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

NO. 1

LABORATORY METHODS FOR DETERMINING COPPER, ZINC, AND LEAD

By

M. A. Gilbert

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

NO. 1. COPPER, ZINC, AND LEAD

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 has been decided to prepare a series of papers outlining the methods used, and 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 "The Principles of Geochemical Prospecting" by Hawkes (1957).

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1956a: Preliminary Treatment of Soil and Sediment Samples for Analysis; Tech. Comm. No. 1, Imperial College of Science and Technology, Geochemical Prospecting Research Centre, London.
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PRELIMINARY REMARKS

Before proceeding with the analytical details it must be pointed out that certain precautions are necessary to maintain the smooth operation and accuracy of a trace-element laboratory. Contamination from reagents and equipment and careless working habits may lead to faulty and, sometimes misleading results.

One of the principal causes of inaccuracy in trace analytical work is contamination from outside sources, and this should be borne constantly in mind. It is essential to run one or two blanks with every batch of analyses, coupled with two or three standard samples covering a suitable range of values. Once the value of these samples has been established, any result that falls outside the limits of accuracy of the method, or any increase in the metal content of the blank, requires investigation. The source of the error should be found before proceeding with further analyses, and if necessary, the entire batch should be repeated.

As it is not expedient to carry out the analyses in duplicate, the analyst has no way of detecting a chance result that might be questionable. Accordingly, he must rely on the geologist to ask for a repeat determination on any sample where the result does not seem to fit the geological pattern. In general, it is a good practice to repeat, as a routine procedure, any analysis falling above a certain level. This value should be settled in consultation with the geologist and will vary from one project to the next. Such a policy will serve to ensure that time and money are not wasted in the investigation of apparently anomalous areas that are due entirely to faulty analyses.

Some of the sources of contamination and a few suggestions on how to avoid them are discussed in the following.

Metal-free water must be used for all tests. Pass distilled water through a demineralizing column to remove the last traces of metal.

Pyrex or a similar hard borosilicate-type glassware is essential; soft glass is a source of heavy metal contamination. All glassware must be thoroughly rinsed with metal-free water before use. Test-tubes should be cleaned with a brush, rinsed with metal-free water, and dried in an oven. When in use they should be kept covered whenever possible. Both polyethylene and glass reagent bottles should be washed with strong hydrochloric acid prior to rinsing with water.

Items such as rubber stoppers and tubing (a source of zinc) must be avoided. Stopcock grease can also give rise to contamination and should not be used. Extreme caution must be taken with all metal components on the equipment used to ensure that they do not come in contact with any of the solutions. Whenever a new item is introduced into the laboratory, it must be carefully considered from the viewpoint of contamination.

Care must be taken with stoppers and corks. Corks should always be placed on the bench top end down, never on their sides. It is advisable to tie glass stoppers onto flasks, separating funnels, and cylinders. Pipettes must not be placed carelessly on laboratory benches. A porcelain pipette support or some suitably designed non-contaminating rack should be used. The enamel filling used in the etching on the outside of certain brands of hard glass pipettes has been found to be a serious source of lead contamination.

It is important to maintain regular and tidy working habits to ensure uniformity.

Personnel to supervise and operate a trace-element laboratory must be chosen with care. Although the tests may appear relatively simple, it is recommended that a qualified person, preferably a chemist, be placed in charge of the laboratory, although technicians may be used to make the actual tests.

The standard of accuracy of the tests described in this series of papers depends on the skill and experience of the analyst. For the average operator, over a range of 10 to 200 ppm, a mean accuracy of the order of $\pm$ 20% can be attained.

SAMPLE PREPARATION

Soil and Sediment Samples

Equipment

Kraft paper sample envelopes made with water-resistant glue, approximately 6 x 3"

Oven or other means of drying samples

Porcelain pestle and mortar, 100-mm diameter

Set of 6 non-contaminating sieves ranging from 20 to 200 mesh per lineal inch

This set should include an 80-mesh sieve. The sieves can be constructed from a length of 3-inch plastic tubing and 4-inch squares of Swiss bolting silk.

Stiff paint brush, $1\frac{1}{2}$"

Sample-bag numerator

Procedure

1. Dry the sample in its original envelope either in the air or in an oven at about 100° C.

2. Crush sample lightly with a pestle and mortar and sieve onto a sheet of glossy paper.
   The minus-80-mesh fraction is satisfactory for most purposes but the best mesh size should be determined for each project.
   Clean the pestle, mortar, sieve, and paper with a stiff brush after each sample.

3. Transfer sieved fraction to a numbered sample envelope and discard oversize.
   1 gram of sieved sample is adequate for most analytical requirements.

Rock Samples

Equipment

Steel plate and pestle

Agate mortar and pestle or power mortar

Specimen vials, with plastic molded caps, 10-gram capacity

Procedure

1. Break the sample into small uniform pieces.

2. Roll and mix thoroughly on a large sheet of paper.

3. Cone and quarter to obtain about 10 g of sample.

4. Grind in an agate mortar or power grinder to a fine powder.
   Sample should be fine enough to pass a 200-mesh sieve.

5. Transfer sample to a specimen vial and mix thoroughly by shaking vial.

ANALYTICAL PROCEDURES

General Laboratory Equipment Required for All Tests

Torsion balance, 500-mg capacity, sensitive to 1 mg, or any other type of balance suitable for the rapid weighing of samples

Reagent balance, 1-kg capacity

Glass-writing diamond

Stainless steel spatula, 4" blade

Stainless steel spatula, 8" blade

Water-still and mixed-resin demineralizing unit
Metal-free water must be used in all tests; also for making up standards, buffer solutions, and for rinsing etc.

2 aspirator bottles, pyrex or polyethylene, 5-gal capacity

Tygon tubing

4 racks to hold 50 test-tubes (16 x 150 mm) with asbestos base

2 racks to hold 10 test-tubes (16 x 150 mm)

Fluorescent colour matching tube

Suitably designed data sheets for recording results

Burette, 100-ml

Glass rod and tubing, pyrex

Miscellaneous items, such as Bunsen burners, tripods, wire gauze, triangles, tongs, retort stands, clamps, rings, clamp holders, screw clips, corks, wax pencils, labels, glass-cutting file, cork borers, stop-clock, test-tube brushes, Kleenex tissue, porcelain pipette supports, pair of scissors, filter funnels, etc.

Sample Extraction

The metals in the sample can be extracted by either of the following methods:

(a) Digestion with hot nitric acid.

(b) Fusion with potassium bisulphate or pyrosulphate.

Trial runs should be carried out to find the most suitable method for the type of sample collected. The presence of large quantities of iron may give rise to oxidation difficulties in the copper test when using a nitric acid digestion. Metal-free water must be used throughout all tests.

Equipment required for extraction by methods (a) and (b)

Tray covered with 1/2" to 3/4" layer of sand, 12 x 10"
This is conveniently made from an electric hot-plate.

Rack to support about 100 test-tubes (16 x 150 mm) on the sand tray

Measuring cylinder, pyrex, 500-ml

Wash bottle, polyethylene, 500-ml

(a) Digestion with Nitric Acid

Additional equipment required

150 test-tubes, rimless, pyrex, 16 x 150 mm

Wash bottle, polyethylene, 500-ml

Reagents required for 1,000 determinations

1 litre nitric acid, concentrated, analytical-grade

Metal-free water

Preparation of equipment and reagents

1. Number the test-tubes and calibrate at the 3-ml and 10-ml levels using a glass-writing diamond.

2. Prepare a 1:3 nitric acid solution by diluting 125 ml of the concentrated acid to 500 ml with metal-free water in a cylinder. Transfer solution to a polyethylene wash bottle.

Procedure

1. Weigh 0.2 g of sieved sample into a test-tube.
   Smaller weight may be taken if high values are expected. Operate in batches of 30-50 samples.
   Note sample and test-tube number.

2. Add 3 ml of 1:3 nitric acid.

3. Simmer for 1 hour on the sand tray.
   Add more nitric acid if necessary to correct for evaporation.
   During this period a further batch of samples may be weighed and the standard colours prepared (see Preparation of Standards under the various determinations).

4. Remove tubes from sand tray and dilute to 10 ml with water.
   Dispense water from a wash bottle.

5. Mix well and allow to settle for 15 minutes.

6. Proceed as described under the appropriate test.

(b) Fusion with Potassium Bisulphate of Pyrosulphate

Additional equipment required

150 test-tubes, rimless, pyrex, 16 x 150 mm

1 plastic scoop for measuring 0.5-g flux, made by drilling a small cavity in a lucite bar

2 automatic pipettes to deliver 5 ml

2 reagent bottles, pyrex, 500-ml

5 corks 7/8" diameter at narrow end

1 Coleman gasoline stove covered with wire mesh to support 6 tubes in the flame or alternatively a multiple burner unit with a suitably designed rack

Reagents required for 1,000 determinations

600 g potassium bisulphate, fused, powdered, analytical-grade

600 ml hydrochloric acid, concentrated, analytical-grade

Metal-free water

Preparation of equipment and reagents

1. Number the test-tubes with a glass-writing diamond.

2. Prepare a 1N hydrochloric acid solution by diluting 50 ml of concentrated acid to 500 ml with metal-free water in a cylinder. Transfer to a pyrex bottle fitted with a 5-ml automatic pipette.

Procedure

1. Weigh 0.2 g of sieved sample into a test-tube.
   Smaller weight may be taken if high values are expected. Operate with a batch of 80-100 samples. Note sample and test-tube number.

2. Add 0.5 g of flux by means of scoop.

3. Mix flux and sample by tapping bottom of the tube on the palm of the hand.

4. Fuse until frothing ceases (usually 1 minute to 3 minutes).
   Tubes must be rotated during fusion. If unfused material collects on the sides of the tube, fusion must be completed by holding the tube in the flame manually.

5. Allow the melt to cool and add 5 ml of 1N hydrochloric acid.

6. Digest 5 to 10 minutes on a sand tray until the melt has broken up into separate particles.

7. Add 5 ml of water and mix well.
   Dispense from a pyrex bottle fitted with an automatic pipette.

8. Proceed as described under the appropriate test.

Determination of Copper

Equipment required

30 test-tubes, pyrex, rimless, 16 x 150 mm

50 corks, $\frac{1}{2}$" diam at narrow end

1 polyethylene wash bottle, 500-ml

1 polyethylene reagent bottle, 250-ml

1 polyethylene reagent bottle, 500-ml

1 polyethylene reagent bottle, 1-litre

1 automatic pipette to deliver 5 ml
Fit with a cork (not rubber) and attach to the top of a thermos flask.

3 thermos flasks, 1-pint
Cups can be used to construct sieves.

1 automatic pipette to deliver 1 ml

2 pipettes, graduated, serological, pyrex, 1 x 0.01 ml

1 pipette, graduated, serological, pyrex, 5 x 0.1 ml

1 flask, volumetric, pyrex, 500-ml

1 flask, volumetric, pyrex, 100-ml

1 reagent bottle, pyrex, 250-ml

1 measuring cylinder, pyrex, 100-ml

1 separating funnel, Squibb, pyrex, 2-litre

1 beaker, pyrex, 1-litre

1 beaker, pyrex, 100-ml

1 stirring-rod, pyrex

Reagents required for 1,000 determinations

0.15 g diphenylthiocarbazone (dithizone), analytical-grade

0.1 g thymol blue or 10 ml of solution (0.04%)

150 g ammonium citrate (dibasic)

150 g hydroxylamine hydrochloride

150 ml concentrated hydrochloric acid, analytical-grade

3 pellets of sodium hydroxide

0.2 g copper sulphate ($CuSO_4.5H_2O$), analytical-grade

8 litres of carbon tetrachloride, analytical-grade
Carbon tetrachloride can be recovered, see end of this paper for details.

Other solvents can be used in the test. Some of these are:
Xylene and white spirit (Shellsol)
These tend to give unstable solutions and are, therefore, not generally suitable.
Benzene and toluene
These are commonly used in the field, but indoors their volatility and the inflammable and poisonous nature of their vapours create fire and health hazards.

Carbon tetrachloride is also toxic, but, unlike the solvents mentioned above, has a specific gravity greater than water and is usually shielded from direct contact with the atmosphere by an aqueous layer. Nevertheless, it is essential that the laboratory be well ventilated.

Preparation of equipment and reagents

1. Mark the top of 9 corks — 0, 1/2, 1, 1 1/2 .... 4 (this denotes the number of micrograms of copper in the standards) and the top of 10 corks from a to j. Remove any copper impregnated in the cork by shaking with dithizone and citrate solution as in steps 2 to 5, under procedure (below).

2. Prepare a 0.01% solution of dithizone in carbon tetrachloride by dissolving 0.04 g dithizone in 400 ml carbon tetrachloride. Shake thoroughly and stand overnight. Store in a thermos flask.

3. Prepare a 0.001% dithizone solution in carbon tetrachloride by diluting the 0.01% solution daily as required. Store in a thermos flask.

4. Prepare a 0.04% thymol blue solution by dissolving 0.1 g of solid in 2 ml of 0.1N Na OH. Dilute to 250 ml with water. Store in a pyrex reagent bottle.

5. Prepare a citrate solution by dissolving 100 g of ammonium citrate and 100 g of hydroxylamine hydrochloride in about 600 ml of water. Add 10 ml of thymol blue solution. Shake for 2 or 3 minutes in a separating funnel with successive 50-ml parts of 0.01% dithizone solution until the lower carbon tetrachloride layer remains green. Remove the excess dithizone by shaking with successive 50-ml portions of carbon tetrachloride until the organic phase remains colourless. Make up to 1 litre with metal-free water and transfer solution to a polyethylene reagent bottle.

6. Prepare a 1N hydrochloric acid solution by diluting 50 ml of concentrated acid to 500 ml with water in a measuring cylinder. Transfer solution to a polyethylene wash bottle.

7. Prepare a standard copper solution containing 100 µg /ml by dissolving 0.2 g of copper sulphate in a little water, adding 50 ml of 1N hydrochloric acid, and diluting to 500 ml with water in a volumetric flask. Store in a polyethylene reagent bottle. This is the stock solution.

8. Prepare a copper solution containing 5 µg /ml by pipetting 5 ml of the stock solution into a 100-ml volumetric flask and diluting to the mark with water. Prepare this solution freshly once a week.

Procedure

1. Pipette 1 ml of the test solution into a test-tube. Operate in batches of 10.

2. Add 1 ml of citrate solution.

3. Add 1N hydrochloric acid until the colour just turns pink (pH 2.0).
   If the solution is already pink add 2N ammonia until it just turns yellow and then add the acid to bring it back to pink.

4. Add 5 ml of 0.001% dithizone solution.
   Use automatic pipette fitted to the top of the thermos flask.

5. Cork the tube and shake vigorously for 2 minutes.
   Shake in batches of 10.

6. Compare the colour in the carbon tetrachloride layer with standards obtained from known amounts of copper. (See below for preparation of standards.)
   Unless the colour is above the top standard it is unnecessary to rinse tubes between determinations.

7. When the colour obtained is above the top standard repeat steps 1 to 6 using a smaller volume of test solution.
   In that case clean cork and tube by following steps 2 to 5 above.

8. Record the volume of test solution used and the number of micrograms of copper in the matching standard.
   Calculate the copper content, in parts per million (ppm), of the original sample.

$$\text{Cu content (ppm)} = \frac{\mu g \text{ of matching standard} \times 10}{\text{sample weight (g)} \times \text{volume of test solution used (ml)}}$$

Preparation of Standards

Pipette 0, 0.1, 0.2, 0.3 ..... 0.8 ml of the 5 µg/ml copper solution into test-tubes and proceed as in steps 2 to 5 above. The standard colours range from green through blue to pink covering a copper content of 0 to 4 micrograms. The standards should be prepared freshly each day and stored in the dark when not in use. Standards and samples should be treated with the same batch of diluted dithizone solution.

Productivity

80 to 90 determinations per 8-hour man-day.

Determination of Zinc

Equipment required

30 test-tubes, pyrex, rimless, 16 x 150 mm

50 corks, 1/2" diameter at narrow end

1 polyethylene wash bottle, 500-ml

1 polyethylene reagent bottle, 1-gal

1 polyethylene reagent bottle, 500-ml

1 polyethylene reagent bottle, 250-ml

1 automatic pipette to deliver 5 ml
Fit with a cork (not rubber) and attach to the top of a thermos flask.

3 thermos flasks, 1-pint

2 pipettes, graduated, serological, pyrex, 1 x 0.01 ml

1 pipette, graduated, serological, pyrex, 5 x 0.1 ml

1 volumetric flask, pyrex, 500-ml

1 volumetric flask, pyrex, 100-ml

1 separating funnel, Squibb, pyrex, 2-litre

1 measuring cylinder, pyrex, 100-ml

1 beaker, pyrex, 1-litre

1 beaker, pyrex, 600-ml

1 beaker, pyrex, 100-ml

Reagents required for 1,000 determinations

0.15 g diphenylthiocarbazone (dithizone), analytical-grade

8 litres carbon tetrachloride, analytical-grade
Carbon tetrachloride can be recovered, see end of this paper for details.

600 g sodium thiosulphate, ($Na_2S_2O_3 \cdot 5H_2O$)

1,500 g sodium acetate, ($CH_3COO\,Na \cdot 3H_2O$), crystalline, analytical-grade

300 ml glacial acetic acid

10 ml concentrated hydrochloric acid, analytical-grade

0.05 g zinc, analytical-grade

Preparation of equipment and reagents

1. Mark the top of 8 corks — 0, 1/4, 1/2, 1, 1 1/2, 2, 2 1/2, and 3 (this denotes the number of micrograms of zinc in the standards) and the top of 10 corks from a to j.
   Remove any zinc impregnated in the cork by shaking with buffer and dithizone solution as in steps 1 to 4 under procedure.

2. Calibrate 18 tubes at the 8-ml level with a glass-writing diamond.

3. Prepare 0.01% and 0.001% dithizone solutions as described under copper test reagent preparation.

4. Buffer solution: (a) Dissolve 250 g of sodium thiosulphate in about 500 ml of water. Shake for 2 to 3 minutes in a separating funnel with successive 50-ml parts of 0.01% dithizone solution until the dithizone remains green. Remove suspended dithizone by shaking with successive 50-ml parts of carbon tetrachloride until the organic phase remains colourless. (b) Dissolve 610 g of sodium acetate in about 700 ml of water to which 120 ml of glacial acetic acid has been added. Remove any zinc present as described under (a). Combine solutions (a) and (b) and make up to 4 litres with water. Store in a polyethylene reagent bottle.

5. Prepare a standard zinc solution containing 100 µg/ml by dissolving 0.05 g of zinc in 2 to 3 ml of concentrated hydrochloric acid and diluting to 500 ml with water. This is the stock solution. Store in a polyethylene reagent bottle.

6. Prepare a zinc solution containing 5 μg/ml by pipetting 5 ml of the stock solution into a 100-ml volumetric flask and diluting to the mark with water. Store in a polyethylene bottle. Prepare this solution freshly once a week.

Procedure

1. Add 8 ml of buffer solution to a test-tube.
   Dispense buffer from a polyethylene wash bottle. Operate in batches of 10.

2. Pipette 1 ml of test solution into the tube.

3. Add 5 ml of 0.001% dithizone solution.
   Use an automatic pipette fitted to the top of the thermos flask.

4. Cork the tube and shake vigorously for 1 minute.
   Shake in batches of 10.

5. Compare the colour in the carbon tetrachloride layer with standards obtained from known amounts of zinc. (See below for preparation of standards.)
   Unless the colour is above the top standard it is unnecessary to rinse tubes between determinations.

6. When the colour obtained is above the top standard repeat steps 1 to 5 using a smaller volume of test solution.
   In this case, tube and cork must be freed from zinc by shaking with buffer and dithizone solution.

7. Record the volume of test solution used and the number of micrograms of zinc in the matching standard. Calculate the zinc content of the original sample.

$$\text{Zn content (ppm)} = \frac{\mu\text{g of matching standard} \times 10}{\text{sample weight (g)} \times \text{volume of test solution used (ml)}}$$

Preparation of standards

Pipette 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 ml of the 5 μg/ml zinc solution into 8 tubes to which 8 ml of buffer has been added. Add 5 ml of 0.001% dithizone solution and shake vigorously for 1 minute. The standard colours range from green through blue to pink corresponding to a zinc content of 0 to 3 micrograms. The standards should be prepared freshly each day and stored in the dark when not in use. Standards and samples should be treated with the same batch of diluted dithizone solution.

Productivity

100 determinations per 8-hour man-day.

Determination of Lead

Equipment required

20 test tubes, pyrex, rimless, 16 x 150 mm

20 corks, 1/2" diameter at narrow end

2 polyethylene wash bottles, 500-ml

1 polyethylene reagent bottle, 500-ml

2 polyethylene reagent bottles, 250-ml

1 automatic pipette to deliver 5 ml
Fit with a cork (not rubber) and attach to the top of a thermos flask.

3 thermos flasks, 1-pint

1 pipette, graduated, serological, pyrex, 1 x 0.01 ml

1 pipette, graduated, serological, pyrex, 2 x 0.1 ml

1 pipette, graduated, serological, pyrex, 5 x 0.1 ml

1 flask, volumetric, pyrex, 500-ml

1 flask, volumetric, pyrex, 100-ml

1 reagent bottle, pyrex, 1-gal

2 reagent bottles, pyrex, 250-ml

1 measuring cylinder, pyrex, 100-ml

1 separating funnel, pyrex, Squibb, 2-litre

5 separating funnels, pyrex, Squibb, 125-ml

1 beaker, pyrex, 1-litre

1 beaker, pyrex, 600-ml

1 beaker, pyrex, 100-ml

1 book of pH indicator papers, range 2 to 10.5

1 shaking rack
This should be constructed of some non-contaminating metal (e.g. aluminum) with clips for securing 5 separating funnels, 125-ml.

Reagents required for 1,000 determinations

0.15 g diphenylthiocarbazone (dithizone), analytical-grade

8 litres carbon tetrachloride, analytical-grade
Carbon tetrachloride can be recovered, see end of this paper for details.

0.1 g thymol blue or 40 ml of solution (0.04%)

500 ml ammonium hydroxide, sp gr 0.900, analytical-grade

500 ml chloroform, analytical-grade

600 g ammonium citrate (dibasic)

150 g potassium cyanide, analytical-grade

100 g hydroxylamine hydrochloride

2 or 3 pellets of sodium hydroxide

20 ml nitric acid, concentrated, analytical-grade

0.2 g lead nitrate, $Pb(NO_3)_2$

Preparation of equipment and reagents

1. Mark the top of 7 corks — 0, 1/2, 1, 1 1/2 ... 3 (this denotes the number of micrograms of lead in the standards) and the top of 10 corks from a to j.

2. Calibrate 17 test-tubes and the 125-ml separating funnels at the 10-ml level using a glass-writing diamond.

3. Draw out a dropping tube from a piece of pyrex glass tubing.

4. Prepare 0.01% and 0.001% dithizone solutions as described under copper test reagent preparation.

5. Prepare a 0.04% solution of thymol blue as described under copper test reagent preparation.

6. Prepare a 2N ammonium hydroxide solution by diluting 60 ml of concentrated solution to 500 ml with water. Transfer to a polyethylene wash bottle.

7. Prepare a 10% solution of potassium cyanide by dissolving 25 g of KCN in 250 ml of water.
   Potassium cyanide is extremely poisonous. Solutions must NEVER be pipetted by mouth. Always wash hands thoroughly after handling the reagent or its solutions.

8. Prepare a citrate solution having pH 8.5 by dissolving 200 g of ammonium citrate, 40 g of potassium cyanide and 32 g of hydroxylamine hydrochloride in about 800 ml of water. Add 10 ml of 0.04% thymol blue solution. While stirring continuously, carefully add concentrated ammonium hydroxide solution until a blue-green colour is obtained. The pH should be about 8.5. Check with indicator paper. Add a further 30 ml of thymol blue. Shake the solution in a separating funnel with successive 50-ml parts of 0.01% dithizone solution until the dithizone remains green. Remove excess dithizone from the aqueous phase by extracting with successive 50-ml parts of chloroform until the chloroform layer remains colourless. Extract the residual chloroform by shaking twice with 50-ml parts of carbon tetrachloride. Dilute the aqueous phase to 4 litres with metal-free water and store in a pyrex reagent bottle.

9. Prepare a 7.5% nitric acid solution by diluting 15 ml of the concentrated acid to 200 ml with water. Store in a polyethylene reagent bottle.

10. Prepare a standard lead solution containing 100 μg/ml by dissolving 0.08 g of dry lead nitrate in a little water containing a drop of concentrated nitric acid. Dilute to 500 ml with water. This is the stock solution. Store in a polyethylene reagent bottle.

11. Prepare a zinc solution containing 5 μg/ml by pipetting 5 ml of the stock solution into a 100-ml volumetric flask and diluting to the mark with water. Prepare this solution freshly once a week.

Procedure

1. Add 10 ml of citrate solution (pH 8.5) to a 125-ml stoppered separating funnel.
   Dispense citrate solution from a wash bottle. Operate in batches of 5.

2. Pipette 2 ml of the test solution into the separating funnel.

3. Add 2N ammonium hydroxide until a blue-green colour is obtained indicating pH 8.5.

4. Add 5 ml of 0.001% dithizone solution.
   Use an automatic pipette fitted to the top of the thermos flask.

5. Stopper funnel and shake gently in a horizontal motion for 15 seconds.
   Shake 5 funnels at a time using rack.

6. Add 10 ml of water to a test-tube, 16 x 150 mm.
   Dispense from a wash bottle.

7. Add 2 drops of 10% potassium cyanide.
   Use a pyrex dropping tube.

8. Run off the lower organic phase from the separating funnel into the test-tube.
   Care must be taken not to allow any of the aqueous phase to pass into the test-tube.

9. Cork the tube and shake vigorously for 10 seconds. Operate in batches of 5 or 10.

10. Compare the colour in the carbon tetrachloride layer with standards obtained from known amounts of lead. (See below for preparation of standards.) Unless the colour is above the top standard it is unnecessary to rinse funnels or tubes between determinations.

11. When the colour obtained is above the top standard repeat steps 1-10 using a smaller volume of test solution.

12. Record the volume of test solution used and the number of micrograms of lead in the matching standard. Calculate the lead content, in parts per million (ppm), of the original sample.

$$\text{Pb content (ppm)} = \frac{\mu g \text{ of matching standard} \times 10}{\text{sample weight (g)} \times \text{volume of test solution used (ml)}}$$

Preparation of standards

Pipette 0, 0.1, 0.2, 0.3 .... 0.6 ml of the 5 µg/ml lead solution into separating funnels containing 10 ml of citrate solution (pH 8.5). Add 2 ml of 7.5% nitric acid solution and proceed as in steps 3 to 9 above. The standard colours range from colourless through varying intensities of pink corresponding to a lead content of 0 to 3 micrograms. The standards should be prepared freshly each day and stored in the dark when not in use.

Productivity

80 to 100 determinations per 8-hour man-day.

RECOVERY OF CARBON TETRACHLORIDE

Equipment and reagents required

1 all-pyrex distillation apparatus with a 5-litre flask

1 electric heating mantle and energy regulator

2 polyethylene funnels, 6" diam

1 separating funnel, pyrex, 2-litre

1 polyethylene reagent bottle, 1-gal

Ammonium hydroxide solution

Calcium oxide

Powdered activated charcoal

Filter paper, Whatman No. 1, 24-cm diam

Procedure

Accumulate the spent liquid in an empty gallon reagent bottle. When full, shake the carbon tetrachloride with dilute ammonia solution (100 ml of concentrated ammonia diluted to 4 litres with tap water) for about 1 minute. Run the organic phase into a fresh bottle. Add about 20 g of activated charcoal and let stand for 2 or 3 days. When the carbon tetrachloride is colourless, filter into a 5-litre distilling flask. Add 20 g of lime, some glass beads, and distil. Collect fraction coming over between 76 - 77°C.