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FIELD AND LABORATORY METHODS USED BY
THE GEOLOGICAL SURVEY OF CANADA
IN GEOCHEMICAL SURVEYS

No. 2

A METHOD FOR DETERMINING READILY-SOLUBLE COPPER
IN SOIL AND ALLUVIUM

R. H. C. Holman



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No. 2. A METHOD FOR DETERMINING
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By

R. H. C. Holman

D E P A R T M E N T O F
M I N E S A N D T E C H N I C A L S U R V E Y S
C A N A D A

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INTRODUCTION

Described here is a rapid method for determining readily-soluble copper in soil and alluvium during geochemical exploration.

The sample is shaken in a test-tube at air temperature with an acidified solution of ammonium citrate and dithizone reagent dissolved in a light, immiscible organic solvent. After shaking, the suspended solids settle into the aqueous layer, leaving the floating organic solvent clear enough for its colour to be observed. An approximate measure of the amount of copper reacting under the conditions of the test may be made at the sampling site by a simple titration with dithizone solution. A more precise determination can be made in the field laboratory by colorimetric comparison with a set of standards prepared from known amounts of copper.

The method has been widely and successfully used under various conditions in different parts of the world (see references listed below).

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LABORATORY PROCEDURE

1. Weigh 0.2 g of the sample into a test-tube.
2. Add 5 ml of the buffer solution.
3. Add 2 ml of the 0.001-per-cent dithizone solution.
4. Cork the tube and shake vigorously for 2 minutes.
5. Place the tube flat on a bench and allow the solvents to separate.
6. Compare the colour of the organic liquid layer with those of standards containing known amounts of copper.
7. Should the colour lie outside the range of the standards, add measured increments of 0.001-per-cent dithizone solution, shaking between each addition for 30 seconds, until a match is possible.
8. Calculate the amount of copper reacting in the sample by the following formula:

$$\text{Cu (ppm)} = \frac{\text{Micrograms of Cu in matching standard}}{\text{sample weight (g)}} \times \frac{\text{ml dithizone solution added}}{5}$$

Preparation of Standards

Dilute the standard copper solution (100 micrograms/ml) with water to 5 micrograms/ml.

Pipette the following quantities of the 5 microgram/ml copper solution into test-tubes. Add 5 ml of buffer solution and 5 ml of 0.001-per-cent dithizone solution to each, cork, and shake vigorously for 2 minutes.

Ml of 5 micro-gram/ml copper solution	0	0.01	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
Copper in micrograms	0	0.50	1.00	1.50	2.00	2.50	3.00	3.50	4.00	4.50

The standards should be prepared freshly each day and kept in subdued light.

FIELD PROCEDURE

1. Take a level scoopful of the sample as collected, and transfer it to a 25-ml graduated stoppered cylinder.
2. Add 5 ml of the buffer solution and 1 ml of the 0.001-per-cent dithizone solution.
3. Stopper the cylinder and shake vigorously for 2 minutes.
4. Observe the colour of the organic layer as soon as sufficient has separated. Record as 1 ml if the colour is blue-grey, 1/2 if blue-green, and 0 if unchanged green.
5. Should the colour be purple or pink, add further increments of dithizone solution, shaking vigorously between each addition for 30 seconds until a blue-grey colour is obtained. Record the volume of dithizone solution added as an index of the amount of copper reacting.

PREPARATION OF REAGENTS

Thymol Blue Solution

Prepare a 0.04-per-cent solution of the sodium salt in water by dissolving 40 mg in 100 ml of water.

Buffer Solution

Dissolve 50 g of ammonium citrate and 20 g of hydroxylamine hydrochloride in 800 ml of water. Using thymol blue as an

indicator, adjust the pH to 2.0 by adding concentrated hydrochloric acid until the first definite pink colour is permanent; about 48 ml is usually required. Dilute to 1 litre and readjust the pH if it has changed.

Wash the solution free of copper by shaking vigorously in a separatory funnel with successive 15-ml portions of 0.01-per-cent dithizone solution until no colour change is observed in the organic liquid layer. Finally, wash the buffer solution free of dithizone with 15-ml portions of benzene, and store in a polyethylene bottle.

Standard Copper Solution

Dissolve 196 mg of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in water. Add 5 ml of concentrated hydrochloric acid and dilute to 500 ml. One ml of this solution contains 100 micrograms of copper.

Dithizone Solutions

Prepare the 0.01-per-cent solution by weighing 0.04 g dithizone into a Thermos flask, adding 400 ml of benzene and shaking vigorously to dissolve.

Prepare the 0.001-per-cent solution daily by diluting the 0.01-per-cent solution with benzene. Store in a Thermos flask.

Other solvents such as toluene, xylene and the petroleum distillates 'Shellsol', 'Varsol' and 'White Spirit' may be used if benzene is unobtainable, but they will probably require purification. For purification procedures see Holman (1956a).

EQUIPMENT AND REAGENTS*

Equipment—for Reagent Preparation

- 1 reagent balance, 250-g capacity
- 1 graduated cylinder, 500-ml
- 2 graduated cylinders, stoppered, 50-ml
- 1 beaker, 1000-ml, and stirring rod
- 1 separatory funnel, 2000-ml
- 3 polyethylene bottles, 2000-ml
- 2 polyethylene bottles, 500-ml
- 2 polyethylene bottles, 250-ml

*All glass to be 'Pyrex'; all chemicals to be A. C. S. reagent-grade.

- 2 'Thermos' flasks, 1-pint
- 1 polyethylene funnel, 6-inch diameter
- 1 pipette, graduated, 1-ml x 0.01-ml
- 1 pipette, graduated, 10-ml x 0.1-ml
- 1 resin demineralizer, to supply metal-free water, with tubing
- 1 spatula, stainless-steel, 8-inch
- 1 dropping bottle, 10-ml

Equipment—for Analysis

- 1 graduated cylinder, stoppered, 25-ml
- 1 pipette, graduated, 1-ml x 0.01-ml
- 1 automatic pipette or dispenser, 2-ml
- 150 test-tubes, rimless, 16-mm x 150-mm
- 150 corks, select grade, size No. 5, to fit above test-tubes
- 2 polyethylene wash bottles, 250-ml
- 1 test-tube rack to hold 12 tubes
- 1 test-tube rack to hold 50 tubes
- 1 scoup, aluminum or plastic, 0.1-g capacity, or as required
- 1 torsion balance, 500-mg capacity, graduated in 1-mg divisions
- 1 small palette knife
- 1 fluorescent matching tube

Reagents—Sufficient for 1,000 Determinations

Ammonium citrate	500 g
Hydroxylamine hydrochloride	150 g
Hydrochloric acid (concentrated)	300 ml
Benzene, or any other suitable solvent for dithizone	12 pints
Thymol blue, sodium salt	1 g
Copper sulphate (CuSO ₄ ·5H ₂ O)	1 g
Dithizone (diphenylthiocarbazone)	1 g

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