Field Determination of Uranium in Natural Waters

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By F. N. WARD *and* A. P. MARRANZINO

CONTRIBUTIONS TO GEOCHEMISTRY

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A semiquantitative method for use in hydrogeochemical prospecting

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By F. N. Ward and A. P. Marranzino

ABSTRACT

A simple and moderately accurate method for determining traces of uranium in natural waters has been devised to facilitate the development of hydrogeochemical prospecting techniques. The procedure eliminates the present practice of transporting bulky water samples from field to laboratory and the time-consuming evaporation of samples, preliminary to analysis. Under field conditions the uranium is separated from a water sample by means of a phosphate collector, and, after a paper-chromatographic separation, is determined by its reaction with ferrocyanide. The lower limit of the method is 2 ppb (parts per billion) and without modification it can be used to determine as high as 200 ppb of uranium in natural waters. Recoveries of 2, 5, and 10 micrograms of uranium added to 500 ml portions of a water sample are respectively 1, 5, and 7 micrograms. The analyses of 7 different binary mixtures prepared from natural water samples compare favorably with the values calculated from the mixture composition and the known uranium contents of the components. Five repeat determinations on a water sample containing 5 ppb agree within 1 ppb of the mean; similar determinations on a sample containing 30 ppb agree within 4 ppb of the mean. Results by the proposed method on samples containing from 2 to 30 ppb of uranium compare reasonably well with the fluorimetric results obtained by another laboratory of the United States Geological Survey.

INTRODUCTION

A field method for determining traces of uranium in natural waters was needed to facilitate uranium exploration by hydrogeochemical techniques. To date these techniques have been hampered by the labor involved in collecting enough samples and by the cost of transporting the samples from field to laboratory. Moreover, during the time required to transport the samples to the laboratory the metal content of the water may change because of adsorption on the inner surface of the container or by reaction with the algae which frequently develop after the samples are taken, with the result that even the most efficient sampling techniques are often nullified.

The term "natural waters" as used in this paper connotes fresh water uncontaminated by human activities; the present paper presents a simple means of filtering a sample of such water at the sampling site to collect the uranium from the water in a small wad of paper pulp and describes a procedure for determining the quantity of collected uranium at either a nearby field station or in a laboratory. The collection of the uranium from a water sample in the field by such a technique effectively eliminates the labor involved in transporting bulky water samples, and the field determination of the collected uranium decreases the cost per analysis to a negligible part of the total exploration costs.

The uranium concentration in natural waters commonly ranges from a fraction of 1 ppb to a few parts per billion, but in water moving through mineralized ground the concentration may reach several thousand parts per billion. Analytical methods useful in exploration by hydrogeochemical techniques should cover the entire range above 2 ppb. Because the actual quantity of uranium that can be detected ranges from 1×10^{-5} gram for colorimetric to 1×10^{-10} gram for fluorimetric methods (Grimaldi and others, 1954), useful analytical methods require some type of collection or other means to concentrate the uranium.

In most of the published methods for determining uranium in water the collected uranium is measured by the fluorescence of a sodium fluoride bead. These measurements require special equipment to measure the fluorescence emitted by small amounts of uranium; other elements in the water, however, interfere by enhancing or quenching the fluorescence. Uranium is usually separated from most of the interfering elements by extraction into ethyl acetate, and is recovered after evaporation of the extractant. Fluorescent measurements are widely used (Grimaldi and others, 1954) because of their great sensitivity. If enough uranium could be isolated and concentrated, however, other kinds of measurements might be useful.

The chromatographic procedure developed by Hunt, North, and Wells (1955) and modified by Thompson and Lakin (1957) seems to be another useful way of measuring the uranium. In brief, the uranium in a sample aliquot is dried on a strip of filter paper and then moved in a solvent front away from possible interferences from other elements, such as iron. The strip is sprayed with aqueous ferrocyanide to produce a brown-colored band, the color and width of the band being proportional to the uranium present. The lowest amount detectible by this reaction is about 0.1 microgram.

If the uranium can be collected rapidly and easily from a large enough water sample, the chromatographic separation on filter-paper strips followed by the reaction with ferrocyanide offers distinct advantages over fluorescent measurements, especially under field conditions.

COLLECTION OF URANIUM

Hecht and others, (1956) employ the strongly basic resin IRA 400 to collect the uranium from a natural-water sample and to effect a separation of the uranium from iron, thorium, and cerium. More often traces of uranium in natural waters are collected by precipitation as the hydroxide (Hernegger and Karlik, 1934), (Urry, 1941), or the phosphate (Tschernichow and Guildina, 1934) with suitable carriers, such as iron or aluminum. When the uranium is collected as the hydroxide or the phosphate, the finely divided and often gelatinous precipitate has to be separated from the liquid phase by filtration or centrifugation. The slowness of the filtration of gelatinous precipitates precluded their use under field, conditions, and suitable centrifuges cannot be considered field equipment.

In the proposed procedure the uranium is collected in the following manner: A saturated solution of dibasic sodium phosphate is added to the acidified sample solution until the pH is about 6. The natural-water samples collected to date, remain clear even after the pH adjustment; however certain mine waters contain enough calcium, aluminum, iron, and other chemical constituents to precipitate under these conditions. If any precipitation occurs during the pH adjustment, a 5 percent aqueous solution of disodium ethylenediaminetetraacetic acid (EDTA) is added drop by drop until the precipitate is redissolved. When the sample solution so prepared is filtered through paper pulp, the paper collects almost all the uranium present. In the absence of phosphate, a variable amount but generally less than 50 percent of the uranium present will be found in the paper pulp.

The present writers have not made a detailed study of the mechanism of the collection, but the following facts are pertinent: Rodden (1950) stated that "even 12 percent nitric acid will not redissolve uranyl phosphate," and in a study of the distribution of uranium during an ether extraction process, he recommended ferric or aluminum nitrate to complex the phosphate and thus overcome its inhibiting influence. Thompson and Lakin were unable to separate the uranium from a phosphate rock sample solution on a chromatographic paper strip, until they added aluminum nitrate to the sample solution. The present writers also observed that, unless the nitric acid used to dissolve the collected uranium contained a large amount of aluminum nitrate, no uranium moved in the solvent front during the subsequent chromatographic separation. These facts provide a basis for concluding that in the method proposed here, the uranium is collected as a phosphate complex.

The use of aluminum nitrate effectively breaks up the uranium phosphate complex and furnishes a high concentration of nitrate ion which seems necessary to cause the uranium to move in the solvent front.

EXPERIMENTS

MAXIMUM SALT CONCENTRATION

The phosphate needed to effect complete collection of the uranium and the aluminum nitrate needed to break up the uranyl phosphate contribute to the salts present in the sample solution prepared for chromatographic separation. Large amounts of salts are not only difficult to keep in solution, but they inhibit the drying of the sample aliquot, and improper drying leads to poor separations. Thus the quantity of salts which can be tolerated is limited.

Because the phosphate is added to change the pH through a fixed range, the quantity of phosphate present after the uranium collection from a natural-water sample is practically constant and cannot be decreased appreciably, but the aluminum nitrate may be decreased to the minimum amount needed to break up the uranium phosphate formed in the collection step. In order to determine the minimum amount needed, 0.2 ml portions of dilute nitric acid solutions (1+3) containing from 20 to 90 percent (weight per volume) of aluminum nitrate enneahydrate were used to break up the uranyl phosphate formed from 5 micrograms of added uranium. The 0.2 ml portion of the 80 percent solution effected complete recovery of the added uranium.

EFFECT OF EDTA

The disappearance of the yellow-green color of a 0.5 molar sulfuric acid solution of uranium standard when EDTA is added indicates the formation of some kind of complex. The formation of such a complex explains the poor recoveries observed when uranium and EDTA were added to samples of demineralized water, and the samples taken through the entire procedure. The complex between uranium and EDTA must be relatively weak because, in the presence of calcium, iron, or aluminum, recoveries of added uranium are satisfactory. Presumably these elements form stronger complexes with EDTA and inhibit or prevent a reaction between uranium and EDTA. In the proposed procedure, EDTA is added only in sufficient quantity to redissolve any precipitate of calcium, iron, or aluminum that forms during the pH adjustment.

EFFECT OF RELATIVE HUMIDITY ON DRYING OF SAMPLE ALIQUOTS

Before the paper-chromatographic separation, the sample aliquot is placed near one end of the paper strip and dried. Proper drying is essential for good separation, and suitable conditions were determined experimentally.

Hunt, North, and Wells (1955) dried 0.01 and 0.05 ml aliquots in the atmosphere for 1 hour, and successfully carried out chromatographic analyses. Following the same procedure Thompson and Lakin, working in the dry atmosphere of the Western United States, found that no separation of the uranium occurred. Different drying conditions had to be established to compensate for the lower relative humidities, but the rather close control of the drying time set by them proved to be a handicap in the proposed field method.

The present writers prepared dilute nitric acid solutions of uranium collected from a natural water and dried 0.01, 0.02, and 0.05 ml aliquots for different periods of time at relative humidities varying from 9 to 81 percent. The results of these experiments are shown in table 1.

TABLE 1.—*Effect of relative humidity on drying of chromatographic papers*

Relative humidity over saturated solutions (percent)	Salt used [1]	Temperature (°C)	Appearance after given drying times, in minutes (D, detectable band; I, iron movement; F, fair band; G, good band)			
			10	15	30	1,200
9	$CaCl_2$.anh	24.5	G	D, I	D, I	D, I
31	$CaCl_2.6H_2O$	24.5	G	D, I	D, I	D, I
43	$K_2CO_3.2H_2O$	24.5	G	G	G	D, I
47	KSCN	20	G	G	G	D, I
52	$NaHSO_4.H_2O$	20	G	G	G	G
52	$Mg(NO_3)_2.6H_2O$	24.5	G	G	G	G
81	$(NH_4)_2SO_4$	20.25	F	F	G	F

[1] Lange, 1952.

A drying time of 10 minutes at relative humidities below about 50 percent seems to be satisfactory, but longer times cause uncertain separations of the uranium from the iron with resulting poor band development. To avoid the highly problematical question of whether 10 minutes is long enough for the atmosphere within the usual desiccator to reach equilibrium and to make the drying step more objective, the writers prefer to dry the sample aliquots for at least 30 minutes. The data show that sample aliquots can be dried for 30 minutes at relative humidities varying from about 40 to 80 percent.

Presumably the relative humidity becomes more critical with longer drying times. However, at a 52 percent humidity the sample aliquots can be kept for several weeks before proceeding with the chromatographic separation.

Saturated solutions of both sodium bisulfate and magnesium nitrate hexahydrate provide a 52 percent relative humidity at temperatures of 20° to 25°C. The latter desiccant was selected for the work reported in the rest of this paper because the vapor pressure is less sensitive to changes in temperature. In fact, satisfactory chromatograms have been prepared from paper containing 0.02 ml aliquots of sample solutions kept over the magnesium nitrate hexahydrate desiccant for as long as 3 months.

SOLVENT MIXTURES

Arden, Burstall, and Linstead (1949) used a solvent consisting of 90 percent ethyl acetate and 10 percent concentrated nitric acid (volume per volume) to separate uranium chromatographically. In a procedure for determining uranium in soils, Hunt, North, and Wells (1955) used the same solvent modified by the addition of 5 percent of water (volume per volume). Thompson and Lakin used a 2-phase solvent prepared by mixing 30 ml of ethyl acetate, 3.5 ml concentrated nitric acid, and 10 ml of water. Obviously the various workers in the field have modified the solvent to meet their particular need.

Using the definite drying conditions given in the previous section and 30 ml of ethyl acetate in the solvent, the present writers investigated the effect of different amounts of acid in the solvent on the chromatographic separation of 0.2 microgram of uranium on paper strips. The results are as follows:

Percent nitric acid volume per volume	*Appearance after development (D, detectable band; T, trailing behind solvent front; F, fair band; G, good band)*
6	D
10	F, T
12	F, T
14	G
17	G
19	F
21	G, T
23	F, T
25	F, T

Varying amounts of water were added to the solvent mixtures containing respectively 14 and 17 percent nitric acid (volume per volume). The characteristics of the bands obtained by making chromatographic separations with these solvents are given in table 2.

It is evident that a wide range in the composition of solvent mixtures can be tolerated under normal conditions. However, if the ratio of the acid to the water is much greater than 2, the solvent becomes a 2-phase system which may not provide enough nitrate to stabilize the uranyl ion and thereby cause it to move in the solvent front. All the separations described in the rest of this paper were made with a single phase solvent (see "solvent mixture" below).

TABLE 2.—*Effect of water in solvent at 14 and 17 percent acid concentration on chromatographic separations*

Water added (ml)	Appearance after development (D, detectable band; F, fair band; G, good band; T, trailing behind solvent front)	
	14 percent nitric acid	17 percent nitric acid
0	G, T	G, T
0.5	G, T	G
1.0	G	G
1.5	G	F
2.0	G	F
2.5	F, T	D
3.0	F	D, T

REAGENTS AND APPARATUS

Ammonium hydroxide, concentrated, reagent grade.

EDTA, Ethylenediaminetetraacetic acid, disodium salt. 5 percent aqueous.

Magnesium nitrate hexahydrate, reagent grade. A saturated aqueous solution is used as the desiccant for drying sample and standard aliquots.

Nitric acid, Sp. G. 1.42, reagent grade.

Nitric acid-aluminum nitrate reagent. Dissolve 80 grams of aluminum nitrate enneahydrate in mixture of 25 ml concentrated nitric acid and 75 ml water.

Potassium ferrocyanide, 5 percent aqueous.

Phosphate reagent. Sodium phosphate, dibasic, saturated aqueous solution of the dodecahydrate.

Solvent mixture. To a clean dry 600 ml beaker, add in this order: 30 ml ethyl acetate, reagent grade; 6 ml concentrated nitric acid; and 0.5 ml water. Swirl to obtain clear solution and cover. The mixture can be used immediately, and it is good for 4 to 5 chromatograms or 4 hours, depending on whichever involves the shorter time.

Standard uranium solution, 0.1 percent. Dissolve 0.211 gram of uranyl nitrate hexahydrate in 100 ml of nitric acid-aluminum nitrate reagent. Prepare dilute standard solutions by adding 0.1, 0.2, 0.4, 0.8, 1.5, 3, and 6 ml of 0.1 percent standard to a series of 10 ml volumetric flasks—0.1 ml to first flask, 0.2 ml to second flash, etc., and making volume up to mark with nitric acid-aluminum nitrate reagent.

Atomizer.

Beakers, 600 ml. Two or more are used for greatest efficiency.

Bottles, dropping, 30 and 60 ml capacity.

Crucibles, porcelain no. 0. High form.

Desiccator, 150 mm in diameter. For efficient operation two or more are required: one for standards and other for samples.

Filter apparatus, shown in figure 18. Before using, prepare slurry of one Whatman ashless tablet and collect pulp on filter paper circle placed over small holes in *D*, after connecting *B* and *D*.

Paper, *Whatman* no. 1–2½ cm circles for retention of item *C* in figure 18.
Paper, *Whatman* CRL–1 Chromatographic, ten chromatograms can be made on each sheet.
Pipettes, micro, capacity 0.05, 0.02, and 0.01 ml.
Pipette, measuring, calibrated in tenths of a ml.
pH test paper, long range from pH 1–6 and short range from pH 5.8–6.2.
Rods, small glass stirring.
Stove, gasoline portable, with steel plate to serve as hot plate.

PROCEDURE

To a 500 ml sample of natural water add 2 ml concentrated nitric acid. Add concentrated ammonium hydroxide drop by drop until the pH is 2.5. Add phosphate reagent until pH is 5.9 to 6.1. If a precipitate forms on the addition of phosphate, add EDTA drop by drop to the stirred sample solution until the precipitate redissolves, and then alternately titrate the sample solution drop by drop, first with phosphate reagent and then with EDTA until pH is 5.9 to 6.1. Filter water through paper pulp in the filter apparatus shown in figure 18. After water filters through paper pulp, separate item *B* from *A* and cover with stopper *E*.

To determine the uranium collected, transfer the paper pulp to a porcelain crucible. Add 4 to 5 drops of concentrated nitric acid and dry on hot plate. Heat over open flame until only a white ash remains. Cool. Add 0.5 ml of concentrated nitric acid to the ash, heat gently to dryness, and ignite to expel nitric oxide fumes. Cool. Repeat the addition of concentrated nitric acid. Police the sides of the crucible with a small glass stirring rod and evaporate the liquid in the crucible to dryness. Dissolve all residue in the cool crucible in 0.2 ml of nitric acid-aluminum nitrate reagent and warm gently for 20 seconds. Avoid boiling.

Transfer a 0.02 ml aliquot of the warm sample solution to a strip of chromatographic paper. Place strip in the desiccator and allow it to remain for at least 30 minutes. Remove paper from desiccator and place lower end of the paper in the solvent mixture. Allow solvent to rise through the dried sample aliquot to within 1 inch of the top of the paper. Remove strip from solvent, dry, and spray both sides of the paper with potassium ferrocyanide reagent.

Preparation of standard bands—Place 0.01 ml aliquots from each of the 10 ml volumetric flasks containing dilute standard uranium solutions on strips of chromatographic paper and allow to dry one-half hour in desiccator. Place paper strips in solvent and continue as with samples. These standard bands contain, respectively, 0.1, 0.2, 0.4, 0.8, 1.5, 3.0, and 6.0 micrograms of uranium.

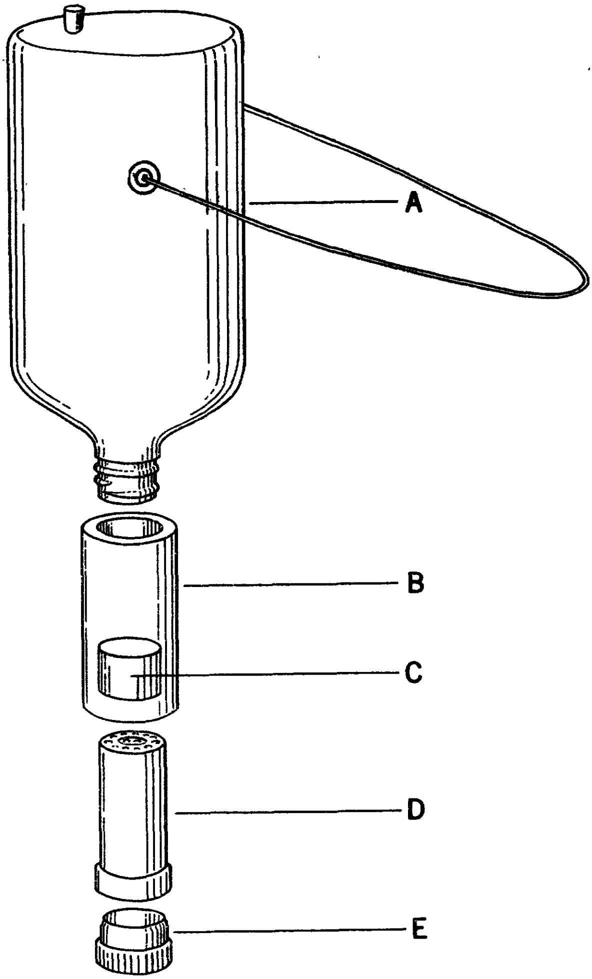

FIGURE 18.—Filter apparatus.

Estimation—Compare chromatograms of samples with those of standard solutions to determine uranium content of aliquot. Multiply the uranium content of the corresponding standard chromatogram by 20 to convert the results into parts per billion in original sample.

RESULTS

The proposed procedure was tested by adding different amounts of uranium to 500 ml portions of 3 different natural-water samples of known uranium content and taking the portions through the entire procedure. The results are shown in table 3.

TABLE 3.—*Recovery of added uranium*

Laboratory no.	Uranium present (micrograms in 500 ml)	Uranium added to 500 ml micrograms	Uranium found micrograms	Uranium recovered micrograms
CR-2-566	3	2	4	1
		5	8	5
		10	10	7
CR-2-568	10	10	20	10
CR-2-5618		2	2	1
		4	4	3
		8	7	6
		16	12	11
		32	28	27
		40	40	39
		50	50	49

The recoveries of added uranium shown in column 5 are good, and they provide evidence that little uranium is lost during the various steps.

For additional evidence of the validity of the proposed method, mixtures were prepared from 2 different natural-water samples whose uranium content had been established by a laboratory method. The results obtained by analyzing these mixtures are given in table 4.

TABLE 4.—*Determination of uranium in binary mixtures*

Laboratory no.	Composition of mixture Component 1 Component 2	Uranium content [1] Component 1 (ppb)	Uranium content Component 2 (ppb)	Uranium content of mixture (ppb)	Uranium found (ppb)
CR-2-5612	3/7	30	2	10.4	8
CR-2-5613	1/1	25	<2	12.5	10
CR-2-5614	2/3	30	2	13.2	10
CR-2-5615	1/1	30	2	16	16
CR-2-5616	1/19	320	<2	16	16
CR-2-5617	4/1	25	<2	20	16
CR-2-5618	1/1	240	<2	120	120

[1] Analyses made in laboratory of Quality of Water Branch, U. S. Geological Survey, Denver, Colo.

The agreement between the calculated uranium content and that found by the proposed method shown, respectively, in columns 5 and 6 is quite satisfactory.

The proposed method was tested for repeatability by making 5 separate uranium determinations at different times on 5 different natural-water samples. The determinations were made from large bulk samples acidified with nitric acid to permit storage without loss in uranium content. The concentration of uranium ranged from 5 to 300 ppb, and the results of these determinations are shown in table 5.

TABLE 5.—*Repeatability of uranium determinations*

Laboratory no.	Uranium, ppb					
	1	2	3	4	5	Mean
CR-2-566	6	5	4	6	5	5. 2
CR-2-5610	16	16	10	12	16	14. 0
CR-2-5611	30	30	25	30	30	29. 0
CR-2-5612	160	120	160	160	140	148. 0
CR-2-568	300	320	300	300	320	308. 0

The repeatability of the proposed method is good over the concentration range covered.

The accuracy of the field procedure was tested by comparing the results obtained on 8 water samples with those obtained by a laboratory procedure. The comparison is shown in table 6.

TABLE 6.—*Determination of uranium in water*

Laboratory no.	Uranium, ppb	
	Laboratory[1]	Field
CR-2-562	0. 5	<2
CR-2-563	1. 5	<2
CR-2-564	2. 6	2
CR-2-565	2. 8	2
CR-2-566	5. 9	6
CR-2-567	15	10
CR-2-568	27	25
CR-2-569	60, 85	60, 75

[1] Analyses made in laboratory of Quality of Water Branch, U. S. Geological Survey, Denver, Colo.

The laboratory results were obtained by another laboratory of the U. S. Geological Survey using a procedure in which the uranium is concentrated by evaporation of the water sample and subsequently determined fluorimetrically. The favorable comparison shown in table 7 is good evidence that the proposed field method is moderately accurate.

The proposed method is reasonably precise and relatively fast. It permits the easy determination of uranium in natural waters under field conditions and thus eliminates the collection and costly transportation of bulky water samples from field to laboratory. With the proposed method, research on principles of hydrogeochemical prospecting is facilitated, but, perhaps of greater importance, hydrogeochemical prospecting for uranium now becomes practicable for the individual prospector.

LITERATURE CITED

Arden, T. V., Burstall, F. H., and Linstead, R. P., 1949, A new method for the detection and determination of uranium: Chem. Soc. London Jour. Suppl. issue 2, p. S 311–313.

Grimaldi, F. S., May, Irving, Fletcher, M. H., and Titcomb, Jane, 1954, Collected papers on methods of analysis for uranium and thorium: U. S. Geological Survey Bull. 1006, p. 126.

Hecht, F., Korkish, J., Patzak, R., and Thiard, A., 1956, Zur Bestimmung kleinster Uranmengen in Gesteinen and natürlichen Wassern: Mikrochim. Acta, nos. 7–8, p. 1287.

Hernegger, F., and Karlik, B., 1934, Die quantitative Bestimmung sehr kleiner Uranmengen und der Urangehalt des Meerwassers: Akad. Wiss. Wien, Math. naturwiss. Kl., Sitzungsber., Abt. IIa, 144 Band, p. 217.

Hunt, E. C., North, A. A., and Wells, R. A., 1955, Application of paper chromatographic methods of analysis to geochemical prospecting: Analyst, v. 80, p. 172–194.

Lange, N. A., 1952, Handbook of chemistry: Sandusky, Ohio, Handbook Publishers, Inc., 8th ed., p. 1454–1455.

Rodden, S. J., 1950, Analytical chemistry of the Manhatten Project: New York, McGraw-Hill Book Co., p. 37.

Thompson, Charles E., and Lakin, H. W., 1957, A field chromatographic method for the determination of trace quantities of uranium in soils and rocks: U. S. Geological Survey Bull. 1036– [in preparation].

Tschernichow, J. A., and Guldina, E., 1934, Colorimetrische Bestimmung von Uran in uranarmen Erzen: Zeitschr. anal. Chemie, v. 96, p. 260.

Urry, W. D., 1941, The radioactive determination of small amounts of uranium: Am. Jour. Sci., v. 239, p. 191–203.

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