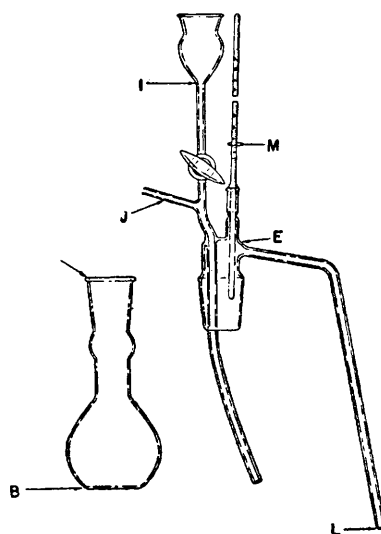


Agricultural

Routine Method for Determining Selenium in Horticultural Materials. J. S. McNulty (*Anal. Chem.*, 1947, **19**, 809-810)—Perchloric acid and a vanadium catalyst with nitric and sulphuric acids destroy selenium-containing organic matter. The selenium is distilled with hydrobromic acid and the distillate titrated by a modified Norris - Fay procedure. Recovery is improved and the working time reduced. The procedure is as follows.

DIGESTION—Tissues—Quickly moisten 10 g. of the prepared sample with 30 ml. of "starting solution" and 5 ml. of water in a digestion flask. (Prepare the starting solution by dissolving 1.6 g. of ammonium metavanadate in 300 ml. of water and 1500 ml. of concentrated nitric acid. When seething stops, add 75 ml. of concentrated nitric



acid, 5 ml. of 60 per cent. perchloric acid, and 50 ml. of concentrated sulphuric acid.) Heat the flask slowly to 140° to 150° C. and when nitrogen peroxide ceases to be evolved raise the temperature slowly to 210° C.; cool, and rinse the thermometer with 10 ml. of water. If the solution becomes green during digestion, add 1 ml. of perchloric acid and 10 ml. of nitric acid, and heat less strongly.

Soils—Heat 50 g. of soil with 30 ml. of starting solution. When the foam breaks add 75 ml. of concentrated nitric acid, 7 ml. of perchloric acid, and 100 ml. of sulphuric acid. Incline the flask in a 600-ml. Moroney anti-bumping cup and digest as for tissues.

Nutrient solutions—Evaporate an appropriate volume to 30 or 40 ml. with 0.5 g. of sodium peroxide in a digestion flask. Add 50 ml. of sulphuric acid, 1 ml. of 60 per cent. perchloric acid, and 5 to 10 mg. of ammonium metavanadate. Add nitric acid only if the colour of the solution turns green. Heat to 210° C.

DISTILLATION—Tissues and solutions—Apply silicone grease to the joints and assemble on a ring stand the apparatus shown in the figure. Pass air in J so that 2 or 3 bubbles per sec. emerge from L, which is immersed in 50 ml. of 0.1 per cent. aqueous hydrazine sulphate solution in a cooled 250-ml. Berzelius beaker. Add 5 ml. of 48 per cent. hydrobromic acid solution to the digested sample through I. Heat the flask until most of the bromine is driven off, and allow 10 ml. of hydrobromic acid to be drawn into the flask at a rate of 1 ml. per min.; maintain a vapour temperature of 125° to 135° C. Heat E when necessary to remove the condensate.

Soils—Distil as above, after mixing with 10 ml. of hydrobromic acid, and add only 5 ml., while heating, at a rate of 0.5 ml. per min.

TITRATION—Add 3 g. of urea and 2.5 ml. of 90 per cent. formic acid solution to the receiver and heat to reduce the bromine: add 45 per cent. sodium hydroxide solution until the solution is neutral to phenolphthalein. Add 13 ml. of 18 N sulphuric acid and cool, then add 5 ml. of a 1 per cent. solution of potassium iodide in 0.1 per cent. wheat starch paste, and immediately titrate with 0.005 to 0.01 N sodium thiosulphate. The end-point is taken when the purple to pink colour change is stable for more than 7 sec. Standardise the thiosulphate against a pure selenite or selenium dioxide by the above titration method.

The employment of the vanadium-catalysed digestion is necessary to effect complete selenium recovery in the presence of high concentrations of organic material as in pot soils. The use of a small amount of potassium iodide favours a sharp end-point, as it avoids a high concentration of free selenium and iodine. Elimination of transfer between distillation and titration, hydrolysis of selenium tetrabromide before contact with air, and more effective oxidation all contribute to greater recovery.

Results—Of six values for selenium added to alfalfa meal, ranging from 50 to 330 p.p.m., five were correct to within 1 p.p.m. Of seven values for selenium added to pot soil, ranging from 2 to 50 p.p.m., five were correct to within 0.1 p.p.m.

M. E. DALZIEL

New pH Indicators for Determination of Total Alkalinity in Water. Disodium 4:4'-bis(p-dimethylaminophenylazo)-2:2'-stilbene-disulphonate and Disodium 4:4'-bis(o-tolyl-triazeno)-2:2'-stilbene-disulphonate. M. Taras (*Anal. Chem.*, 1947, 19, 339-341)—In an investigation of the indicator properties of the disazostilbeneamine-disulphonate series of dyes, amines of the aniline and naphthylamine series were coupled with 4:4'-diaminostilbene-2:2'-disulphonic acid. Some of the indicators formed have pronounced colour changes that make them suitable for use in

coloured solutions. Two of these compounds are discussed.

Disodium 4:4'-bis(p-dimethylaminophenylazo)-2:2'-stilbene-disulphonate—The colour change of this indicator is from orange-red at pH 5.5 to blue at pH 4.0. Because the indicator becomes progressively less soluble as the colour change proceeds, the titration is best carried out in a dish, the blue rings of dye deposited on the sides assisting in the detection of the end-point. In the range pH 4.0 to pH 5.0 the change of colour is sufficiently pronounced for titration to be performed to intermediate pH values. Because the colour change begins at pH 5.0 as against pH 4.5 for methyl orange, the indicator gives a more correct end-point in the titration of dilute carbonate solutions. It may be used in yellow carbonate solutions, e.g., marshy water, in which methyl orange does not give a good end-point. Use 2 drops of a 0.1 per cent. solution of the indicator in each 100 ml. of liquid.

Disodium 4:4'-bis(o-tolyltriazeno)-2:2'-stilbene-disulphonate—The indicator changes from deep yellow at pH 5.0 to muddy at pH 4.0. It is more soluble than the above compound and more suited for use in colourless solutions. The colour change is marked only if titrations are performed in a porcelain dish. Use 5 drops of a 0.5 per cent. solution of the indicator in each 100 ml. of liquid.

Preparation of the indicators—Dissolve a paste of 9.25 g. of 4:4'-diaminostilbene-2:2'-disulphonic acid and 50 ml. of distilled water by adding a solution of 2.5 g. of sodium hydroxide in 100 ml. of water. Add, with stirring, a solution of 3.45 g. of sodium nitrite in 10 ml. of water. Run the liquid slowly, with stirring, into a mixture of 25 ml. of crushed ice and 25 ml. of concentrated hydrochloric acid. Allow the beaker to stand in a refrigerator for 1 hr., remove the supernatant liquid, and add the slurry to a solution of 7.3 ml. of dimethylaniline or, for the other indicator, to 6.0 ml. of o-toluidine in 25 ml. of glacial acetic acid. Stir for 1 hr., filter, and dry the precipitate. Add the calculated volume of 0.5 N sodium hydroxide and dilute the solution to the required concentration.

B. ATKINSON

Colorimetric Determination of Free Chlorine with Methyl Orange. M. Taras (*Anal. Chem.*, 1947, 19, 342-343)—The method described is for the determination of chlorine in tap water. It makes use of the reaction by which two molecules of chlorine oxidise one of methyl orange.

Procedure—Fill a 100-ml. Nessler cylinder to the mark with the sample containing not more than 0.65 p.p.m. of chlorine. Add 2 drops of 5 N hydrochloric acid and exactly 3 ml. of 0.005 per cent. methyl orange solution and mix. Compare immediately against permanent standards prepared as follows. Calculate the volume of methyl orange solution in excess when portions of 3 ml. of 0.005 per cent. methyl orange solution are added to samples containing 0.1, 0.15, 0.20 . . . 0.65 p.p.m. of chlorine. Add these amounts of 0.005 per cent. methyl orange solution to 100 ml. of water acidified with 2 drops of 5 N hydrochloric acid. Keep the standards in the dark.

The method is sensitive to 0.1 p.p.m. of chlorine. By using more methyl orange, up to 1.3 p.p.m. of chlorine can be estimated. The solutions compared should be at pH 3, at which point the colour of methyl orange does not vary with pH , and the amount of acid added may have to be increased if the water is alkaline. The bleaching reaction is slow if sulphuric or acetic acid is used for the acidification. Up to 1.25 p.p.m. of chloramine does not interfere if the comparison is made quickly, and substantial amounts of ferric chloride can be present. As the methyl orange is equally sensitive to manganic ion and elementary chlorine, only 0.05 p.p.m. of manganic ion can be tolerated.

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