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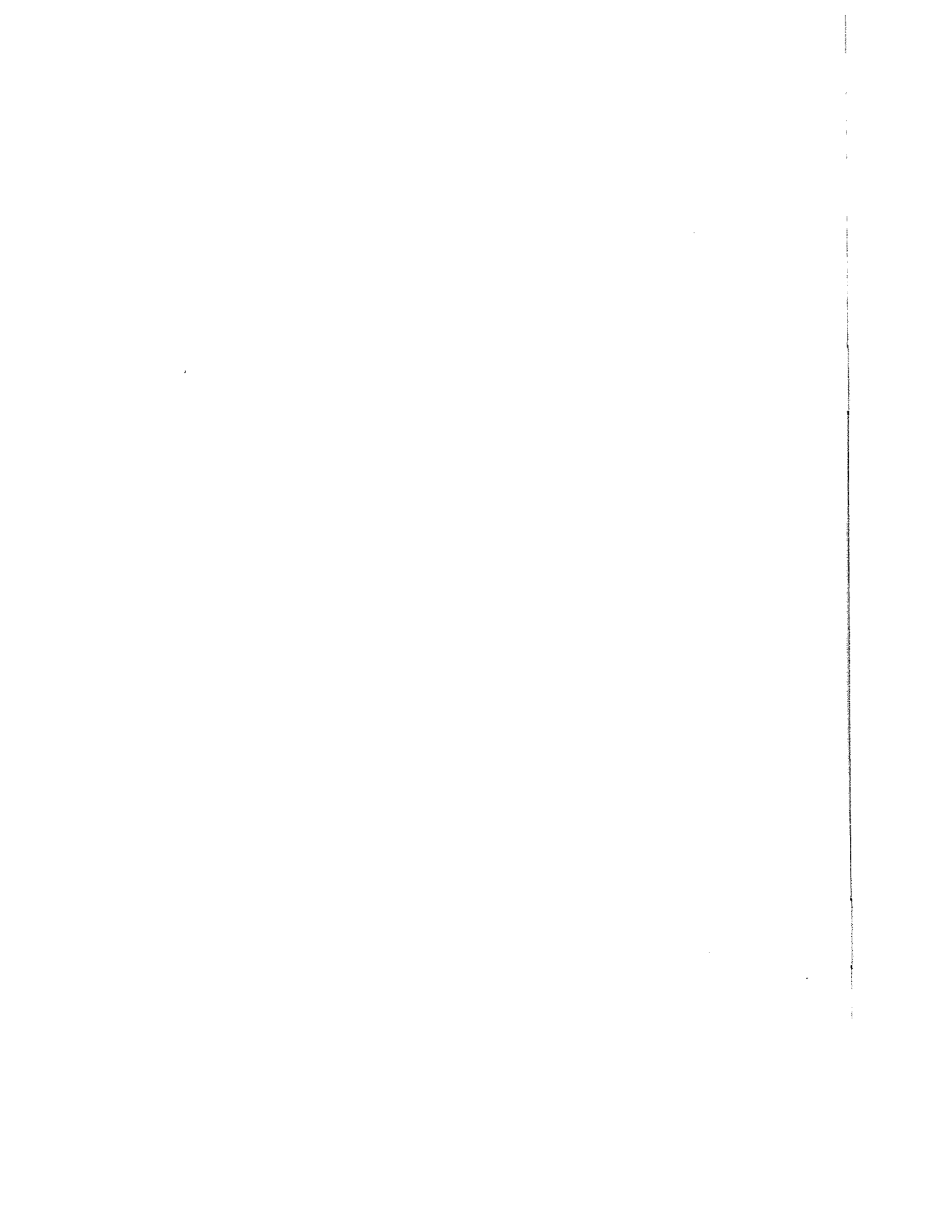
A FIELD METHOD FOR DETERMINING URANIUM  
IN NATURAL WATERS

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CANADA



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### ABSTRACT

The following procedure has been used by the Geological Survey of Canada for field determinations of the amount of uranium in solution in natural water. A cold water sample is filtered, acidified and placed in a separatory funnel. Sodium chloride is added to lower the solubility of carbon tetrachloride in the aqueous phase; EDTA solution is added to complex interfering metals; diphenyl propanedione solution is added to complex the uranium; and pyridine and carbon tetrachloride are added to dissolve this complex. The carbon tetrachloride solution forms a separate phase and its colour is compared with standards to determine the amount of uranium present.

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INTRODUCTION

This paper is one of a series describing methods of analysis used in geochemical surveys by the Geological Survey of Canada. The test described is essentially unchanged from that developed by Smith and Chandler (1958) and by Hunt (1958)<sup>1</sup>.

The method is admirably suited to field conditions as no heat is required. Two men working in a field laboratory can analyze about thirty water samples in a normal work day once a production schedule is established.

DESCRIPTION OF METHOD

A 1-litre cold water sample is filtered, acidified with hydrochloric acid, and placed in a 2-litre separatory funnel. The following reagents are added to the sample in rapid sequence, with intermittent agitation: sodium chloride, to lower the solubility of carbon tetrachloride in the aqueous phase; EDTA solution, to complex interfering metals; diphenyl propanedione solution, to complex the uranium; pyridine, to act both as a solvent for the diphenyl propanedione and as a buffer to obtain the correct final pH; and carbon tetrachloride, which acts as a solvent for the uranium complex.

The carbon tetrachloride, generally referred to as the 'organic phase', settles to the bottom of the separatory funnel, carrying the uranium complex with it, and is drawn off into a glass specimen vial. The uranium concentration of the organic phase is proportional to the intensity of the yellow colour of the extract, which is compared visually with a set of colorimetric standards previously prepared in an identical manner. The lower limit of sensitivity of the method is between 1 and 2 ppb (parts per billion) uranium.

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<sup>1</sup> Names and dates refer to publications listed in the Selected Bibliography.

## ANALYTICAL PROCEDURES

### Sample Preparation

1. Place a finger over the stem of the 6-inch-diameter funnel and fill the funnel about one-third full with uranium-free water. Insert a perforated ceramic disc in the funnel and add two heaping tablespoons of cellulose floc above the disc. Allow the water to drain and press a moist pad of floc gently around the edges with fingers.

2. Filter a raw 1-litre water sample through the floc into a clean 1-litre sample bottle (or directly into a 2-litre separatory funnel if analysis is to be done immediately) and add 10 ml of 1:1 hydrochloric acid.

### Analysis

1. Transfer a previously filtered and acidified 1-litre water sample to a 2-litre separatory funnel and add 20 grams of sodium chloride by means of a scoop. Shake until dissolved.

2. Add 15 ml of EDTA solution and shake gently.

3. Add 10 ml of carbon tetrachloride and shake vigorously for 1 minute. Allow to stand until the carbon tetrachloride has settled to the bottom. Globules of carbon tetrachloride floating on the aqueous phase can be brought down by gentle swirling of the funnel or by submerging them with a plastic knitting needle. Extract the carbon tetrachloride and discard it. Repeat the extraction with another 10 ml of carbon tetrachloride, again discarding the organic phase. This step may be by-passed where waters contain little or no organic material, but most waters in the Canadian Shield from areas of low topographic relief require it. The step is necessary when brownish colours appear in the final extract, or when samples emulsify when shaken with carbon tetrachloride. In the first case, the brown colour masks the yellow uranium complex, and in the second, the final yield of organic phase is too low to make a reliable colour comparison with standards.

4. Add 5 ml of diphenyl propanedione solution and shake well.

5. Add 15 ml of pyridine and shake gently.

6. Add 10 ml of carbon tetrachloride and shake vigorously for 3 minutes by the clock.

7. Allow the organic phase to settle out.

8. Dry the stem of the separatory funnel with a rolled filter paper and insert a second rolled filter paper into the stem. Allow the organic phase to drip out slowly through the paper into a clear glass specimen vial.

9. In daylight, but not in direct sunlight, compare the colour of the sample with the prepared standards, looking down the lengths of the tubes against a white background. Estimate the uranium content of the unknown directly in parts per billion.

## EQUIPMENT AND REAGENTS

### Equipment

Supply of polyethylene water-sample bottles with screw tops,  
1-litre capacity  
Six funnels, 6-inch diameter, with 5-inch ring stand for each  
Six perforated ceramic filter discs, 1-inch diameter  
Whatman's ashless filter floc, cellulose  
One wash bottle, polyethylene, 500-ml  
Reagent bottle, 500-ml-capacity  
Two separatory funnels, 2-litre capacity, with teflon stopcocks,  
and ring stands  
One plastic knitting needle, 14 inches long  
One scoop, made to measure 20 grams of sodium chloride  
Two automatic pipettes to deliver 15 ml, with 500-ml-capacity  
reagent bottles  
Two automatic pipettes to deliver 10 ml, with 500-ml-capacity  
reagent bottles  
Twenty clear glass specimen vials, 45 x 15 mm diameter with  
screw tops  
One graduated cylinder, pyrex, 5-ml capacity  
One graduated cylinder, pyrex, 50-ml capacity  
One pipette, pyrex, serological, capacity 1 ml, with 0.1-ml  
subdivisions  
One pipette, pyrex, serological, capacity 10 ml with 0.1-ml  
subdivisions  
One reagent bottle, 250-ml capacity, with glass stopper  
One glass-writing diamond-tipped pencil  
2,000 sheets of filter paper, 10-cm diameter, any permeability

The following equipment, in addition to that listed above, is intended as a general guide to equipment required for setting up a field laboratory. Some of the items could be omitted or modified to suit local conditions.

Two water bottles, polyethylene, 5-gallon capacity, for storing uranium-free water  
Tubing, tygon, 6 feet  
Pinch cocks  
Balance, sensitive to 0.01 gram  
Spatula, stainless-steel, 4-inch blade  
Interval timer, spring wound, to signal 3 minutes elapsed time  
Grease pencils  
Cork stoppers, select quality, various sizes  
Cork borer  
Bottle-cleaning brushes  
Detergent  
Plastic wash basin, large enough to immerse 2-litre separatory funnel  
Cleaning tissue

#### Reagents<sup>1</sup> for 1,000 Determinations

10 litres of hydrochloric acid, concentrated  
20 kg of sodium chloride  
150 grams of ethylenediamine tetra-acetic acid (disodium salt) (EDTA)  
30 litres carbon tetrachloride  
15 litres of pyridine  
50 grams of 1,3-diphenyl-1,3-propanedione  
5 litres of absolute ethyl alcohol  
0.1 grams of uranyl nitrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )  
Supply of uranium-free water for reagent preparation, rinsing glassware and preparation of standards. A two-man laboratory will require at least 5 gallons per week if there is an additional local supply of water with uranium content 1 ppb or less. If no such local source exists, the laboratory will require at least 15 gallons per week of demineralized water. (See also note under "General Comments".)

#### PREPARATION OF REAGENTS AND STANDARDS

##### Hydrochloric Acid Solution

Prepare a 1:1 volume for volume hydrochloric acid solution by adding 250 ml of concentrated acid to 250 ml of uranium-free water.

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<sup>1</sup> Chemicals should be A.C.S. reagent-grade if possible.



#### EDTA Solution

Prepare a 1 per cent EDTA solution by dissolving 10 grams ethylenediamine tetra-acetic acid (disodium salt) in 1 litre of uranium-free water.

#### Diphenyl Propanedione Solution

Prepare a 1 per cent diphenyl propanedione solution by dissolving 1 gram of the reagent in 100 ml of absolute alcohol. (Note: 1,3-diphenyl-1,3-propanedione obtained as reagent number 2197 from Eastman Organic Chemicals, Rochester 3, N.Y., does not require the purification procedures described by Smith and Chandler, 1958.)

#### Stock Uranium Solution

Prepare a stock uranium solution containing  $100\mu$  grams of uranium per ml in 1:1 hydrochloric acid. To obtain this concentration, dissolve 0.105 grams of uranyl nitrate in 500 ml of the acid.

#### Standard Uranium Solution

Prepare a standard uranium solution containing  $1\mu$  gram of uranium per ml by pipetting 10 ml of the stock solution (above) into a 1,000-ml sample bottle and filling with uranium-free water acidified with 100 ml of 1:1 hydrochloric acid. (Note: This standard solution should be freshly prepared every 3 or 4 days.)

#### Colorimetric Standards

The following seven standards should be prepared daily in hot weather and every second day in cool weather: 0, 1, 2, 3, 5, 10, and 20 ppb uranium, respectively. To do this, take seven 1-litre sample bottles and designate the desired uranium content on each with a grease pencil. For each ppb uranium required, pipette 1 ml of standard uranium solution (containing  $1\mu$  gram of uranium per ml as described above) into the appropriate sample bottle. Acidify each sample with 10 ml of 1:1 hydrochloric acid and fill to the 1,000-ml level with uranium-free water. Proceed with the analyses as described under "Analytical Procedures", extracting the organic phases into the specimen vials on which the corresponding uranium content has been inscribed.

## GENERAL COMMENTS

Great care must be taken to provide maximum ventilation in the field laboratory because of the toxic effects of the organic solvents carbon tetrachloride and pyridine both of which are used extensively in the test.

The writer found it expedient to use mimeographed sheets (see specimen on opposite page) for recording collection of water samples. The sheets were made up on 5-by-8-inch paper, punched to fit field notebooks.

The filtering process is slow, taking up to 20 minutes per sample, and it was found advantageous to have four to six samples filtering simultaneously in a field laboratory.

Uranium-free water can be stored in the 5-gallon polyethylene bottles listed under "Equipment". One bottle can be used in the field laboratory while the other is being refilled. If the laboratory is in an isolated area, provision for water can be made either by bringing in sufficient water for the required number of analyses at the start of the project, or by passing a local soft water source through an ion-exchange column.

### Sources of Error

One possible error arises from the fact that waters high in natural organic constituents tend to give brown final extracts. Although these mask the colour of the uranium complex, the two should not be confused: the uranium complex is lemon yellow, quite distinctive from the brown caused by the organic solute. The difficulty is largely removed by "scrubbing" with carbon tetrachloride as described in step 3 of "Analytical Procedure".

Contamination should not offer a problem provided normal precautions are taken. Glassware should be washed with detergent in water containing little or no uranium and then triple-rinsed: first with uranium-free water, second with a few ml of concentrated hydrochloric acid and, finally, with uranium-free water.

The glass vials containing the colorimetric standards (which are freshly prepared daily) should have their respective uranium contents indicated by figures inscribed with the glass-writing diamond. This avoids possible false colour effects caused by labels or grease-pencil markings during comparison of the standards with unknowns.

WATER SAMPLE No. _____			
Date .....	General Area		
Sampled by .....			
Location data	Lat ..... Long ..... NTS ..... Elev ..... Prov .....  Geographic name ..... Map sheet ..... Plotted .....		
Access			
Type water	<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;">                     SURFACE                      Lake .....                      Creek .....                      River .....                      Swamp ....                      Sea .....                      Other .....                 </td> <td style="width: 50%; vertical-align: top;">                     UNDERGROUND                      Well .....                      Spring .....                      U/G .....                 </td> </tr> </table>	SURFACE Lake ..... Creek ..... River ..... Swamp .... Sea ..... Other .....	UNDERGROUND Well ..... Spring ..... U/G .....
SURFACE Lake ..... Creek ..... River ..... Swamp .... Sea ..... Other .....	UNDERGROUND Well ..... Spring ..... U/G .....		
Weather			
General	Volume of sample ..... Rate of flow nil .... slow .... mod .... rapid ..... Country rocks .....  Distance to U occurrence ..... Misc.		
Physical character of water	Colour .....  Temp. vc .... c .... tep .... wm .... hot ..... Special odour, taste, solid matter or other features ..... .....		
ANALYSIS:	Date ..... Analyst .....  Method .....  ppb U .....  <div style="text-align: right;">                     pH .....                      Eh .....                 </div> Plotted .....		

Form used to record sample data



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