are relatively clean, and have a pH of about 2, but they sometimes contain significant amounts of sediment, or in some cases, crystalline salts. The samples are shaken thoroughly before aliquots are taken.

Since July 1, 1975, over 20 000 samples have been analyzed by this method. The present rate of analysis is in excess of 3 000 samples per month, or about 8 samples per man-hour.

VI. POTENTIAL FUTURE DEVELOPMENT WORK

Development work on this method before applying it to sample analysis was very limited. Additional work needs to be done as time permits. The optimum HNO_3 concentration for standards and blanks should be established. If the acid concentration has a significant effect, samples should be adjusted to this optimum acidity, preferably in the field. Optimum ratios for the flux mixture should be determined for our particular adaptation, and alternate flux materials should be considered. Standards of suitability for flux materials should be established, and should include flux purity, density, and cohesive properties.

Possibly our most serious source of analytical variability at the present time is the sample fusion. Optimum burner conditions, heating and cooling cycles, burner design, or other variables which might affect the precision of the method need further investigation. Other heat sources should be considered in order to eliminate the problems inherent in the gas burner.

Additional investigation is needed on the effects of diverse materials on the fluorometric determination of uranium. Further effort is needed to eliminate interfering elements by extractions, ion exchange, or other separations.

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REFERENCES

1. F. A. Centanni, A. M. Ross, and M. A. DeSesa, "Fluorometric Determination of Uranium," Anal. Chem. 28, 1651 (1956).
2. N. I. Sax, Dangerous Properties of Industrial Materials, 4th ed., (Van Nostrand Reinhold Co., New York, 1975), Section I, p. 19.
3. C. H. Gray, Ed., Laboratory Handbook of Toxic Agents, (The Royal Institute of Chemistry, London, 1961), p. 90.
4. C. E. Michelson, "The Preparation of Fluoride Melts for Use in the Fluorometric Method of Uranium Analysis," AEC Research and Development report HW-36831 (July 1955).