

***o*-Dithiols in Analysis**

Part VIII.* Use of the Zinc Complex of Toluene-3:4-dithiol in the Field Testing of Ores and Minerals†

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The zinc complex of toluene-3:4-dithiol is recommended as a reagent for testing for copper, silver, gold, zinc, tin, lead, vanadium, arsenic, antimony, bismuth, molybdenum, tungsten, sulphur (free), selenium, tellurium, manganese, iron, cobalt and platinum in their ores and minerals. By carrying out simple procedures, which are suited to field conditions, most of these elements can usually be detected in the coarsely powdered mineral in 1 minute. The procedures are standardised, as far as possible, to permit the maximum information to be gained from the tests. Interferences are rare and can usually be readily avoided.

It was shown by one of us in previous papers in this series^{1,2,3,4} that the zinc complex of toluene-3:4-dithiol (zinc dithiol) can be used in place of toluene-3:4-dithiol (dithiol) as a selective reagent for many thiophilic cations. The tests can be applied rapidly and easily, and the advantages of using a single reagent in place of many are so great that we decided to investigate the use of zinc dithiol in the field testing of ores. Our aim has been to devise simple and rapid preliminary tests for the metals present, which may be of service in the identification of ores.

Almost all the proposed tests can be carried out on the crushed ore in 30 to 60 seconds, except those for noble metals, which take 2 to 3 minutes. The necessary apparatus consists of test-tubes (7.5 cm × 0.95 cm and 12.5 cm × 1.6 cm), a microscope slide, a dropper (teat pipette), a spatula, a polythene wash-bottle and a source of heat. A few common reagents are required.

In most of the tests, zinc dithiol is added to the test solution by means of a spatula. In acid solution, the presence of excess of reagent is revealed at once by the smell of free dithiol. For the few tests in which zinc interferes, a solution of zinc-free dithiol is used, which is prepared as follows—

To 1 ml of 2 *N* hydrochloric acid in a test-tube add a suitable amount of zinc dithiol. Heat to decompose the zinc complex, add 1 ml of ethylene dichloride, and shake. Insert a plug of cotton-wool, and, by pressing the end of a dropper into its fibres, filter, and remove drops of the lower layer as required.

Filtration, which was resorted to sparingly, was carried out by forcing a piece of cotton-wool down a 7.5-cm × 0.95-cm test-tube and removing the clear liquid with a teat pipette. If the solid was required for testing, the cotton-wool was dried as much as possible by suction, wash liquid was added and the procedure was repeated twice. The colour reaction was then given by the precipitate enmeshed in the cotton-wool.

In the preparation of test solutions, no attempt was made to dissolve ores completely. The proposed tests must therefore be regarded as of a preliminary nature. If, in particular, trace amounts of elements are sought, complete dissolution or attack of the ore would normally be necessary. Nevertheless, in no instance did the extremely rapid treatment cause misleading results.

The procedures used with most ores were as follows—

1. *Preparation of ore*—Reduce a fragment of the ore to powder in a small 1-cm × 2-cm (internal dimensions) percussion mortar. The aim should be to prepare a coarse powder (30 to 80 mesh), which will immediately settle from solution without the need for filtration in subsequent tests.

* For details of previous parts of this series, see reference list, p. 23.

† Presented at the meeting of the Society on Wednesday, November 5th, 1958.

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2. *Preparation of test solution*—Place 1 to 5 mg of the prepared ore in a 7.5-cm \times 0.95-cm test-tube. Add 5 drops of concentrated hydrochloric acid, and warm. If there is no immediate sign of reaction, add a trace of potassium chlorate, warm until gas is freely evolved, shake for 10 to 15 seconds and then boil gently for 5 to 10 seconds to remove the smell of chlorine. (Complete removal of chlorine is not necessary.) Allow the undissolved ore to settle, and remove drops of supernatant liquid for testing as required. The arrangement of the ores tested follows that of Read.⁵

COPPER ORES

The presence of copper is indicated by dissolving the ore in acid (procedure 2), diluting the solution and adding zinc dithiol; a black precipitate is formed if copper is present.

TESTS—

A and B—Mix a few milligrams of ore (prepared by procedure 1) with about twice its bulk of zinc dithiol on a microscope slide. Divide the mixture into two heaps. Moisten one heap with 1 drop of pyridine (test A) and the other with 1 drop of 2 *N* sodium hydroxide (test B). Note any reactions in the cold, and then warm gently. A deep green colour in test A or an orange colour in test B indicates the presence of copper. When there is any doubt, the reaction in test B can be intensified by evaporating the drop to dryness, re-moistening with alkali and re-warming.

NOTE—A pale yellow colour with no orange tinge in test B indicates sulphur or pyrites (see "Sulphur Ores," p. 21).

RESULTS—

Test A was given in the cold by copper (native), cuprite, tenorite, covellite, bornite, tennantite (slow—1 minute), enargite (slow—1 minute), malachite (extremely rapid) and azurite (extremely rapid). When warmed gently, chalcopyrite, chalcocite, chrysocolla (slow) and atacamite gave the reaction. (Tennantite and enargite also gave the reaction when warmed gently.)

Test B was given by all the ores that gave test A, tetrahedrite, bournonite (somewhat slow), polybasite, stannite (slow), torbernite and an unidentified cobalt ore containing copper, cobalt and a trace of silver (from a disused mine 4 miles N.W. of Leedstown, Cornwall).

In test B, good reactions were given by bournonite, wolframite (containing copper) and stannite when the mixture was dried, re-moistened and warmed a second time.

SILVER ORES

TESTS—

A—Carry out procedures 1 and 2. To 3 drops of test solution add excess of zinc dithiol, and warm. Add water dropwise (2 to 5 drops are necessary), when, in presence of silver, a bright yellow precipitate appears suddenly.

NOTE—Confusion with antimony, which forms a yellow precipitate at greater dilution, can be avoided (*a*) by heating the liquid, when the antimony complex, but not that of the silver, melts to an orange-yellow oil, or (*b*) by adding a few drops of ethylene dichloride, in which the silver complex is insoluble, but that of the antimony dissolves to give a yellow solution.

Noble metals and tellurium form dark colours with zinc dithiol and interfere in test A. When there is any difficulty, silver is first separated as silver chloride; this is test B.

B—To 3 drops of test solution add 2 to 3 drops of water, and cool. Filter the solution in the way described on p. 16, and wash the cotton-wool twice with 2 *N* hydrochloric acid. Add 2 *N* hydrochloric acid and zinc dithiol, and warm. The cotton-wool is stained yellow in presence of silver.

Nitric acid is often a better solvent for silver ores than is hydrochloric acid; this is the basis of test C.

C—Carry out procedure 1. To a few milligrams of the ore add 3 drops of concentrated nitric acid, and maintain the solution at its boiling-point for 15 to 30 seconds. Add 6 drops of water and zinc dithiol in excess. Re-heat. In presence of silver, the suspended white zinc dithiol suddenly becomes yellow; the yellow precipitate remains unchanged when the solution is boiled.

RESULTS—

Test A was given by cerargyrite. Test B was satisfactory for the complex ores polybasite and sylvanite and when only traces of silver were present, as in the unidentified cobalt ore referred to under "Copper Ores." Test C was more satisfactory than test A for silver (native), stephanite, pyrargyrite and proustite.

GOLD MINERALS

TEST—

Carry out procedure 1. Place 5 to 20 mg of the ore in an ignition tube, and mix with approximately 100 mg each of barium peroxide and barium nitrate. Fuse gently for 30 to 60 seconds, and, while it is still hot, drop the tube into a 15-cm \times 1.6-cm test-tube containing 1 ml of 2 *N* hydrochloric acid so that the ignition tube breaks. Boil for a few seconds, pour the liquid into a second tube, add zinc dithiol, and heat. A brownish pink precipitate indicates gold. To confirm, add 0.5 ml of ethylene dichloride, and shake. By means of a dropper, transfer the lower orange layer to a small hard-glass tube. Evaporate the solvent, and heat the residue, which becomes an intense purple. When heated to redness, the glass becomes gilded in patches.

RESULTS—

The test was given by gold (native), sylvanite, calaverite (purple colour not always obtained), petzite and nagyagite.

Sufficient native gold, in the form of grains, could be dissolved in hydrochloric acid and potassium chlorate in 1 minute to give the reaction, but the proposed fusion method was superior.

ZINC ORES

TEST—

Carry out procedures 1 and 2. To 1 drop of test solution add 3 drops of water and sodium acetate crystals in excess. To the cold solution add 5 drops of zinc-free dithiol solution. Hold the tube nearly horizontal, rotate and then shake. In presence of zinc, a bulky white filamentous precipitate forms at the interface, which may cause the ethylene dichloride to appear almost solid.

RESULTS—

The test was given by smithsonite (with darkening), zinc blende and hemimorphite. Lead, manganese and iron commonly occur in zinc ores. The lead complex, being soluble, does not interfere. Small amounts of iron and manganese do not interfere, but iron darkens the precipitate. Cadmium gives the same reaction, but its ores are rare. Most interferences can be prevented by making the solution alkaline, filtering it and then acidifying with acetic acid, but this was not found to be possible within the time limit imposed.

MERCURY ORES

No improvements on existing tests were found.

TIN ORES

TESTS—

A—Carry out procedure 1. Heat a few milligrams of the ore with 1 pellet (0.1 g) of potassium hydroxide and 1 drop of water for 30 seconds. Cool slightly, and add 3 to 5 drops of water. Acidify with 2 *N* hydrochloric acid, add zinc dithiol, and warm. In presence of tin, a red colour or precipitate forms immediately.

B—Carry out procedures 1 and 2. To 3 drops of test solution add 5 drops of water, 3 to 5 drops of ethylene dichloride and zinc dust to neutralise the acid. Add 3 drops of concentrated hydrochloric acid, and warm. Shake well. Add several drops of water and then zinc dithiol. A red colour or precipitate indicates tin.

RESULTS—

Test A was given by cassiterite (samples from Cornwall, Nigeria, Uganda and Malaya). It failed when antimony, indicated by formation of a yellow precipitate that melted when heated, was present. Test B was given by stannite (much antimony and little tin), but, with cassiterite, the colour was pale pink.

LEAD ORES

TESTS—

A—Carry out procedures 1 and 2. To 3 drops of test solution add 5 drops of water and zinc dithiol in excess. If a coloured precipitate forms, maintain at the boiling-point and shake for 10 seconds, during which the precipitate will usually coagulate and leave an almost colourless but often cloudy supernatant liquid. (The cloudiness is caused by the presence of arsenic or an oxidising agent.) Add sodium acetate crystals in excess. In presence of lead, a bright yellow precipitate forms immediately.

NOTE—The colour of the initial precipitate often indicates the presence of other elements. If the aqueous solution does not rapidly become colourless (as with wulfenite), add an equal volume of ethylene dichloride, warm, shake, and add sodium acetate as before.

B—Carry out procedure 1. Heat a few milligrams of the ore with 1 pellet (0.1 g) of potassium hydroxide and 1 drop of water for 20 to 30 seconds. Add 5 drops of water and then zinc dithiol. A bright yellow precipitate, which forms immediately, indicates lead.

NOTE—Alkali dissolves sufficient copper from reactive copper ores, *e.g.*, azurite, to give an orange solution with excess of zinc dithiol. If lead is present, however, the lead complex coagulates when heated and collects on the surface of the liquid.

If, after applying the test, the liquid is acidified with hydrochloric acid, the presence of other metals may be indicated, *e.g.*, with wulfenite, the lead precipitate immediately becomes green, thus indicating the presence of molybdenum.

Similar reactions are given by thallium, which is, however, rare in ores.

RESULTS—

Test A was given by galena, minium, cerussite, anglesite, pyromorphite, mimetite, vanadinite, crocoisite, wulfenite, jamesonite, bournonite, nagyagite and a mixture representative of freieslebenite. The slow formation of the tungsten complex made it difficult to achieve a satisfactory rapid reaction with stolzite.

Test B serves immediately to distinguish between non-sulphidic and sulphidic lead ores. It was given by all the non-sulphidic ores that gave test A, including stolzite, but not by the sulphide ores, *viz.*, galena, jamesonite, bournonite and nagyagite.

VANADIUM ORES

TESTS—

A—Carry out procedures 1 and 2. To 3 drops of test solution add 7 to 10 drops of water. Add excess of sodium acetate crystals and a few drops of isoamyl acetate. Add zinc-free dithiol solution dropwise, warm gently, and shake. In presence of vanadium, the upper layer darkens and becomes blue, purple or blue-black and almost opaque.

Copper and molybdenum (black and green precipitates, respectively) interfere with this test, but can be removed by dithiol in acid solution, possibly with some loss of vanadium.

B—To 3 drops of test solution add 7 to 10 drops of water and zinc dithiol in excess. Heat, and maintain at the boiling-point for 10 to 20 seconds. Decant or filter the solution, and proceed as in test A.

RESULTS—

Test A was given by carnotite and vanadinite. With vanadinite, a yellow precipitate was also formed, owing to the presence of lead, but it caused no interference. Test B was given by vanadate in presence of nickel and molybdenum (representative of patronite) and of copper and lead (representative of motramite) as well as by solutions containing mixtures of copper, lead and molybdenum.

Cobalt interferes, but is apparently not found in vanadate ores. If suspected, it is easily removed. When a mixture containing copper, cobalt, vanadium^{IV} and iron^{III} in 2 *N* hydrochloric acid was treated with sodium acetate and zinc dithiol, both in excess, the resulting liquid was highly coloured. However, when boiled and shaken, the soluble complexes were decomposed by air and heat in less than 1 minute, and, when the solution was filtered, the filtrate was colourless and gave test A for vanadium^V. The removal of iron was incomplete, but the amount remaining did not interfere.

ARSENIC ORES

TEST—

Carry out procedures 1 and 2 (see Note). To 2 drops of test solution add 3 drops of water and 20 to 50 mg of analytical-reagent grade stannous chloride crystals. Heat for 5 to 15 seconds or until the colour of iron^{III} or copper^{II} has been discharged. Immediately add zinc dithiol, and boil for 15 to 20 seconds with shaking. The liquid becomes milky white in presence of arsenic. Pale yellow droplets of the arsenic complex may form on the surface if a large amount of arsenic is present, and the liquid may then redden after a further 10 to 20 seconds, with subsequent precipitation of metallic arsenic.

NOTE—In procedure 2, insert cotton-wool, and filter if necessary. The presence of undissolved sulphide ore may cause precipitation of stannous sulphide.

RESULTS—

The test was given by arsenic (native), arsenolite, arsenopyrite, cobaltite, enargite, erythrite, mimetite, niccolite, orpiment, polybasite, proustite, realgar, smaltite and tennantite. It was not given by sperrylite (platinum arsenide), which was scarcely attacked in the time allowed. (For detection of arsenic in sperrylite see "Platinum Minerals," p. 22.) Results were negative for all non-arsenical ores tested, including complex ores such as bournonite, jamesonite, sylvanite, pyrargyrite and tetrahedrite.

ANTIMONY ORES

TESTS—

A—Carry out procedures 1 and 2. To 1 drop of test solution add 3 drops of water. If a precipitate (silver chloride) forms, remove it by filtration. Add zinc dithiol in excess, and heat. An orange-yellow precipitate, which melts to droplets or to a yellow film on the surface and solidifies when cooled to about 80° C, indicates antimony or selenium (see Note).

NOTE—If little or no reaction occurs during procedure 2, repeat with nitric acid. The concentration of antimony must be fairly high, as the colour intensity given by antimony is weaker than that given by most other elements here considered by a factor of 10 or more.

If desired, selenium (which is rare in ores) may be distinguished by the fact that the reaction with this element is given if zinc dithiol is added *before* dilution of the test solution.

B—Proceed as in test A. If the addition of zinc dithiol gives a dark precipitate (which indicates the probable presence of copper), dilute a further 2 drops of test solution with 2 drops of water, add 2 pellets (0.2 g) of potassium hydroxide, heat to the boiling-point, and filter. Acidify the filtrate with excess of 2 N hydrochloric acid, add zinc dithiol, and heat. As in test A, the formation of the yellow complex indicates antimony.

NOTE—If ethylene dichloride is added to remove the antimony complex from the aqueous layer and sodium acetate is then added in excess, the formation of the brilliant yellow lead complex in the aqueous layer indicates the presence of lead as well as antimony (jamesonite).

RESULTS—

Test A was given by antimony (native), valentinite, antimonite and jamesonite. Test B gave good reactions with bournonite and tetrahedrite, but, with pyrargyrite and polybasite, reactions were weak unless nitric acid was used as solvent (see Note to test A).

BISMUTH ORES

TEST—

Carry out procedures 1 and 2. To 1 drop of test solution add excess of zinc dithiol. Warm, and add 5 drops of water. In presence of bismuth, a dark red precipitate forms. Boil for a few seconds until the liquid is clear. Chill in water. A red colloidal precipitate of the bismuth complex appears, the colour being discharged by heat.

RESULTS—

The test was given by bismuth (native), bismuth ochre, bismutite, bismuthinite and eulytite.

MOLYBDENUM ORES

TEST—

Carry out procedures 1 and 2. To 1 drop of test solution add 3 drops of water and then zinc dithiol. A brilliant green colour or precipitate forms immediately in the cold.

NOTE—Tungstate gives no reaction in the cold.

RESULTS—

The test was given by molybdenite and wulfenite. Sufficient molybdenum to give the reaction could be dissolved from a single flake of molybdenite treated with hydrochloric acid (without potassium chlorate) for 30 seconds, although the flake appeared to be unchanged.

TUNGSTEN ORES

TEST—

Carry out procedures 1 and 2. To 3 drops of test solution add 10 drops of concentrated hydrochloric acid and excess of zinc dithiol. Heat, and maintain at the boiling-point. A blue-green colour develops within 10 to 20 seconds and becomes more intense if the solution is set aside. If molybdenum is present, add 30 to 50 mg of analytical-reagent grade stannous chloride before adding zinc dithiol.⁶

RESULTS—

The test was given by tungsten (metal), wolframite, scheelite and stolzite, none of which contained molybdenum.

SULPHUR ORES

TEST—

Proceed as for copper (test B, p. 17). A pure yellow colour is formed if sulphur is present.

RESULTS—

The test was given by sulphur and iron pyrites, but not by other sulphidic ores that were tested. Copper interferes.

SELENIUM

When selenium dioxide is sublimed in the vicinity of zinc dithiol, the latter immediately becomes bright yellow. No selenium ores were available, but the element and available compounds (dioxide, potassium selenate and potassium selenocyanate) immediately respond to the following test. Tellurium gives no reaction.

TEST—

Mix a trace of the powder or ore with excess of potassium nitrate in a small test-tube. Dust the upper part of the interior of the test-tube with zinc dithiol. Heat to sublime selenium dioxide; the zinc dithiol becomes bright yellow.

For possible confusion of selenium with antimony, see "Antimony Ores," p. 20.

TELLURIUM ORES

TEST—

Carry out procedures 1 and 2. To 3 drops of test solution add 3 drops of concentrated hydrochloric acid, 2 to 3 drops of ethylene dichloride and zinc dithiol in excess. Heat, and shake. The drops of solvent darken, become black and take on a characteristic metallic appearance.

RESULTS—

The test was given by tellurium (metal), sylvanite, calaverite, petzite, nagyagite and by mixtures representative of tellurite, tetradyomite and hessite.

MANGANESE ORES

TEST—

Carry out procedures 1 and 2. To 3 drops of zinc-free dithiol in ethylene dichloride add 3 drops of pyridine and then 1 drop of test solution. An intense dark greenish brown colour (reddish brown in presence of traces of iron) indicates manganese.

NOTE—If an intense red colour is obtained, iron is present in excess and must be removed. To 3 drops of test solution add excess of ammonium chloride, make alkaline with ammonia, dilute, boil, filter, and add drops of the filtrate to the dithiol in pyridine as described above.

RESULTS—

The test was given directly by pyrolusite and psilomelane, and by a sample of rhodonite after removal of iron.

IRON ORES

Iron can be so readily detected by other means that detection by dithiol is in itself of little interest. The following test may, however, be of use in distinguishing between ores, despite the widespread occurrence of iron in ores of other metals.

TEST—

Carry out procedure 1. To a few milligrams of ore add 2 drops of zinc-free dithiol in ethylene dichloride and 1 drop of pyridine. A red colour may develop almost immediately in the cold, or only when warmed, or not at all.

RESULTS—

The sulphidic ores pyrrhotite and pyrites formed a red colour instantly in the cold. The carbonate and phosphate ores, chalybite (including ironstone) and vivianite rapidly formed a pink colour on warming. The oxidised and less soluble oxide ores, magnetite (including specular iron), limonite (the sample contained only a trace of iron^{II}), hematite and garnet failed to react. For comparison, ferrous sulphate reacted instantly in the cold, and ammonium ferric sulphate slowly developed a pale pink colour on heating.

For the detection of sulphur and cobalt in iron pyrites, see "Sulphur Ores," p. 21 and "Cobalt Ores," respectively.

COBALT ORES

TEST—

Carry out procedure 1. Place a few milligrams of the ore and twice its bulk of zinc dithiol in a test-tube. Add 1 drop of pyridine. Warm if necessary. If there is no strong reaction, add 1 drop of 2 *N* sodium hydroxide, and heat to the boiling-point. An intense blue colour indicates cobalt.

RESULTS—

The test was given immediately in the cold by cobaltite (from Cobalt, Ontario). Smaltite and an unidentified cobalt ore (see p. 17) gave a pale blue when warmed and an intense blue after the addition of sodium hydroxide.

Iron pyrites containing cobalt (from Kirembe, Uganda) gave a pale blue colour, which was not intensified by addition of alkali. When a small pile of zinc dithiol was placed on a lump of this ore and moistened with pyridine, the ore became covered with red and blue patches.

PLATINUM MINERALS

TEST—

Proceed as for gold (p. 18). To a few drops of test solution in dilute hydrochloric acid add 2 to 5 mg of hydroxylamine hydrochloride and excess of zinc dithiol. Maintain at the boiling-point for 1 minute. A violet precipitate, which forms slowly, indicates platinum. Add a few drops of ethylene dichloride, shake, and remove the upper layer. The colour of the solvent (violet) remains unchanged on addition of concentrated hydrochloric acid.

RESULTS—

The test was given by platinum (native—two samples) and by sperrylite. With sperrylite, a marked cloudiness was immediately observed when zinc dithiol was added, which indicates the presence of arsenic. No method of dissolving enough osmiridium in 1 minute to give a satisfactory dithiol reaction could be found.

We thank Mr. P. S. Jewell and Mr. S. F. Everiss of the Cambridgeshire Technical College for their encouragement and help, Dr. S. O. Agrell, Curator of the Museum of Mineralogy and Petrology, University of Cambridge, for his interest and for the supply of many minerals, and Hopkin and Williams Ltd. for a gift of zinc dithiol.

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NOTE—References 1, 2, 3 and 4 are to Parts III, IV, V and VII, respectively, of this series.

Received June 24th, 1958

DISCUSSION

DR. J. H. HAMENCE remarked that Dr. Clark had referred to the fact that dithiol was superior to hydrogen sulphide from the point of view of diagnostic tests. In his own experience, this was in fact a very fair statement and was the origin of his paper on the use of dithiol for the detection of molybdenum and tungsten. In the course of some toxicological work, an odd brownish sulphide precipitate had been obtained, which it was thought might be tin, but which when examined by the dithiol reagent gave, not the expected red precipitate, but a brilliant green. The precipitate was subsequently identified as being due to molybdenum.

Clearly, Dr. Clark had produced a useful advance by the introduction of zinc dithiol as the reagent for testing purposes. One of the objections that was frequently raised to the use of dithiol was in respect of its instability and lack of keeping properties. The use of zinc dithiol would obviously remove this snag.

Finally, he asked whether Dr. Clark had worked out any systematic scheme for the detection of metals with dithiol similar to those that had been suggested from time to time with hydrogen sulphide.

DR. CLARK replied that he had made several attempts to do so, but that these had so far been unsuccessful. One of the difficulties arose in connection with iron and cobalt. These metals were easily precipitated by dithiol in weak acid, but with excess of dithiol the precipitates re-dissolved in part, thereby preventing complete separation. Because of the greater cost of dithiol, he thought that at present its more useful role was as a confirmatory reagent. The addition of diacetyldithiol to acid mixtures, in any case, removed most of the difficulties encountered in the precipitation of sulphides.

DR. W. STROSS said that, if he had understood Dr. Clark correctly, the specificity of the reactions consisted in the production of certain colours with certain metals only at certain acid concentrations. As these concentrations seemed to come close to each other (one range being 10 to 6 *N*, the other 6 to 1 *N*), was there not danger of overlaps, and, in consequence, of practical errors.

DR. CLARK replied that although, in the chart he had shown, many cations had for convenience been grouped together within the ranges 10 to 6 *N* and 6 to 1 *N*, no suggestion was intended that cations precipitated at, say, 4 *N* would come down at, say, 2 *N*. This was not so. When dithiol was added to a mixture of two such cations in acid solution, it was, in general, easy to effect a clear-cut separation as shown by the respective colours of the precipitates.

As the colours of precipitates were spread rather evenly over the spectrum and as the complexes were formed under widely different conditions of acidity, any overlap was hard to find. No serious ambiguities arose with the metals discussed in the paper. In the few instances that arose, notably silver and antimony, the properties of the precipitates (solubility in solvent or low melting-point) served to indicate their nature.

DR. R. F. MILTON enquired whether any of the metal dithiols were solvent-soluble and if so would it be possible to use chromatographic methods of separation and determination.

DR. CLARK replied that a number of the complexes were soluble and that doubtless chromatographic methods could be applied. He thought, however, that quicker and better methods of determination, based on the direct addition of dithiol, might be developed and he had already experimented in this direction. However, it was probably desirable to investigate more fully the nature of the complexes formed and the conditions of their formation. A single cation did not always give the same product. Tin gave a number of complexes; at least one was yellow and at least two were red. Thus, in acid solution, according to the conditions, the red product might contain either 2 or 3 atoms of tin combined with 5 dithiol residues. Unless a single type of molecule was formed, chromatography might give misleading results.