

# Determination of Uranium in Natural Waters

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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-C



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F. B. BARKER, J. O. JOHNSON, K. W. EDWARDS, *and* B. P. ROBINSON

RADIOCHEMICAL ANALYSIS OF WATER

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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1696-C



**UNITED STATES DEPARTMENT OF THE INTERIOR**

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# RADIOCHEMICAL ANALYSIS OF WATER

## DETERMINATION OF URANIUM IN NATURAL WATERS

By F. B. BARKER, J. O. JOHNSON, K. W. EDWARDS, and  
B. P. ROBINSON

### ABSTRACT

A method is described for the determination of very low concentrations of uranium in water. The method is based on the fluorescence of uranium in a pad prepared by fusion of the dried solids from the water sample with a flux of 10 percent NaF 45.5 percent  $\text{Na}_2\text{CO}_3$ , and 45.5 percent  $\text{K}_2\text{CO}_3$ . This flux permits use of a low fusion temperature and yields pads which are easily removed from the platinum fusion dishes for fluorescence measurements. Uranium concentrations of less than 1 microgram per liter can be determined on a sample of 10 milliliters, or less. The sensitivity and accuracy of the method are dependent primarily on the purity of reagents used, the stability and linearity of the fluorimeter, and the concentration of quenching elements in the water residue. A purification step is recommended when the fluorescence is quenched by more than 30 percent. Equations are given for the calculation of standard deviations of analyses by this method. Graphs of error functions and representative data are also included.

### INTRODUCTION

The Water Resources Division of the U.S. Geological Survey is studying the occurrence and distribution of uranium, radium, and other radioelements in natural waters (Scott and Barker, 1962). This study is important principally because (1) it furnishes data basic to studies of the hydrogeochemistry of radioelements, (2) it provides a basis for the geochemical prospecting of uranium ore deposits, and (3) it permits evaluation of the pollution of natural waters by uranium mining and milling operations. Previous papers in this series (Barker and Robinson, 1963; Barker and Johnson, 1964) have described the determination of gross beta activity and radium in water.

Uranium is usually regarded as one of the rarer elements, but it is actually present in the earth's crust in greater amounts than such "common" elements as cadmium, bismuth, mercury, and iodine. The average uranium concentration in the earth's crust is estimated to be about  $4 \times 10^{-6}$  g per g of rock (Katz and Rabinowitch, 1951, p. 69). Uranium as well as thorium is concentrated in crustal rocks of

high silica content such as pegmatite and granite, but concentrations are less in mafic rocks, especially those in the deeper parts of the crust; very little is thought to occur below 16 km.

Uranium is widely disseminated in the lithosphere; concentrations in igneous rocks range from  $0.001 \times 10^{-6}$  to  $30 \times 10^{-6}$  g per g of rock (Adams, Osmond, and Rogers, 1959, p. 312). Although uranium-bearing rocks are extensively distributed in nature, substantial ore deposits are uncommon. Three types of minerals dominate most large deposits: (1) the oxides, primarily pitchblende, (2) the vanadates, primarily carnotite and tyuyamunite, and (3) the silicates, of which coffinite is the most important. In terms of economic geology, uranium is at present the most important of the radioelements. Its chief use is in the field of nuclear energy.

Most natural waters contain detectable amounts of uranium. The average concentration in the ocean is about 3  $\mu\text{g}$  per l (micrograms per liter) (Rona and others, 1956). The uranium concentration of ground and surface waters varies greatly, from a low of less than 0.1  $\mu\text{g}$  per l to several mg per l (milligrams per liter). In the great majority of surface and ground waters the concentration is less than 10  $\mu\text{g}$  per l. The concentration in ground waters associated with secondary uranium deposits (such as the Shirley Basin uraniumiferous area in Wyoming) sometimes exceeds several milligrams per liter, however.

#### METHODS OF URANIUM ANALYSIS

The analytical chemistry of uranium has been reviewed recently by Booman and Rein (1962). This copiously referenced work contains a comprehensive coverage of analytical methods available for a wide range of concentrations of uranium in various chemical forms.

Many of the conventional titrimetric, gravimetric, and electro-metric methods of analysis are obviously unsuitable for very low uranium concentrations unless the uranium in a large volume of water is concentrated by techniques such as ion exchange, solvent extraction, and coprecipitation. Such processes, although frequently used, are not only somewhat time consuming but also may introduce errors from the additional manipulations required.

Fortunately, trace amounts of uranium can be determined by practical methods which partially or completely avoid tedious concentration and separation procedures. Such methods may be based on (1) the formation of a characteristic colored complex whose concentration may be determined directly with a suitable spectrophotometer, (2) the radioactivity of uranium, its daughters, or its neutron-activation products, or (3) the fluorescence of various uranium ions or compounds. All of these methods have certain disadvantages and limitations, but each also has its particular areas of usefulness.

Many of the chromogenic agents used for uranium determinations are useful only in organic solvents into which the uranium is extracted. Dibenzoyl methane is probably the most frequently used of such compounds. Many metallic cations interfere unless the composition of the extraction solvent and the aqueous solution are carefully controlled. Of the reagents useful for direct spectrophotometric determination in aqueous solution, the one that has perhaps been studied most extensively is 3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid (arsenazo). However, this substance forms stable complexes with many other metallic ions and hence has limited applicability. Specific chromogenic agents for uranium have been much sought but have not yet been found.

Determination of uranium by measurement of radioactivity is a highly sensitive technique; it requires, however, a knowledge of the other radionuclides present in the sample. Either the uranium must be separated from interfering radionuclides, or it must be possible to make appropriate corrections for their interference. Uranium in equilibrium with its decay products may be determined conveniently by measurement of the gamma activity of its daughters.

Alpha-counting methods are available for uranium that has been separated from other alpha-emitting nuclides. A source of error results from the variation in abundance of the uranium isotopes. The abundance ratios vary more in natural waters than in primary uranium minerals, as is to be expected from geochemical consideration of the uranium series. Alpha spectrometry, using solid-state detectors, is a promising method for determining the individual uranium isotopes, even when other alpha emitters are present. Neutron-activation methods are suitable for analyzing uranium in very low concentrations; 0.3  $\mu\text{g}$  of uranium-238 can be detected after irradiation with a flux of  $10^{12}$  neutrons per  $\text{cm}^2$  per sec and subsequent beta counting of neptunium-239 (Koch, 1960, p. 190). Haskin, Fearing, and Rowland (1961) have determined as little as  $10^{-10}$  g of uranium in limestone by measurement of the beta activity of xenon-133 resulting from the fission of uranium-235 in a thermal neutron flux as high as  $10^{13}$  neutrons per  $\text{cm}^2$  per sec. Irradiation for periods of 4 to 12 days was used.

The determination of uranium concentrations by the isotope-dilution method of Rona and others (1956) is probably the most precise method yet developed. However, it requires concentration steps and the use of a mass spectrometer and would not be suitable for routine analyses.

The fluorimetric method for uranium is among the most sensitive and specific methods available. Various techniques for the measurement of uranium fluorescence have been used, ranging from direct

measurement of mineral and solution fluorescence to measurements on materials of carefully controlled composition in the solid phase. Measurement of the fluorescence of uranium in fused pads containing sodium fluoride appears to be the most sensitive, accurate, and reproducible of such methods. The principles of this method and its advantages and disadvantages as used by the Water Resources Division of the U.S. Geological Survey are discussed in the following sections.

### THE FLUORIMETRIC URANIUM METHOD

The intense green or yellow-green fluorescence of uranium minerals under excitation by ultraviolet light has been known for many decades, and fluorescence measurements have been extensively used for detection and qualitative identification of uranium in nature. There is a considerable variation in the fluorescence spectra of uranium minerals and compounds, however. Uranium silicates, micas, and compounds which contain exclusively U(IV) are not fluorescent (Booman and Rein, 1962, p. 60).

Nichols and Slattery (1926) discovered that uranium will fluoresce very strongly when fused in sodium fluoride. This fluorescence is stronger than that of the most highly fluorescent uranium minerals. Since this discovery, many investigators have studied the quantitative determination of uranium by measurements of its fluorescence in fused pads containing sodium fluoride (see Price and others, 1945 and 1953; Jacobs, 1950; Grimaldi and others, 1954). Numerous investigators have demonstrated that the fluorescence is directly proportional to the amount of uranium over a wide concentration range.

Price, Ferretti, and Schwartz (1953) found the fluorescence spectrum of uranium pads, prepared by fusion with fluoride salts, to consist of four bands having peaks at 5456, 5546, 5571, and 6016 Å. The band at 5546 Å is the most intense and hence the most sensitive for quantitative analysis. The wavelength of the exciting light may be varied over a considerable range, but the 3650 Å region seems to give maximum excitation and is also conveniently obtained from a mercury-arc lamp. Most fluorimeters employ primary filters to limit the incident ultraviolet light to this wavelength region. A phototube or photomultiplier sensitive to the 5546 Å region is used as detector, and appropriate filters are used to exclude light of other wavelengths. Excitation of uranium in fused pads that contain fluoride by means of 3650 Å ultraviolet light and measurement of the 5546 Å fluorescent radiation permits a very specific quantitative determination. No other elements are known to interfere in fluxes containing more than 90 percent sodium fluoride, but cadmium fluorescence has been reported for high carbonate fluxes (Booman and Rein, 1962, p. 102).

Numerous instruments have been designed for fluorimetric determinations (see Byrne, 1957; Morrison and Galvanek, 1955; Price and others, 1953; Parshall and Rader, 1957). Of these, the commercially available instruments of the Galvanek-Morrison type are satisfactory for most routine work. Instruments having greater stability of response may be desirable where the maximum in accuracy and reproducibility is desired. The Water Resources Division Laboratory at Denver uses a Galvanek-Morrison fluorimeter manufactured by the Jarrel-Ash Co., Newtonville, Mass.

A variety of flux compositions have been used by other investigators. All fluxes in common usage contain sodium fluoride in amounts ranging from about 8 to 100 percent. Pure sodium fluoride gives high sensitivity but has the disadvantage of requiring a high fusion temperature (about 1000°C), and the resultant pellet cannot be easily removed from the fusion dish without breakage. Interference due to the presence of certain heavy metals which may cause quenching or enhancement of the fluorescence seems to be lowest with this flux. Centanni, Ross, and DeSesa (1956) reported that the use of a 98 percent NaF-2 percent LiF flux permits use of a lower fusion temperature (850-900°C), gives a pellet which is easily removed from the fusion dish, and improves the accuracy and reproducibility of the method.

The Geological Survey has found the use of a high carbonate flux generally satisfactory. The flux composition used is 45.5 percent  $\text{Na}_2\text{CO}_3$ , 45.5 percent  $\text{K}_2\text{CO}_3$ , and 9 percent NaF by weight. This flux has a relatively low fusion temperature (605° C) which permits the use of a less elaborate fusion apparatus. It also gives a pad which is easily removed from the fusion dish for fluorescence measurements.

Fluxes of this type have certain disadvantages, however; these are: (1) a slightly reduced fluorescence sensitivity, (2) formation of a hygroscopic pellet that requires dessication, and (3) a somewhat greater interference by elements that quench the uranium fluorescence. The increased quenching generally is regarded as the most serious of these factors.

Dessication of the pellet after fusion does not generally present any particular difficulties. Unless the humidity is very high, the pellet may be removed from the dessicator and read on the fluorimeter in the normal atmosphere without a noticeable drift in the reading over short time intervals. In areas of high humidity, it may be desirable to keep the fluorimeter in a low-humidity environment.

Quenching of fluorescence by various elements occurs in any type of flux, although it seems to be most pronounced in high carbonate fluxes. Grimaldi and others (1954) list Cr, Mn, Co, Ni, Ag, La, Pt, Au, Pb, Ce, Pr, and Nd as strong quenchers (1-10  $\mu\text{g}$  quench uranium

fluorescence by 10 percent or more) and Fe, Cu, Zn, Sn, and Th as moderately strong quenchers (10–50  $\mu\text{g}$  quench fluorescence by 10 percent). The quenching of uranium fluorescence by iron, copper and manganese is shown in figure 1. The solubility of iron in the flux determines the maximum quenching possible by this element. The pads containing manganese are highly colored at moderate to high concentrations of this element, and part of the quenching may be attributed to a reduction in the reflectivity of the pad. (For highly colored pads the calculation of the blank factors, discussed on p. C18, may not be valid.)

One of two methods is generally employed to avoid errors due to quenching; either the sample is diluted sufficiently to reduce quenching to negligible levels, or the uranium is separated from the quenching elements before analysis by techniques such as ion exchange or solvent extraction. The dilution method is useful when the amount of uranium in the sample is large enough to permit a rather large sample dilution. Figure 1 shows that the fluorescence intensity of the

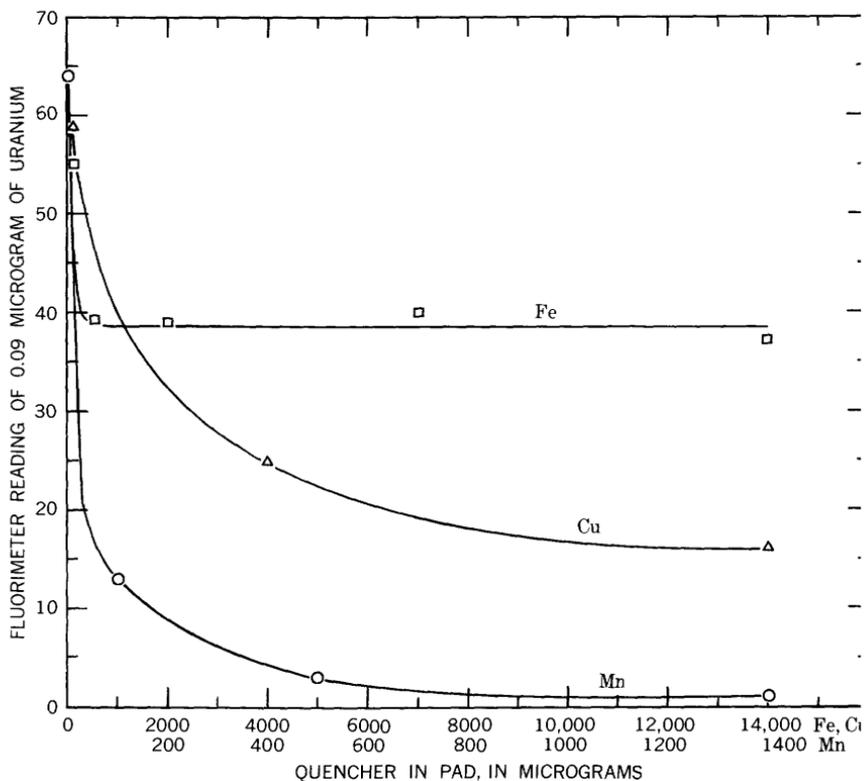


FIGURE 1.—Quenching of uranium fluorescence by iron, copper, and manganese. Fluorimeter readings of 0.09  $\mu\text{g}$  of uranium for various amounts of added quencher

sample drops off rapidly with the addition of small amounts of quenching elements and more slowly with further additions. Thus, if quenching occurs in the undiluted sample, a rather large dilution may be necessary to reduce the concentration of quenching elements to a point where their interference is negligible. Excessive dilution will reduce the fluorimeter reading and result in an increase in the probable error of the measurement.

In general, separation of uranium from quenching elements by solvent extraction or ion exchange is preferable to making a large dilution. Both techniques may be avoided, however, if the quenching does not reduce the fluorescence by more than about 30 percent. Thatcher and Barker (1957) noted that moderate amounts of quenching can be dealt with mathematically. Most nonsaline natural waters can be analyzed for uranium by this procedure without preliminary treatment. Computation of uranium concentrations in water containing quenching elements is discussed on page C13.

#### APPARATUS

Much of the apparatus needed in fluorimetric uranium determinations is standard in most chemical laboratories. The special equipment needed is described below.

*Fusion apparatus.*—The fusion machine (fig. 2) was designed by Stevens and others (1959) of the Geological Survey and has been described in the literature. The machine is a device for passing the

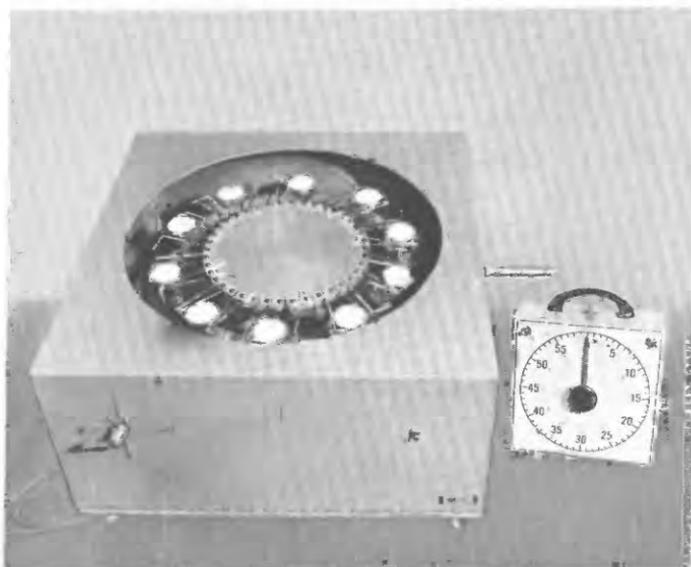


FIGURE 2.—Stevens rotary fusion machine.

fusion dishes over an air-natural gas burner in a manner that ensures complete mixing of the melt and formation of uniform pads. The fusion dishes are mounted on quartz rods that extend from a central platform. As the platform rotates, the dishes pass over the circular burner at a constant speed (10.8 rpm) and a constant elevation ( $\frac{7}{8}$  in.). The gas pressure is regulated by means of a four-way valve having settings of off, low, medium, and high. The temperature obtainable with the burner in the high position is approximately  $650^{\circ}\text{C}$ , although the actual temperature will vary somewhat, depending on outside usage of natural gas. With the valve in the medium position, the temperature in the platinum dishes is near the melting point of the flux, approximately  $605^{\circ}\text{C}$ . In the low position the temperature is approximately  $550^{\circ}\text{C}$ . The medium and low settings are used to permit slow solidification of the pad after the fusion has been completed. The fusion machine is mounted so that it may be tilted during the initial fusion interval to ensure complete mixing of the melt.

*Fluorimeter.*—Many instruments have been built for fluorimetric uranium analysis. Production fluorimeters of the Galvanek-Morrison type made by the Engineering Equipment Co., Boynton Beach, Fla., and the Jarrel-Ash Co., Newtonville, Mass. (fig. 3) are suitable for routine work.



FIGURE 3.—Galvanek-Morrison reflection-type fluorimeter.

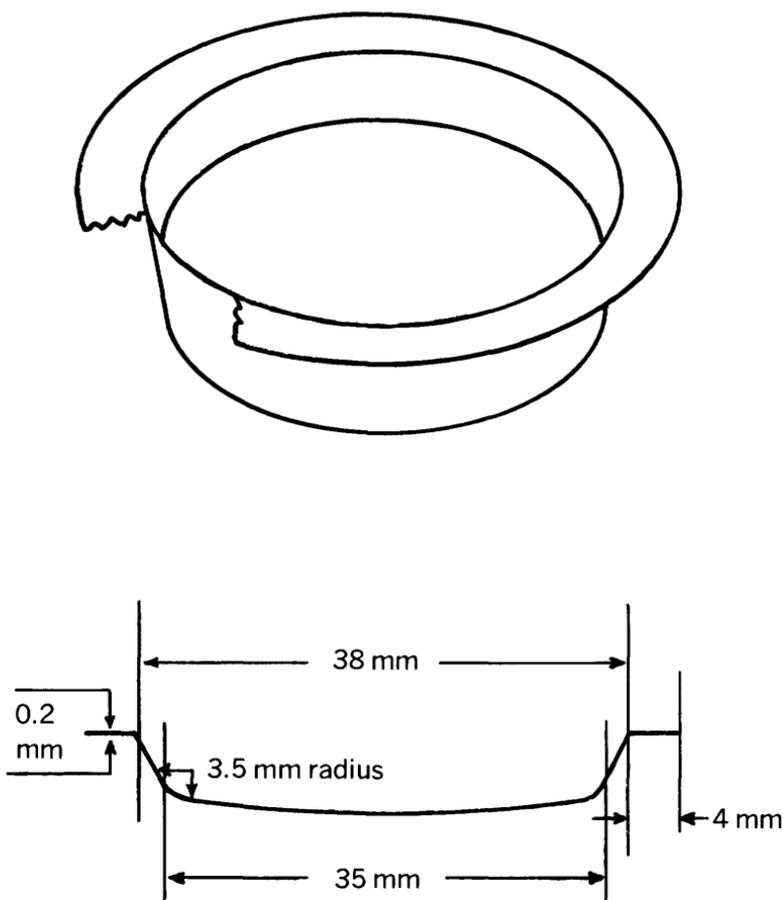


FIGURE 4.—Platinum fusion dish.

*Fusion dishes.*—Platinum dishes of approximately 10 ml capacity are used (fig. 4). The lips on the dishes permit mounting on the quartz rods of the fusion mashine.

*Rod or ball mill.*—Both a heavy glass jar mill containing lucite rods and an aluminum oxide ball mill are satisfactory for grinding and mixing the flux. Other mills may be equally satisfactory, however.

*Infrared drying lamps.*—Suitable infrared lamps having protective shields are available from most chemical supply companies.

*Glass-stoppered test tubes.*—Tubes of 30 ml capacity are used in the extraction procedure.

#### REAGENTS

Aluminum nitrate reagent (saturated): Add excess reagent grade  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  to 2 liters dilute nitric acid (7 percent conc.  $\text{HNO}_3$ , by volume). Heat gently on a hot plate for an hour, stirring fre-

quently. Cool to room temperature, allow the crystals to settle, and decant. Extract any uranium in the saturated solution with three 100-ml portions of diethyl ether by using a 3-liter separatory funnel. Store in a polyethylene bottle over crystals of uranium-free  $\text{Al}(\text{NO}_3)_3$ .

Aluminum nitrate reagent (0.4 molar): Dissolve 15 g of purified  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled water and dilute to 100 ml. The  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  is purified by dissolving reagent grade  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled water, extracting with ether, and recrystallizing.

Ammonium hydroxide: Concentrated, reagent grade.

Ammonium nitrate solution (1 percent): Dissolve 10 g of reagent-grade ammonium nitrate in distilled water and dilute to 1 liter.

Diammonium hydrogen phosphate solution: Dissolve 12 g of reagent-grade diammonium hydrogen phosphate in distilled water and dilute to 1 liter.

Diethyl ether: Reagent grade.

Ethyl acetate: Reagent grade.

Flux: Using anhydrous reagent-grade chemicals, prepare a flux consisting of 9 percent sodium fluoride, 45.5 percent sodium carbonate, and 45.5 percent potassium carbonate by weight. Dry-mix the chemicals for approximately 12 hours in a rod or ball mill and then fuse the mixture in platinum evaporating dishes over Fisher burners. Cool the fused flux, break it into small pieces and then pulverize it for 72 hours in a rod mill. Store the pulverized flux in a desiccator until it is needed.

Methyl-red indicator solution: Dissolve 0.1 g of methyl red (dimethylaminoazobenzene-carboxylic acid) in 18.6 ml of 0.02N sodium hydroxide solution and dilute with water to 250 ml.

Nitric acid: Concentrated, reagent grade.

Sodium fluoride solution (1 percent): Dissolve 10 g of reagent grade sodium fluoride in distilled water and dilute to 1 liter.

Standard uranium stock solution (100  $\mu\text{g}$  U per ml): Dissolve 0.1782 g of reagent-grade uranyl acetate dihydrate in approximately 500 ml of distilled water. Add 2 ml of reagent-grade concentrated nitric acid and dilute to 1 liter. Store in a polyethylene bottle. From this stock solution, prepare a dilute standard containing 0.050  $\mu\text{g}$  U per ml.

#### PROCEDURE FOR NONSALINE WATER

1. Using one platinum dish for a blank, one for a standard, and one for each sample, make a survey run (steps 2-8) to determine suitable volumes of samples for analysis. (If the approximate concentrations of uranium in the samples are known, proceed directly to step 9).

2. Add 1 ml of a 1 percent sodium fluoride solution to each dish and evaporate to dryness under an infrared lamp or other suitable heat source. In this step and in succeeding evaporations, remove the dishes from heat immediately after reaching dryness. Do not bake. The purpose of the sodium fluoride is to minimize the loss of uranium during subsequent evaporations.
3. To the standard dish, add 1 ml of 0.050  $\mu\text{g}$  U per ml standard solution. This amount of uranium usually gives a reading near midscale on the fluorimeter used by the Denver laboratory; more or less uranium should be used depending on the properties of the fluorimeter and flux. To each of the sample dishes add 2 ml of sample. Again evaporate to dryness. Should any solids be deposited on the vertical sides of the dishes, they must be polished down with distilled water and the water evaporated before continuing with succeeding steps of the procedure.
4. To each of the dishes (including the blank dish containing only sodium fluoride) add 2 g of the flux mixture. Spread and bank the flux so that any solids on the vertical walls of the dishes will be covered.
5. Place the dishes on the rotating fusion table and tilt the table to the inclined position by pulling the positioning lever at the right side of the box until the stop is reached. Turn the heat to the high position, giving a temperature slightly above the flux melting point ( $605^{\circ}\text{C}$ ), and heat the dishes until the flux is melted. This requires approximately 5 minutes. Allow the fusion table to rotate in the inclined position for an additional 1–3 minutes. The swirling action scrubs the sides of the dishes and ensures the formation of a homogeneous melt. Return the table to the level position and heat the melt for an additional 3 minutes at the same temperature. Lower the temperature by turning the heat control to the intermediate setting for 3 minutes. This setting maintains the flux at fusion temperature, and crystals continually form and remelt. Lower the temperature still further by turning the heat control to the low setting for 3 minutes. This setting gives a temperature in the range  $550^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ , and allows solidification to occur. Finally, turn off the heat completely and let the melts cool for 8 minutes with the fusion table still rotating.
6. Place the dishes in a desiccator and cool for at least 30 minutes.
7. Remove the blank pad from the dish and adjust the fluorimeter sensitivity so that a reading of 10 (on a scale of 100) is obtained. (Different blank settings on other fluorimeters may give better sensitivities for a given uranium spike).
8. Read the standard and sample pads on the fluorimeter.

9. On the basis of the fluorescence measurements or approximately known concentrations, select a suitable volume of each sample for the determination of uranium. The Denver laboratory uses a maximum volume of 10 ml in the routine determination of uranium. If less than a 1 ml volume of sample is indicated, obtain the aliquot from a diluted sample.
10. The amount of uranium in the samples is now determined by using the procedure of steps 2-8 with the following changes in step 3. Two standards and two blanks are now used for each fusion set. Four aliquots of equal size are used for each sample; to two of these are added spikes of 0.05  $\mu\text{g}$  of uranium. The spike is necessary to determine whether or not quenching is present and, if so, to correct for it.
11. Calculate the uranium concentrations using equation 1 on page C13.

#### **PROCEDURE FOR SALINE WATER OR WATER CONTAINING LARGE AMOUNTS OF QUENCHING ELEMENTS**

The following procedure is similar to that of Smith and Grimaldi (1954) as modified by G. F. Scarbro (written Commun.).

1. Place 250 ml of the sample in an 800 ml beaker. If the dissolved solids exceed  $\approx 35,000$  ppm (parts per million), a smaller volume may be used. Prepare one blank and two standards by using a volume of distilled water equal to the sample volume. (The standard should contain approximately five times the amount of the usual spike for nonsaline water samples, because only about one-fifth of the total amount is carried through to the fused pad).
2. Add 3 ml of concentrated nitric acid, 1 ml of  $\approx 0.2$  molar aluminum nitrate solution, and 5 ml of diammonium hydrogen phosphate solution. Heat to boiling to remove carbon dioxide.
3. Add a few drops of methyl-red indicator and neutralize with ammonium hydroxide to the yellow endpoint. If, on addition of the indicator, a pink color forms and then disappears, the water probably contains excessive iodide or bromide ions. In that event, add ammonium hydroxide, 2 or 3 drops at a time; then add a drop of indicator. Repeat this procedure until the indicator does not turn pink upon hitting the solution but instantly exhibits the yellow color.
4. Digest the precipitate on a steam bath for 10-15 minutes. Allow the precipitate to cool and settle.
5. Using a small pipet connected to an aspirator, draw off as much of the supernatant liquid as possible without disturbing the precipitate.
6. Transfer the precipitate to a 50-ml pyrex centrifuge tube. Police down the beaker and the stirring rod with 1 percent ammonium nitrate solution, adding the washings to the centrifuge tube.

Centrifuge for about 10 minutes. Discard the liquid, wash the precipitate with a few ml of 1 percent ammonium nitrate solution, centrifuge and discard the supernatant liquid.

7. Add 8 ml of the saturated aluminum nitrate reagent and warm gently to dissolve the precipitate.
8. Transfer the solution to a 30-ml glass-stoppered test tube. Drain the centrifuge tube as completely as possible, but do not wash.
9. Add 10.0 ml of ethyl acetate and shake the mixture for 1 or 2 minutes. Allow about 15 minutes for the layers to separate.
10. Draw off about 8 ml of the ethyl acetate and filter through a dry Whatman No. 42 filter paper into a dry test tube.
11. Transfer a 2-ml volume (more or less may be needed depending on the uranium content of the water) of the filtered ethyl acetate into one of the platinum dishes used for fusion. Place the dish on a large watch glass and add water to the watch glass until the dish is about one-fourth submerged. Ignite the ethyl acetate and let it burn completely.
12. Prepare fused pads and read the fluorescence as outlined in the procedure for nonsaline waters.
13. Calculate the concentration of uranium in each sample by using equation 3, page C14.

The efficiency of recovery of the uranium may be determined by comparing the fluorimetric readings of the above standards with direct transfer standards. The direct standards are prepared as described in the procedure for nonsaline waters. The recovery of uranium should be from 80 to 95 percent.

#### CALCULATION OF URANIUM CONCENTRATIONS

Calculation of the concentration of uranium in the sample when the spiking technique is employed can be made by use of the following equation:

$$U = \left[ \frac{(A - Br)S}{D - A} - \frac{BfS}{C - B} \right] \frac{1000}{V} \quad (1)$$

where

$U$  = concentration of uranium in micrograms per liter,

$A$  = fluorimeter reading of sample,

$B = Br + Bf$  = fluorimeter reading of blank (arbitrarily set),

$r$  = fraction of blank reading due to reflected light (or other cause),

$f$  = fraction of blank reading due to uranium in the flux,

$S$  = micrograms of uranium in the spike,

$D$  = fluorimeter reading of sample spiked with  $S$  micrograms of uranium,

$C$  = fluorimeter reading of standard containing  $S$  micrograms of uranium, and

$V$  = volume of sample in milliliters.

The first term in the brackets in equation 1 represents the total amount of uranium in the fused pad; the second term is the amount of uranium in the pad due to impurities in the flux components. The difference between the two terms is obviously the amount of uranium in the sample aliquot used.

From equation 1, it is evident that  $\frac{S}{(D-A)}$  is the fluorimeter sensitivity for the sample in micrograms of uranium per scale division, and  $\frac{S}{(C-B)}$  is the corresponding sensitivity for the standard. When quenching is absent these sensitivities will be the same, and equation 1 reduces to

$$U = \frac{(A-B)S}{D-A} \cdot \frac{1000}{V} \quad (2)$$

In the extraction method for saline waters, quenchers are absent in the final pad, and an equation similar to 2 is applicable. The only modification necessary is correction for the fractions of sample and standard that are carried into the final pads:

$$U = \frac{(A-B)S}{D-A} \cdot \frac{1000}{V} \cdot \frac{F_s}{F_x} \quad (3)$$

where

$F_x$  = fraction of ethyl acetate containing sample transferred to fusion dish, and

$F_s$  = fraction of ethyl acetate containing standard transferred to fusion dish.

A quench factor, defined as the ratio of sensitivity of the standard to that of the sample, is useful as a measure of the extent of quenching and in evaluation of the error which this introduces (see p. C19). Mathematically, the quench factor,  $Q$ , is given by the equation

$$Q = \frac{D-A}{C-B} \quad (4)$$

Experiments show that when the value of  $Q$  is less than 0.7, best results are obtained by dilution of the sample or use of the extraction procedure described for saline waters. Occasionally a slight enhancement of uranium fluorescence may occur ( $Q > 1$ ), but this enhancement may be dealt with mathematically in exactly the same manner as quenching.

The fraction of the blank reading,  $f$ , due to uranium impurities in the flux varies from one batch of flux to another, but seems to be approximately constant for fluxes prepared from the same batch of reagents. This factor determines, to a large extent, the sensitivity

obtainable in the uranium determination with a particular fluorimeter. The lower the value of  $f$ , the greater the sensitivity attainable. Thus, it is important to use highest quality reagents in preparing the flux. The method of determining the flux constants,  $f$  and  $r$ , is described in the following section. The effect of error in these factors on the accuracy of the determination is discussed on page C20.

### DISCUSSION

The extraction procedure described for saline waters is applicable for all water samples whether quenching elements are present or not. The mathematics are simple and straightforward; the net fluorimeter reading (sample-pad reading minus blank-pad reading) multiplied by the sensitivity (micrograms of uranium per fluorimeter scale division) gives the amount of uranium in the pad. Appropriate factors are used to convert this weight into concentration units (micrograms per liter) for the water sample (equation 3).

It is not necessary to perform the rather tedious steps of the extraction procedure, however, when the concentration of quenching elements is not excessively high. As shown in figure 5, the fluorescence intensity is a linear function of uranium concentration for any fixed amount of quenching element(s) in the pad. This fact permits determination of the sensitivity (or slope of the fluorescence intensity-concentration line) for any uranium sample containing quenchers of unknown identity and concentration. The sample fluorescence is measured with and without added uranium. The weight of uranium in the spike divided by the increase in fluorescence intensity due to the spike gives the sensitivity,  $\frac{S}{(D-A)}$ , for that particular sample.

The situation is somewhat complicated by the occurrence of uranium impurity in the flux. In the absence of such impurities, line plots of fluorescence intensity versus uranium weight would intersect in a common point on the zero uranium axis. The point of intersection would be the arbitrary blank setting,  $B$ . However, due to the uranium impurity, part of the blank reading is also subject to quenching. Thus the quench lines have their common point at negative apparent uranium and at a fluorimeter reading below the value,  $B$ , arbitrarily set for the "blank" pad. The blank reading thus has two components;  $Br$ , which is not subject to quenching, and  $Bf$ , due to fluorescence of the uranium impurity in the flux, which is subject to quenching. These are shown in figure 6.

The total amount of uranium in a pad may be calculated from the fluorimeter reading together with the value of  $Br$  if the sensitivity for that pad is known. The net sample reading, that is, the sample reading,  $A$ , minus that portion of the blank reading which is not due

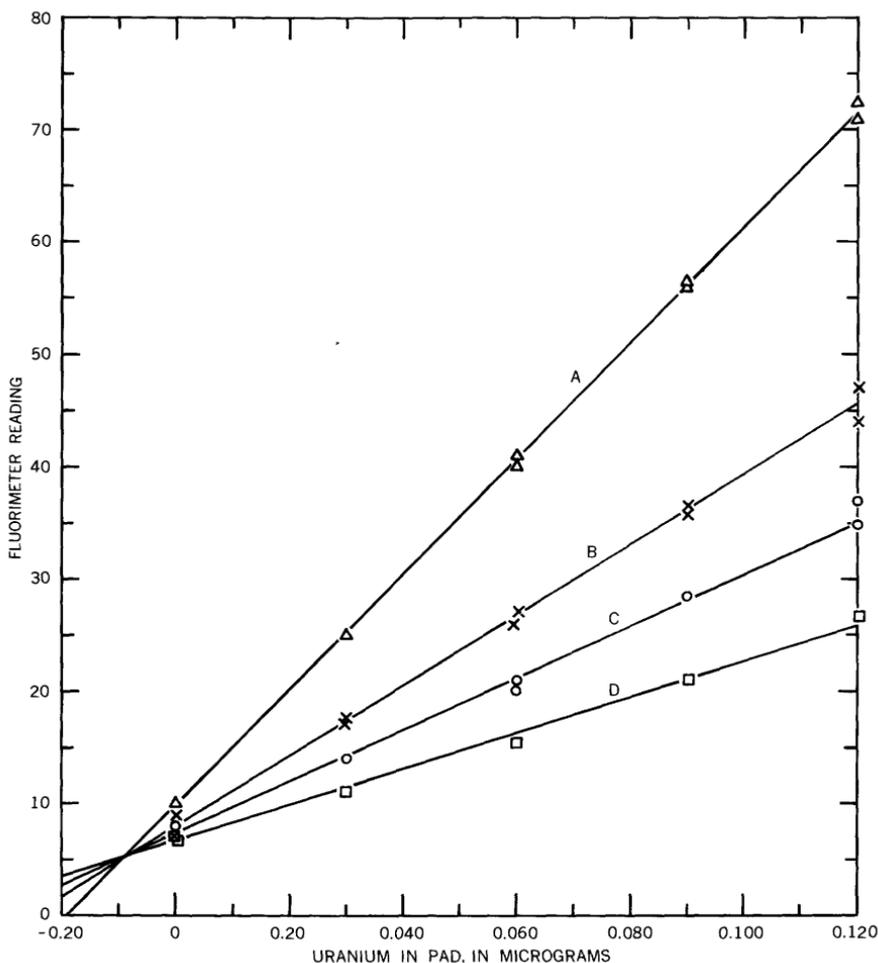


FIGURE 5.—Quenching of uranium fluorescence by chromium. Fluorescence intensity versus amount of uranium for pads containing (A) 0.0  $\mu\text{g}$  of added Cr, (B) 10.0  $\mu\text{g}$  of added Cr, (C) 20.0  $\mu\text{g}$  of added Cr, and (D) 40.0  $\mu\text{g}$  of added Cr.

to uranium,  $Br$ , is divided by the sensitivity to give the total uranium content of the pad.

$$\text{Total U } (\mu\text{g}) = (A - Br) \frac{S}{D - A}$$

The amount of uranium in the pad contributed by the sample is obtained by subtracting the contribution due to flux impurities from the total uranium present. The contribution from the flux should be the same for each pad made from a given batch of flux. This con-

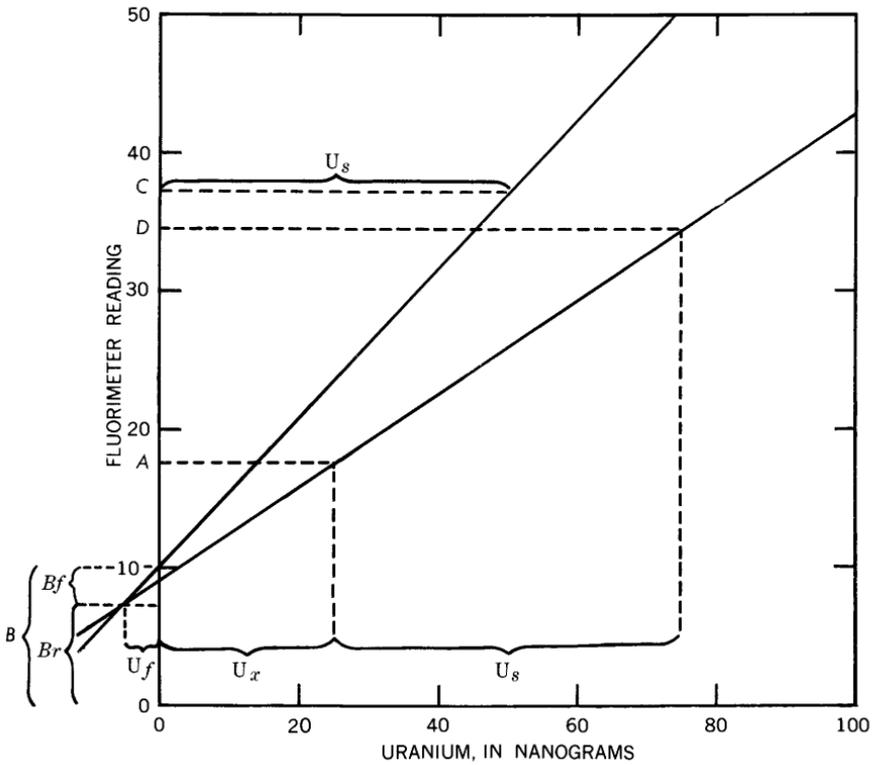


FIGURE 6.—Flux and sample constants. Determination of the quenchable (*Bf*) and unquenchable (*Br*) portions of the blank reading. *B*=arbitrary blank setting, *Bf*=portion of blank due to uranium in flux, *Br*=instrumental portion of blank, *U<sub>f</sub>*=uranium in flux, *U<sub>x</sub>*=uranium in sample, *U<sub>s</sub>*=uranium in spike, *A*=reading of sample, *D*=reading of sample + spike, and *C*=reading of standard.

tribution may be calculated from the quenchable part of the blank,  $Bf = B - Br$ , together with the sensitivity in the absence of quenching

$$\mu\text{g U in flux} = Bf \cdot \frac{S}{C - B}$$

The uranium content of the sample is thus

$$\mu\text{g U} = (A - Br) \frac{S}{D - A} - Bf \frac{S}{C - B}$$

Multiplying by  $\frac{1000}{V}$ , where *V* is the volume of the sample in milliliters, gives the uranium concentration in  $\mu\text{g per l}$

$$[U], \mu\text{g per l} = \left[ (A - Br) \frac{S}{D - A} - Bf \frac{S}{C - B} \right] \frac{1000}{V}$$

As a general rule, duplicate determinations should be made of  $A$  and  $D$  for each sample to check the flux sensitivity,  $\frac{S}{C-B}$ , for each fusion set.

It is desirable to determine  $r$  and  $f$  as accurately as possible to minimize errors. The procedure used by the Denver laboratory is to determine these values from quench curves for three different quenching elements, generally Cr, Mn, and Cu. An amount of each of these elements is chosen that will quench approximately 25 to 50 percent of the fluorescence. Ten different evenly spaced concentrations of uranium are then measured with and without the quenching element present. The intersection of the quenched and unquenched lines (fig. 6) is determined for each element by a least squares calculation. The value of  $Br$  so obtained for each element is divided by the value of  $B$  to obtain the factor,  $r$ , the fraction of the total blank which is not subject to quenching;  $f$  is determined from the relationship  $f+r=1$ . The blank  $B$ , is determined from the least squares equation for the unquenched uranium line, rather than by using the setting for the blank pad. The two values should be nearly identical, however.

The three values of  $r$  (one for each quenching element) determined by this procedure are averaged and the value thus obtained is used in all subsequent analyses using that batch of flux. Since a blank reading of 10 (on a scale of 100) generally is used,  $Br=10r$  and  $Bf=B-Br=10(1-r)$ . Individual determinations of  $r$  usually give values which differ from the average by less than 0.1. Table 1 lists experimental values for the flux constants for two batches of flux.

TABLE 1.—*Experimental constants for two batches of flux*

Batch	Quenching element	Weight of quencher per pad ( $\mu\text{g}$ )	$r$	Constants for $B=10$	
				$Bf$	$Br$
1	Cr	20	0.39	6.1	3.9
	Cr	20	.43	5.7	4.3
	Cu	100	.42	5.8	4.2
	Cu	40	.42	5.8	4.2
	Mn	30	.42	5.8	4.2
	Mn	30	.36	6.4	3.6
Average			0.41	5.9	4.1
2	Cr	20	.96	.4	9.6
	Cu	60	.92	.8	9.2
	Mn	20	.84	1.6	8.4
Average			0.91	0.9	9.1

## ACCURACY OF THE URANIUM DETERMINATION

Several factors affect the accuracy of the uranium determination. Among these are the sensitivity, accuracy of the flux constants, linearity and stability of instrument response, and reproducibility of pads from a given sample.

The sensitivity of the method depends upon the properties of both the fluorimeter and the flux. Ideally, the fluorimeter detector should be sensitive to only the 5546-Å fluorescent radiation from the uranium bearing pads. That this condition is not satisfied is evidenced by the nonquenchable part of the blank reading. This instrumental part of the blank imposes a limitation on the sensitivity and it may be expected, therefore, that sensitivity will vary from one instrument to another. In addition, fluorimeter properties may change with replacement of lamps, photomultiplier tubes, and filters.

The sensitivity attainable by a given instrument depends primarily upon the properties of the flux. The ideal flux would be entirely free of uranium impurities. The blank reading on the fluorimeter would then be entirely instrumental and the sensitivity would be the maximum obtainable with that fluorimeter for a given arbitrary blank setting. As the uranium content of the flux increases, the sensitivity must be reduced in order to obtain the same blank reading. A moderate increase or decrease in the arbitrary value at which the blank is set, although causing a change in sensitivity, has little effect on the accuracy of the uranium determination. Because of the reduced sensitivity caused by uranium in the flux, it should be prepared from reagents of the highest purity. The Denver laboratory has found sensitivities ranging from 0.0004 to 0.003  $\mu\text{g}$  of uranium per fluorimeter-scale division (scale of 100) when the blank is set at 10.

The sensitivity also depends upon the concentration of quenching elements in the water sample (see figs. 1, 5, and 6). The quench factor,  $Q$ , measures the fraction of maximum sensitivity which the sample exhibits. Figures 7 and 8 show the effect of the magnitude of  $Q$  on the precision of the method. This laboratory reruns an analysis either by the dilution or the extraction procedure if more than 30 percent of the fluorescence is quenched ( $Q < 0.7$ ).

The method of determining the flux constants  $f$  and  $r$  (the fractions of the blank that are subject to and free of quenching, respectively) have been described previously. Mathematically, the value of  $Br$  can be determined for each quenching element from the values of the

slope and the  $y$  intercept for the fluorescence versus uranium lines with a given amount of quencher and without quenching.

$$Br = \frac{a_q b_s - a_s b_q}{b_s - b_q}$$

where:

$a_s, a_q$  = the  $y$  intercepts of the unquenched and quenched curves, respectively and

$b_s, b_q$  = slopes of unquenched and quenched curves, respectively.

The uncertainty in  $Br$  for a single determination may be expressed in terms of the standard deviation

$$\sigma Br = \sqrt{\left(\frac{\partial Br}{\partial a_s}\right)^2 \sigma_{a_s}^2 + \left(\frac{\partial Br}{\partial a_q}\right)^2 \sigma_{a_q}^2 + \left(\frac{\partial Br}{\partial b_s}\right)^2 \sigma_{b_s}^2 + \left(\frac{\partial Br}{\partial b_q}\right)^2 \sigma_{b_q}^2}$$

$$\sigma Br = \sqrt{\left(\frac{b_s}{b_s - b_q}\right)^2 \sigma_{a_q}^2 + \left(\frac{b_q}{b_s - b_q}\right)^2 \sigma_{a_s}^2 + \frac{(a_s b_q - a_q b_s)^2}{(b_s - b_q)^4} \sigma_{b_s}^2 + \frac{(a_q b_s - a_s b_s)^2}{(b_s - b_q)^4} \sigma_{b_q}^2}$$

Generally the third and fourth terms of this equation are small and may be neglected.

$$\sigma Br \approx \sqrt{\left(\frac{b_s}{b_s - b_q}\right)^2 \sigma_{a_q}^2 + \left(\frac{b_q}{b_s - b_q}\right)^2 \sigma_{a_s}^2}$$

The variance ( $\sigma^2$ ) of  $a_q, a_s, b_s$  and  $b_q$  are determined from the equations representing the standard deviations of the least square constants of a line subject to error in  $y$  only.

$$\sigma_a^2 = \frac{\sum X_i^2}{n \sum X_i^2 - (\sum X_i)^2} \sigma_y^2 \quad \text{and} \quad \sigma_b^2 = \frac{n}{n \sum X_i^2 - (\sum X_i)^2} \sigma_y^2$$

where the  $X_i$  represent the amount of uranium added to each pad,  $n$  is the number of experimental points, and

$$\sigma_y^2 = \frac{\sum (Y_i - a - bX_i)^2}{n - 2} \quad (\text{Worthing and Geffner, 1943, p. 249}).$$

Because of rather limited experience with this method of determining the flux constants, an evaluation of the overall accuracy is difficult. However, available data indicate that the average standard deviation of the mean  $Br$  (obtained from three different quenching elements) is probably less than  $0.07B$ . The effect of error in  $Br$  on the accuracy of the uranium determination is shown in figure 7.

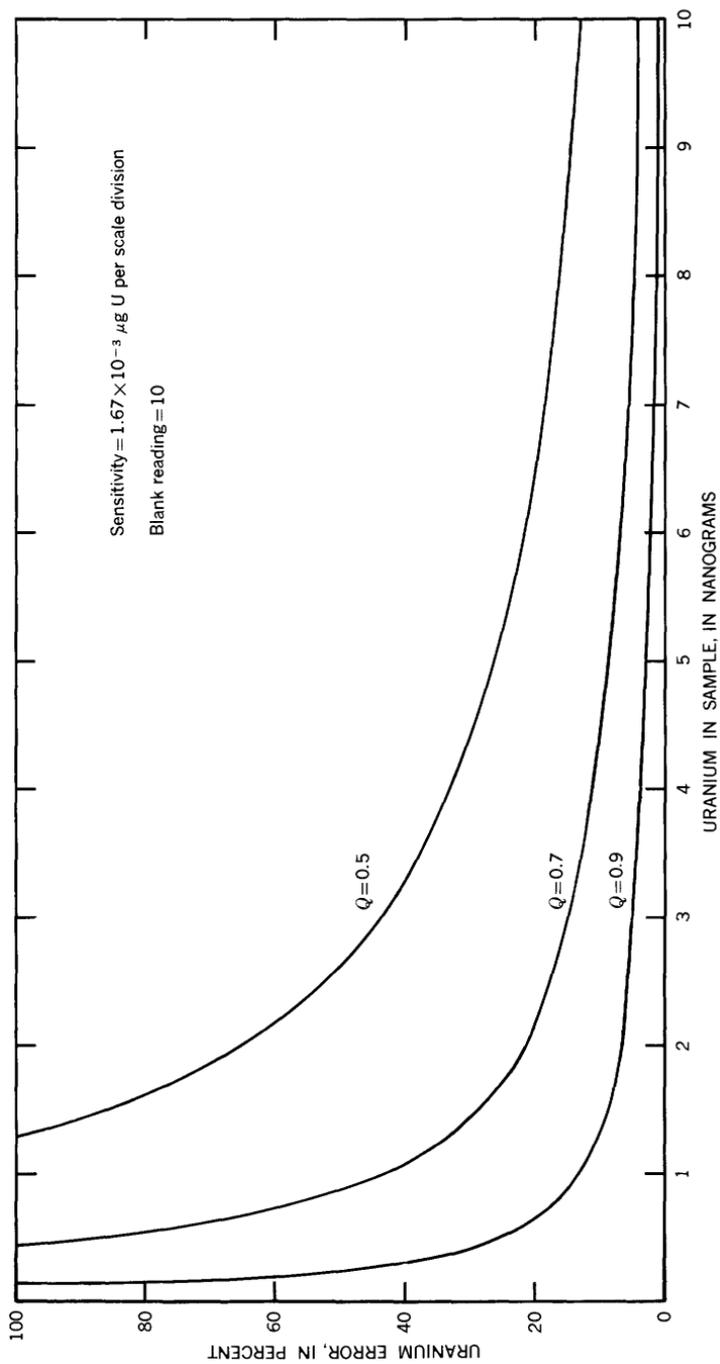


FIGURE 7.—Relative error in the uranium determination due to a 10 percent error in  $B_r$  for quenching factors ( $Q$ ) of 0.5, 0.7 and 0.9.

The linearity and stability of fluorimeters may vary considerably from one instrument to another. The Denver laboratory has found that production instruments of the Galvanek-Morrison type give good linearity and fair stability. Reproducibility of readings of fluorescence standards is about  $\pm 3$  percent of the fluorimeter reading over periods of a few hours or less, and is independent of fluorescence intensity.

Making the assumptions that (1)  $S$  is very precise compared to  $A$ ,  $B$ ,  $C$ , and  $D$  (sample, blank, spiked blank, and spiked sample readings, respectively), (2)  $f$  and  $r$  are constant for any batch of flux, and (3) the fractional deviation,  $\sigma_x/x$ , is approximately constant for all readings, the standard deviation of the uranium determination for samples containing quenchers is:

$$\sigma_U^2 = \left[ A^2 \left( \frac{\partial U}{\partial A} \right)^2 + B^2 \left( \frac{\partial U}{\partial B} \right)^2 + C^2 \left( \frac{\partial U}{\partial C} \right)^2 + D^2 \left( \frac{\partial U}{\partial D} \right)^2 \right] \frac{\sigma_x^2}{x^2}$$

where

$$\frac{\sigma_x^2}{x^2} = \frac{\sigma_A^2}{A^2} = \frac{\sigma_B^2}{B^2} = \frac{\sigma_C^2}{C^2} = \frac{\sigma_D^2}{D^2}$$

Performing the indicated operations yields the following equation for the variance of  $U$ :

$$\begin{aligned} \sigma_U^2 = & \frac{S^2}{(D-A)^4} \left\{ A^2(D-Br)^2 + D^2(A-Br)^2 \right\} \frac{\sigma_x^2}{x^2} \\ & + \frac{S^2}{(C-B)^4} \left\{ B^2 \left[ r \frac{(C-B)^2}{D-A} + fC \right]^2 + f^2 B^2 C^2 \right\} \frac{\sigma_x^2}{x^2} \end{aligned}$$

Figure 8 shows the expected uranium error in percent for different amounts of uranium in the sample pad. A typical sensitivity was used in calculating the curves for different values of  $f$  and  $Q$ . The error in the uranium determination rises rapidly below about 4 nanograms (1 nanogram =  $10^{-9}$  g). A better sensitivity lowers the standard deviation for any given amount of uranium, and consequently improves the detection limit.

The accuracy of the method on actual water samples is shown in tables 2 and 3. The analyses were carried out on water samples which were found in preliminary analyses to contain no detectable uranium within experimental error. A uranium "unknown" of 0.05  $\mu\text{g}$  was added to each sample dish for the analyses reported in table 2, and 0.01  $\mu\text{g}$  for those of table 3.

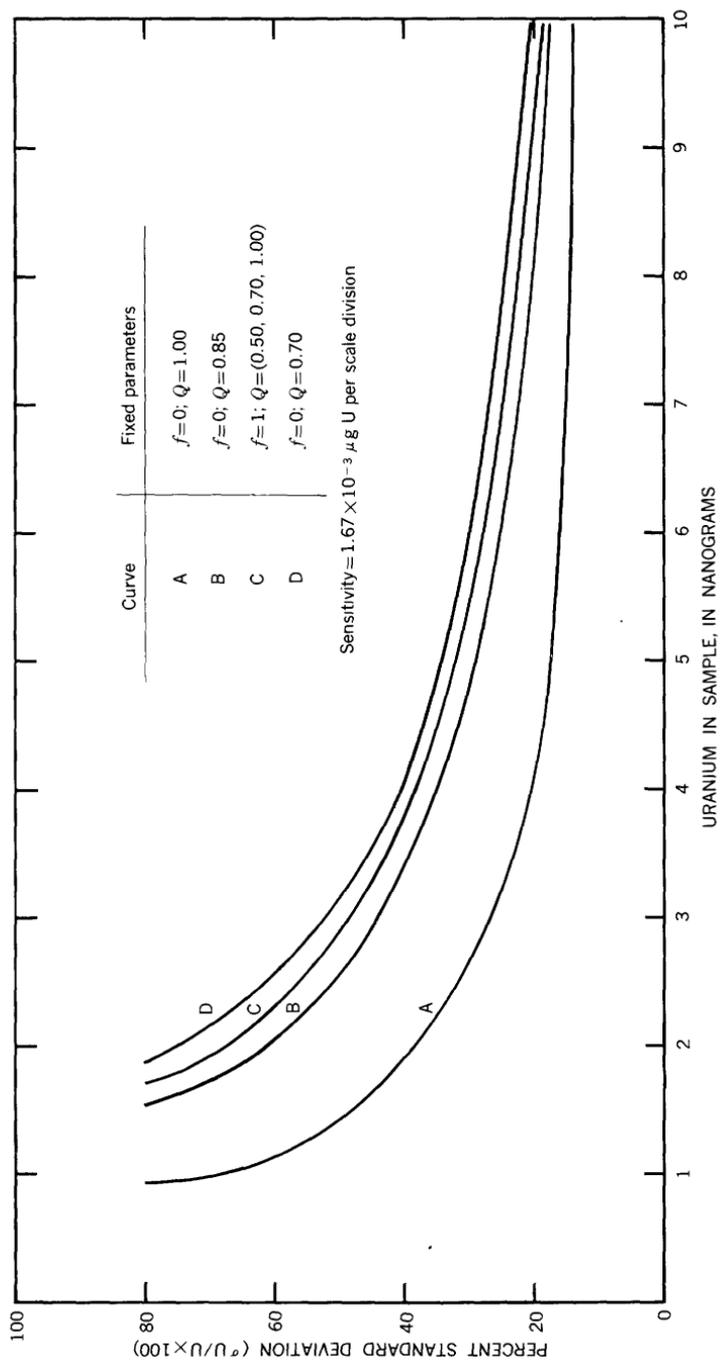


FIGURE 8.—Precision of the uranium determination. Relative standard deviation as a function of the amount of uranium in the pad for various values of  $f$  and  $Q$ .

TABLE 2.—*Determination of 0.05  $\mu\text{g}$  of added uranium in natural waters*<sup>1</sup>

Sample	Dissolved solids (mg per l)	Sample volume (ml)	Quench factor ( <i>Q</i> )	Uranium found	
				( $\mu\text{g}$ )	( $\mu\text{g}$ per l)
4827 .....	60	5	0.98	0.0496	9.9
4804 .....	62	5	1.02	.0510	10.2
4820 .....	95	5	.95	.0529	10.6
4853 .....	194	5	1.09	.0469	9.4
4841 .....	261	5	.92	.0531	10.6
SWS-1 .....	323	5	.95	.0493	9.9
4304 .....	916	5	.73	.0542	10.8
Average .....				0.0510	10.2
4306 <sup>2</sup> .....	1540	5	0.51	0.0414	8.3

<sup>1</sup> The water samples used had previously been found to be free of uranium.

<sup>2</sup> When the quench factor, *Q*, is below 0.7, the analysis should be rerun on a diluted sample, or by the extraction procedure.

TABLE 3.—*Determination of 0.01  $\mu\text{g}$  of added uranium in natural waters*<sup>1</sup>

Sample	Dissolved solids (mg per l)	Sample volume (ml)	Quench factor ( <i>Q</i> )	Uranium found	
				( $\mu\text{g}$ )	( $\mu\text{g}$ per l)
4827 .....	60	5	0.94	0.0095	1.90
4804 .....	62	5	1.02	.0081	1.62
4820 .....	95	5	1.04	.0063	1.26
4853 .....	194	5	1.10	.0127	2.54
4841 .....	261	5	.94	.0100	2.00
SWS-1 .....	323	5	1.09	.0116	2.32
4304 .....	916	5	.93	.0127	2.54
Average .....				0.0101	2.03
4306 <sup>2</sup> .....	1540	5	0.60	0.0143	2.86

<sup>1</sup> The water samples used had previously been found to be free of uranium.

<sup>2</sup> When the quench factor, *Q*, is below 0.7, the analysis should be rerun on a diluted sample, or by the extraction procedure.

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