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Field and Laboratory Methods used by the Geological Survey of Canada in Geochemical Surveys

No. 11. URANIUM IN SOIL, STREAM SEDIMENT AND WATER

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ABSTRACT

Analytical methods used to determine trace quantities of uranium in soil, stream sediment and water are described. These techniques have been tested and used successfully in mobile field laboratories as well as in the headquarters laboratory.

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INTRODUCTION

The Geological Survey of Canada receives frequent requests from the public for outlines of methods of analysis suitable for geochemical surveys. To meet these requests it was decided to prepare a series of papers outlining the methods used, giving a complete list of the equipment and reagents required, and a detailed step-by-step account of the procedures employed.

The tests described in these papers are based on those published in the scientific literature, but, in some cases, slightly modified to speed production. No attempt will be made in this series of publications to discuss the principles of geochemical prospecting, sampling procedures, or the interpretation of the analytical data obtained. For a review of such topics the reader is referred to Hawkes (1957), Ginzburg (1960), and Hawkes and Webb (1962).

Preliminary Remarks

Geochemical methods of prospecting for uranium have received little attention in Canada until recently. With the reactivation of its Uranium Program, the Geological Survey of Canada decided to investigate geochemical methods in an effort to provide the mineral industry with additional exploration tools. The following is a description of the analytical methods used to determine trace quantities of uranium in soil, stream sediment and water, the materials commonly employed in geochemical prospecting. A number of analytical techniques have been tested and found to be less than satisfactory. The present method has been tested and used in mobile field laboratories as well as in the headquarters laboratory with satisfactory results.

The method for uranium given below is based on procedures in use by the United States Geological Survey and developed by them for the United States Atomic Energy Commission (see Grimaldi et al., 1954). Minor modifications in procedure have been made by the writers during use in the field.

Notes on the Method

This method is based on the fact that uranium salts fluoresce in the presence of sodium fluoride. In practice uranium salts are fused with a flux containing sodium fluoride and when the resulting melt is exposed to ultraviolet radiation, a fluorescence is produced the intensity of which is proportional to the concentration of uranium present.

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The method used for soil, stream sediment and water samples is a 'direct' method in that uranium is determined without prior separation from associated elements.

In more elaborate methods separation of uranium from associated elements is necessary because of the phenomenon of quenching. Quenching in fluorescence analysis is a reduction in observed fluorescence due to the presence of certain interfering elements, among which are iron, and manganese. Quenching is dependent on the ratio of the amount of flux to the amount of quenching element and is not related to the uranium content of the sample. In a direct method the concentration of quenching elements is reduced to insignificant amounts by taking a very small sample weight.

Solid samples, that is soil and stream sediment samples, are leached in hot 4N nitric acid for 2 hours. An aliquot of the leach solution is diluted with 4N nitric acid to give the working sample solution. An aliquot of this solution, equivalent to a sample weight of 5 mg is evaporated on a platinum dish. After a quick ashing of the sample dish at red heat to destroy organic matter, three grams of carbonate-fluoride flux are added and fused in a muffle furnace at 650° C for 10 minutes. Samples are cooled in a desiccator for twenty minutes, and the fluorescence read on a Galvanek-Morrison fluorometer. Readings are calibrated in terms of uranium content by comparison with standard curves prepared from uranium solutions of known concentration.

The procedure for water samples is similar to that employed for solid samples. A 5 ml aliquot of sample is evaporated on a platinum dish in two parts. The dish is heated to red heat momentarily to destroy organic matter, and allowed to cool. Three grams of carbonate-fluoride flux are added and fused in a muffle at 650° C for ten minutes. Samples are cooled for 20 minutes in a desiccator and fluorescence read on a Galvanek-Morrison fluorometer. Readings are compared with a standard curve as before.

A number of aspects of these fluorometric techniques must be handled with some care. The first of these is the problem of quenching elements mentioned above. While it is true that the problem is lessened in these 'direct' methods to a considerable extent by the small size of sample taken, the problem is not entirely eliminated. The effect should be suspected where, for example in high Mn samples, the fused flux disc has a bluish cast. In these cases the sample may be repeated taking a smaller aliquot of the final sample solution. This effectively reduces the concentration of the quencher and is satisfactory for those samples where the uranium content is sufficiently high to maintain an adequate limit of sensitivity. A second approach to the problem of quenching elements is the 'spike' method. This entails two determinations on the sample solution, the first in the normal way, the second after the addition of a known amount of uranium standard along with the aliquot of sample solution to the platinum dish. The effect of quenching is in this way observed on a known amount of uranium and a correction applied to the sample determination. Details of this technique are discussed by Ingles (1958) and by Michelson (1955).

Perhaps the most important aspect of fluorometric analysis is the preparation of the sample disc. A number of fluxes have been tested and are in use in various laboratories. Among these are pure sodium fluoride, mixtures of sodium fluoride and lithium fluoride, and carbonate-fluoride. The use of these various fluxes is discussed in Grimaldi et al. (1954), Michelson (1955), Price et al. (1956), and Centanni et al. (1956). In the test described

here we have employed the carbonate-fluoride flux for several reasons. The lower melting point of this flux is a distinct advantage, particularly in a test designed to be used in mobile field laboratories. The lower melting point means that less attack on the platinum dishes takes place. In this way a much smaller amount of platinum, which acts as a quencher, is introduced into the sample disc. Finally, the fused discs are easily tipped out of the platinum dishes leaving them much easier to clean. A possible disadvantage of the mixed carbonate-fluoride flux, perhaps more severe than with other fluxes, is the requirement of very careful control of fusion temperature. With this flux, an increase in fusion temperature results in a marked decrease in sensitivity of the method. For this reason, great care must be exercised during the fusion. This factor has been studied by Fletcher (in Grimaldi et al., 1954).

In general, it may be said that, with careful attention to detail, these procedures are capable of excellent sensitivity and satisfactory precision. For water samples the practical limit of sensitivity is 0.2 part per billion (μg/l), while for soils and stream sediment samples the limit is 0.5 part per million. In the absence of quenching elements, or following separation of uranium from quenching elements, lower limits of sensitivity would be possible. A productivity of 50 samples per man day is easily possible and in our laboratories a production 80-90 samples per man day has been achieved on occasion.

ANALYTICAL PROCEDURE

Determination of Uranium in Soil and Stream Sediment

1. To a clean dry test tube (16 x 150 mm) marked at 10 ml, add a weighed sample of 0.25 g of soil or stream sediment.
2. Add 5 ml of $4N/HNO_3$ to the tube and heat for 2 hours in a water bath at 90-95° C, mixing every 15 minutes.
3. Dilute to the 10 ml mark on the test tube with $4N/HNO_3$, mix and let settle. This is solution A.
4. Pipette 2 ml of the clear solution A to a second test tube (16 x 150 mm) calibrated at 10 ml and dilute to the mark with $4N/HNO_3$ mixing thoroughly. This is solution B.
5. Pipette 1.0 ml of solution B to a platinum dish 1 1/2 inches in diameter by 1/8 inch deep and evaporate to dryness on a hot plate.
6. Heat momentarily to dull red heat over a Meker burner and allow to cool.
7. Using a lucite scoop calibrated to deliver 1 g, dispense 3 g of carbonate-fluoride flux into the platinum dish.
8. Fuse for 10 minutes in a muffle furnace at 650° C, timing from the moment the flux melts. Swirl the dish briefly several times during the fusion to ensure thorough mixing.
9. Remove platinum dish from the furnace, allowing the flux to solidify in a level position, then place in a desiccator to cool for at least 20 minutes.

Note: A table of alternative dilutions is provided in the appendix

10. Warm up and adjust the fluorometer as described below.

11. Remove the flux disc from the platinum dish, place it in the sample receptacle of the fluorometer and measure the fluorescence.

12. By means of a standard graph prepared as directed below, convert fluorometer scale reading to micrograms of uranium.

13. Calculate* uranium content of the sample by: $\mu g\, U \times 200 = U$ in parts per million.

14. If the fluorometer scale reading is greater than 90, take a smaller aliquot of solution B and proceed from step 5 above. Calculate the uranium content of the sample from the table given in the Appendix, or apply the formula.

Determination of Uranium in Water

1. Pipette, in two parts, 5 ml of the water sample on a platinum dish (1 1/2" x 1/8") evaporating to dryness on a hot plate after each addition.

2. Heat momentarily to dull red heat over a Meker burner and allow to cool.

3. Using a lucite scoop calibrated to deliver 1 g, dispense 3 g of carbonate-fluoride flux to the platinum dish.

4. Fuse for 10 minutes in a muffle furnace at 650° C, timing from the moment the flux melts. Swirl the dish briefly several times during the fusion to ensure thorough mixing.

5. Remove platinum dish from the furnace, allowing the flux to solidify in a level position, then place in a desiccator to cool for at least 20 minutes.

6. Warm up and adjust the fluorometer as described in its instruction booklet.

7. Remove the flux disc from the platinum dish, place it in the sample receptacle of the fluorometer and measure the fluorescence.

8. By means of a standard graph prepared as directed below, convert fluorometer scale reading to micrograms of uranium.

9. Calculate the uranium content of the sample by:

$$\mu g\, U \times 200 = \mu g/l \text{ or}$$

U in parts per billion

10. If the fluorometer scale reading is greater than 90, take a smaller aliquot of the sample and proceed from step 1 above.

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*Note: Calculations may be made using the following formula:

$$\frac{a}{b} \times \frac{c}{d} \times \frac{e}{f} = U \text{ in ppm}$$

where a = volume of solution A in ml.
b = sample weight in grams.
c = volume of solution B in ml.
d = aliquot of solution A taken in ml.
e = μg U in sample disc (read from standard graph).
f = aliquot of solution B taken in ml.

11. Calculate the uranium content from:

$$\frac{\mu g \text{ U (from graph)}}{\text{sample volume}} \times 1000 = \text{U in ppb}$$

Preparation of Standard Curve

1. Carefully pipette 0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of 0.1 μg/ml U standard solution into platinum dishes stamped with letters A to H. Prepare two additional blanks.

2. Evaporate to dryness on the hot plate.

3. Add 3 g of carbonate-fluoride flux to each dish.

4. Fuse for 10 minutes in a muffle furnace at 650° C, timing from the moment the flux melts. Swirl the dishes briefly several times during the fusion to ensure thorough mixing.

5. Remove platinum dishes from the furnace, allowing the flux to solidify in a level position, then place in a desiccator to cool for at least 20 minutes.

6. Tip the flux discs from the platinum dishes and write the dish letter on the back of each disc in soft pencil.

7. Having adjusted the zero reading on the fluorometer according to the instruction booklet, insert the 0.1 μg standard disc into the sample holder and adjust the instrument to read 100. Remove the standard disc and check that the zero setting has not changed.

8. Proceed to read the standard discs including the 0.0 μg standard. Reread the 0.1 μg disc after every few readings and adjust the instrument to correct for any drift that might have occurred.

9. Prepare a graph of scale reading as ordinate against micrograms of uranium as abscissa, the points of which should fall on a straight line. Join by a straight line the background scale reading with the 0.1 μg disc scale reading as 100. Establish lines at 5 per cent above and below the first line. Reject those standards which do not fall within these 5 per cent limits. If more than two standards fall outside the ±5 per cent range, repeat the entire set.

10. With careful standardization of procedure and with experience it should be possible to dispense with the preparation of the full set of standards each day. When all points are falling within ±5 per cent of the line consistently, one intermediate standard plus blank and 0.1 μg standard should suffice.

Operation of the Fluorometer

The uranium tests outlined in this paper are based on the use of the Galvanek-Morrison reflectance fluorometer. This instrument is manufactured under license by the Jarrell-Ash Company of Waltham, Massachusetts, U.S.A. as model number 26-000. The directions which follow are taken from the instruction manual supplied with the instrument.

1. Turn instrument on and allow 30 minutes for warm-up.

2. Insert the 0.1 μg U standard disc (without its platinum dish) into the sample holder and push the slide into the reading position.

3. Increase the 'Sensitivity' control (usually to step 5) while depressing the 0.1 scale key until the meter reads approximately mid-scale.

4. Set the meter to read full-scale by adjusting the 'Fine Volts' control.

5. Pull the sample slide out into the loading position and rotate the 'Zero' adjusting knob until the meter reads zero.

6. *Remove the standard disc from the sample receptacle and push the slide into the reading position. Depress the highest sensitivity key (0.01) and adjust the lock-nut control marked 'Background' until the meter reads zero.

7. Repeat steps 4, 5, and 6 until the readings are correct and no change occurs. This should be done at least three times. The instrument is now set up to read unknown samples.

8. When the sample slide is pushed in, the lowest sensitivity key is automatically activated. Operate the scale keys, starting with the highest valued key going from right to left. This is done to prevent the meter from being damaged by a high concentration sample.

The reading obtained corresponds to the output current of the photomultiplier and is, therefore, dependent on the intensity of the fluorescent radiation reaching the tube from the sample. These readings can thus be used as a direct measure of the concentration of unknown present where a linear dependance between sample concentration and fluorescent radiation has been established.

Preparation of Equipment and Reagents

1. Platinum Dishes: The platinum dishes used in the test are of a special design and size to fit the fluorometer used. They are prepared from discs of platinum metal, and formed in a steel dish-forming tool (Jarrell-Ash number 26-090). These dishes conveniently permit evaporation of 2 1/2 ml of sample solution or water, and produce a 3 g flux disc. The platinum dishes should have numbers stamped on their undersides. Fifty platinum dishes are required for the test while an additional 8 are required for standards.

2. Carbonate-Fluoride Flux: Weigh 455 g of sodium carbonate, 455 g of potassium carbonate and 90 g of sodium fluoride. Place the components in a twin shell mixing mill and mix for 8 hours. This mixture is hygroscopic and must be kept in tightly sealed bottles away from moisture when not in use.

3. 4N Nitric Acid: Add 125 ml concentrated nitric acid to 375 ml of metal-free water and mix well.

4. 6N Hydrochloric Acid: Add 250 ml concentrated hydrochloric acid to 250 ml of metal-free water and mix well.

5. Standard Uranium Solutions: Weigh 210 mg of uranyl nitrate ($UO_2(NO_3)_2 . 6H_2O$) into a 100 ml volumetric flask. Add approximately 25 ml of 4N nitric acid and dissolve the uranyl nitrate. Dilute to the mark with 4N nitric acid and mix well. This solution should be prepared every two weeks

*Note: This step is somewhat different from that given in the instruction manual because, in these tests, sample discs are not read in their platinum dishes but are placed directly in the sample slide.

since uranium salts tend to precipitate. This solution contains 1000 μg/ml uranium. From this solution prepare a standard solution containing 0.1 μg/ml U by dilution in the following steps:

Standard used	Aliquot taken	Diluted to	New Standard
1000 μg/ml	10 ml	100 ml*	100 μg/ml**
100 μg/ml	10 ml	100 ml*	10 μg/ml**
10 μg/ml	10 ml	100 ml*	1 μg/ml**
1 μg/ml	10 ml	100 ml*	0.1 μg/ml**

* Dilute with 4N. HNO_3.
** Make the solutions freshly, twice weekly.

6. Test Tubes: Calibrate 100 test tubes (16 x 150 mm) to contain 10 ml with a glass-writing diamond. Number these tubes 1 to 100.

7. Flux Scoop: Prepare a scoop to dispense 1 g of flux by drilling a suitable hole in one end of a lucite plastic bar.

Precautions

1. Fusion conditions must be carefully standardized as mentioned above. Tests should be made to assure that the temperature is uniform throughout the chamber of the muffle furnace and that the temperature is as indicated on the pyrometer. Variation in temperature in different parts of the furnace will adversely affect the sensitivity and precision of the method.

2. Care must be taken to assure cleanliness of the platinum ware for two reasons. Firstly, platinum is an expensive commodity which can be lost through misuse. Secondly, contamination, particularly by quenching elements, can be carried from sample to sample on the platinum dishes. After each use, dishes should be soaked in 1:1 HCl, rinsed with tap water, then with metal-free water. Stains which are not removed in this way may be eliminated by fusing 3 g of potassium pyrosulphate in the dish followed by cleaning with HCl as above.

3. Attention must be paid to spurious fluorescence from other materials in the laboratory. Dust, paper and cloth lint, and vaseline are among common materials which fluoresce strongly under ultraviolet light. Care must be taken to keep such materials away from the sample receptacle of the fluorometer. Similarly chips from the flux discs must be cleaned out of the fluorometer sample slide frequently.

4. The background readings on blank flux discs may increase with time. This may be due to contaminants mentioned in 3 above. It may also be due to scratches on the black coating of the sample receptacle, caused during loading and unloading of the sample discs with tweezers. Should this occur the coating must be renewed.

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APPENDIX

Table of Dilutions

Aliquot from Solution 'A'	Diluted to	Aliquot from Solution 'B'	Effective weight of sample	Factor
4 ml	10 ml	1 ml	10 mg	100
2 ml	10 ml	1 ml	5 mg	200
2 ml	10 ml	0.5 ml	2.5 mg	400
1 ml	10 ml	1 ml	2.5 mg	400
1 ml	10 ml	0.5 ml	1.25 mg	800
0.5 ml	10 ml	1 ml	1.25 mg	800
0.5 ml	10 ml	0.5 ml	0.625 mg	1,600
0.2 ml	10 ml	1 ml	0.5 mg	2,000
0.2 ml	10 ml	0.5 ml	0.25 mg	4,000
0.2 ml	10 ml	0.2 ml	0.1 mg	10,000
0.2 ml	10 ml	0.1 ml	0.05 mg	20,000

Table of dilutions – This table is based on an initial weight of sample of 0.25 g. When dilutions are made as shown, the uranium content of the original sample may be calculated by multiplying the uranium content of the flux disc by the appropriate factor. Thus, from an initial sample weight of 0.25 g solution 'A' was prepared. An aliquot of 2 ml was diluted to 10 ml to give solution 'B'. An aliquot of 1 ml of this solution was evaporated on the platinum dish and its uranium content was found to be 0.04 μg U, from the standard curve. The original sample contained

$$0.04 \times 200 = 8 \text{ ppm U.}$$