COPPER COMPOUNDS + MANCOZEB WETTABLE POWDERS

[*]**44 + 34**/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests

2.1 Copper

REAGENTS

Hydrochloric acid *c*(HCl) = 5 mol/l
Nitric acid *c*(HNO_3) = 5 mol/l
Ammonia solution 25 %
Potassium cyanide 10 % aqueous solution
Ethyne solution in acetone. Saturate acetone 10 ml with ethyne.

PROCEDURE

(i) Cupric compounds. Dissolve a small portion of the sample in hydrochloric acid (5 mol/l). When all the material has dissolved add ammonia solution, a bluish green basic salt is precipitated, add further ammonia solution until the precipitate just dissolves to give a deep blue solution. Add potassium cyanide solution dropwise and the blue colour disappears leaving a colourless solution.

(ii) Cuprous compounds. Dissolve a small portion of the sample in ammonia solution (5 mol/l); a colourless to pale blue solution is formed. Add ethyne in acetone, a red precipitate of copper acetylide is produced. Dissolve a small portion in nitric acid (5 mol/l), add ammonia solution, a bluish green basic salt is precipitated. Continue as for *(i)*.

2.2 Mancozeb

2.2.1 CS_2 evolution. MT 153.

2.2.2 Spot test. MT 130.

2.2.3 Identification of amines. MT 152.

3.1 Copper. As for copper in technical copper compounds **44**/TC/M/3, CIPAC E, *p. 42*.

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[*] Provisional CIPAC method 1973. Prepared by the Dithiocarbamate Panel of PAC-UK. Chairman: A Stevenson (Robinson Bros. Ltd).

3.2 Mancozeb

OUTLINE OF METHOD The sample is decomposed by hydroiodic acid. Hydrogen sulphide is removed by cadmium acetate, the carbon disulphide evolved is absorbed in methanolic potassium hydroxide and determined by iodometric titration.

REAGENTS

Hydrogen iodide solution 55 % (w/w)
Cadmium sulphate solution, 50 g/l
Potassium hydroxide 2 mol/l methanolic solution, RE 21.5
Acetic acid 10 % solution
Phenolphthalein indicator solution RE 19.1
Iodine standard solution $c(½I_2)$ = 0.1 mol/l, RE 16.1
Starch indicator solution RE 27.1
Sodium thiosulphate pentahydrate solution, 30 g/l
Sodium diethyldithiocarbamate trihydrate RE 96

APPARATUS

Weighing funnel consisting of a boat shaped scoop with a hollow handle at one end through which the sample is poured into the flask
Distillation apparatus as shown in Fig. 9. All joints must be absolutely gas tight. Phosphoric acid may be used for this purpose, but petroleum jelly or silicone grease is just as effective, if used in small quantities. The air bleed should reach as near the bottom of the flask as is practicable. Any efficient absorption train can be used. The methanolic potassium absorbers and bubblers should be dry, or should be rinsed with methanol before use.
Beaker 600 ml
Burettes 50 ml

PROCEDURE

(a) Testing of the apparatus. Carry out the whole procedure using sodium diethyldithiocarbamate trihydrate; if correctly carried out recoveries of between 99 and 101 % should be obtained.

(b) Determination. Assemble the apparatus as shown in Fig. 9 with cadmium sulphate (100 ml) in the first absorber, sodium thiosulphate (75 ml) in the second and third, methanolic potassium hydroxide in the fourth and fifth (50 and 25 ml respectively). Keep the main methanolic absorber cold by immersing it in a beaker of melting ice. Be sure that all joints are absolutely air tight. Use phosphoric acid, or small quantities of petroleum jelly or silicone grease.

Turn on the condenser water and heat the water baths surrounding the first three absorbers to, and maintain at 70 to 80 °C throughout the determination. Cool the fourth and fifth absorbers in the ice-water mixture.

Weigh (to the nearest 0.1 mg) from a weighing funnel sufficient sample to contain about 0.4 mg of dithiocarbamate (*w* g) and transfer to the digestion flask. Assemble the dropping funnel and air bleed and add hydroiodic acid (30 ml) from the tap funnel. Connect the tube at the end of the absorption train to a controlled vacuum supply so that approximately five bubblers of air per second pass through the absorbers and regulate the flow of water through the condenser to about six l/h.

Bring the contents of the flask to a gentle boil and steadily heat until the oil bath temperature reaches 140 ± 5 °C. Continue boiling for 30 min. Allow to cool, disconnect the absorption train and, without delay, determine the xanthate as follows: wash the contents of the methanolic potassium hydroxide bubblers into a beaker (600 ml) using distilled water (300 to 400 ml); add one or two drops of phenolphthalein, neutralise with acetic acid from a burette, and add three drops in excess. Then, with continuous stirring, titrate the solution *immediately*, i.e. within 2 min, with the standard iodine solution to near the end point, add starch indicator, and complete the titration (*t* ml). If the titration is not completed within about 2 min after the addition of the acetic acid, the solution should be discarded and the determination repeated. Carry out a blank determination omitting the sample (*b* ml). One ml iodine, $c(\frac{1}{2}I_2)$ = 0.01355 g of mancozeb.

(c) Calculation

$$\text{Mancozeb content} = \frac{135.5 \times N \times (t - b)}{w} \text{ g/kg}$$

where:

N = normality of the standard iodine solution
t = volume of standard iodine used for the sample (ml)
b = volume of standard iodine used for the blank determination (ml)
w = mass of sample taken (g)

4 Suspensibility

(a) Preparation of suspension. MT 15.1 (*i*).

(b) Determination of sedimentation. MT 15.1 (*ii*).

(c) Determination of mancozeb in the bottom 25 ml of suspension

REAGENTS AND APPARATUS As for **3.2** and MT 15 together with:
Büchner funnel or *sintered glass crucible* porosity No 3, average pore diameter 20 to 30 µm
Vacuum desiccator containing P_2O_5 as desiccant

PROCEDURE

After removal of the top 225 ml of suspension, filter the bottom 25 ml using distilled water to wash out the cylinder. If solids or turbidity appear in the filtrate, refilter through the same filter until the filtrate is perfectly clear. Discard the filtrate. Put the funnel or crucible with its contents into a vacuum desiccator overnight or at least for 8 h. Place the funnel or crucible on a dry filter flask. Break up the cake by means of a glass rod, transfer to the reaction flask and determine the mancozeb content by **3.4** above. Mass of mancozeb in the 25 ml of suspension = $0.1355 \times N \times (t - b) = Q$ g. If the mass of residue exceeds 400 mg, then it may be necessary to sub-sample.

(d) Determination of total copper in the bottom 25 ml of suspension. As for copper wettable powders **44**/WP/M/4, CIPAC E, *p. 47*, except that the solution should be made up to 50 ml instead of 250 ml. Mass of total copper in the 25 ml of suspension = $0.0635 \times t \times N = Q$ g.

(e) Calculation

$$\text{Suspensibility} = \frac{111\,(c - Q)}{c}\ \%$$

where:
c = mass of mancozeb or copper in sample taken for preparing the suspension
Q = mass of mancozeb or copper in the bottom 25 ml of suspension

COPPER COMPOUNDS + MANEB WETTABLE POWDERS
[*]**44 + 61**/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/2.

3.1 Copper. As for copper in technical copper compounds **44**/TC/M/3, CIPAC E, *p. 42*.
3.2 Maneb. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/3.2, except:

$$\text{Maneb content} = \frac{132.7 \times N \times (t - b)}{w} \text{ g/kg}$$

4 Suspensibilty. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/4, except:
Mass of maneb in the 25 ml of suspension = $0.1327 \times N \times (t - b) = Q$ g.

COPPER COMPOUNDS + ZINEB WETTABLE POWDERS
[*]**44 + 25**/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/2.

3.1 Copper. As for copper in technical copper compounds **44**/TC/M/3, CIPAC E, *p. 42*.
3.2 Zineb. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/3.2, except:

$$\text{Zineb content} = \frac{137.9 \times N \times (t - b)}{w} \text{ g/kg}$$

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4 Suspensibilty. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/4, except:
Mass of zineb in the 25 ml of suspension = $0.1379 \times N \times (t - b) = Q$ g.

COPPER COMPOUNDS + ZIRAM WETTABLE POWDERS

[*] **44 + 31**/WP/(M)/-

1 Sampling. Take at least 500 g.

2 Identity tests. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/2.

3.1 Copper. As for copper in technical copper compounds **44**/TC/M/3, CIPAC E, *p. 42*.
3.2 Ziram. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/3.2, except:

$$\text{Ziram content} = \frac{152.9 \times N \times (t - b)}{w}\ \text{1g/kg}$$

4 Suspensibility. As for copper + mancozeb wettable powders **44 + 34**/WP/(M)/4, except:
Mass of ziram in the 25 ml of suspension = $0.1529 \times N \times (t - b) = Q$ g.

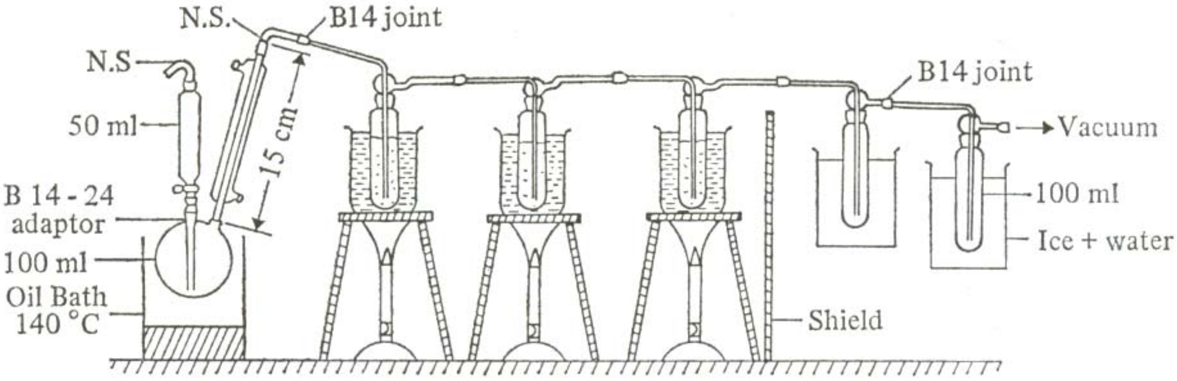

Fig. 9 Apparatus for the determination of dithiocarbamates in presence of copper

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