SCHEDULE 2

METHODS OF ANALYSIS

PART II

11.

DETERMINATION OF MOLYBDENUM

1 SCOPE AND FIELD OF APPLICATION

1. This method is applicable to all fertilisers.

2 PRINCIPLE

2. The sample is dissolved in hydrochloric acid (after ashing if necessary) and the molybdenum complexed with thiocyanate in the presence of stannous chloride. The red coloured complex is extracted into an organic solvent mixture and its absorbance measured at 470 nm.

3 REAGENTS

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3.1 Hydrochloric acid, 50% (V/V): dilute 50 ml concentrated hydrochloric acid solution (d = 1.18 g/ml) to 100 ml with water.

3.2 Hydrochloric acid, 2 N solution.

3.3 Hydrochloric acid, N solution.

3.4 Nitric acid solution, 30% (V/V): dilute 30 ml nitric acid (d = 1.42 g/ml) with water to 100 ml.

(3.5.1) Molybdenum solution (working standard): dissolve 1.84 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in water and dilute with water to 1 litre.

(3.5.2) Molybdenum solution (working standard):

dilute 1.0 ml stock solution (3.5.1) to 1 litre with water.

(1 ml = 1 μg molybdenum).

Prepare this solution immediately prior to use.

3.6 Ammonium ferrous sulphate solution, 4 g per 100 ml.

3.7 Potassium thiocyanate solution, 40 g per 100 ml.

3.8 Sodium sulphate, anhydrous.

3.9 Stannous chloride solution: suspend 40 g stannous chloride dihydrate in 20 ml 6.5 N hydrochloric acid, add water to dissolve and dilute to 100 ml. Filter if turbid.

3.10 Solvent mixture: mix equal volumes of carbon tetrachloride and 3-methylbutan-1-01.

4 APPARATUS

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4.1 Spectrophotometer with 10 mm cells.

5 PREPARATION OF THE SAMPLE

5. See Method 1.

6 PROCEDURE

6

,Preparation of the solution for analysis

In the absence of organic matter

In the absence of organic matter

6.1.—(6.1.1) Weigh to the nearest 0.001 g, 5 g of the prepared sample, place in a 100 ml beaker, add 10 ml hydrochloric acid solution (3.1) and evaporate to dryness on a steam bath. Extract the soluble salts with three successive 10 ml portions of boiling 2 N hydrochloric acid solution (3.2), decanting the solution each time through the same filter paper(**1**) into a 50 ml graduated flask. Wash the filter paper with a little water, cool the solution to room temperature and make up to the mark with water.

In the presence of organic matter

(6.1.2) Weigh to the nearest 0.001 g, 5 g of the prepared sample into a silica dish and place a silica cover on top. Transfer the dish to a cold muffle furnace and gradually raise the temperature to about 475°C (not to exceed 500°C). Maintain at this temperature for at least 16 hours and then open the furnace and allow, the crucible to cool. Add 10 ml hydrochloric acid solution (3.1) and evaporate to dryness on a steam bath. Extract the soluble salts with two successive 10 ml portions of boiling 2 N hydrochloric acid solution (3.2), decanting the solution each time through the same filter paper(**1**) into a 50 ml graduated flask. Add 5 ml hydrochloric acid solution (3.1) and 5 ml nitric acid solution (3.4) to the residue in the dish and evaporate the mixture to dryness on a hot plate at low heat. Add 10 ml boiling hydrochloric acid solution (3.1) to the residue and filter the solution through the same filter paper into the 50 ml graduated flask. Wash the filter paper with water, cool the solution to room temperature and make up to the mark with water.

Determination

6.2.—(6.2.1) Transfer a suitable aliquot of the solution, prepared as in 6.1, to a 125 ml separating funnel, add 1 ml ammonium ferrous sulphate solution (3.6) and sufficient N hydrochloric acid (3.3) to bring the volume to 50 ml (see NOTE), then add 1 ml potassium thiocyanate solution (3.7) and mix. Add 1 ml stannous chloride solution (3.9) and mix again. Add exactly 7 ml solvent mixture (3.1), shake vigorously for two minutes and allow to separate for fifteen minutes. Filter the lower layer through a 7 cm paper into a small stoppered tube. (If the lower layer is not clear or if filtration is difficult, filter through a suitable column packed with anhydrous sodium sulphate (3.8), solid stannous chloride and plugged with cotton wool).

(6.2.2) Carry out a blank determination repeating the procedure but omitting the sample. Measure the absorbance of the solutions at a wave length of 470 nm, in the spectrophotometer (4.1) with water as reference. Determine the quantity of molybdenum in the solution by reference to the calibration curve (6.3).

(**1**) Whatman 541 or equivalent.
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Note:

The acidity of the final solution must not exceed 1.5 N with respect to hydrochloric acid; with more strongly acid conditions, fading of the colour will occur.

6.3 *Calibration curve*

Transfer by pipette, 0,5, 10, 15.20 and 25 ml standard molybdenum solution (3.5.2) into a series of 125 ml separating funnels. To each funnel add 1 ml ammonium ferrous sulphate solution (3.6) and 25 ml of 2 N hydrochloric acid (3.2); dilute to 50 ml with water where necessary and proceed as described at 6.2.1, commencing at "then add 1 ml potassium thiocyanate solution (3.7) and mix ... ... ". Plot a calibration curve of the absorbance of the solutions against the corresponding amounts of molybdenum (µg).

7 EXPRESSION OF THE RESULTS

7. The molybdenum content in me/kg is given by the formula:

$$\frac{A \times 50}{V \times M}$$

where:

A = weight of molybdenum in the aliquot taken for colour development as read from the calibration curve after allowing for the blank reading (µg)

V = volume in millilitres of aliquot taken for colour development

M = weight of sample in grams.