2.9 Determination of methoxyl

The contents of methoxy-groups in an organic substance are assayed by reacting the substance with concentrated hydriodic acid; methyl iodide produced in the reaction is distilled off, absorbed into a suitable absorbing liquid, and its amount determined titrimetrically.

Apparatus

The apparatus consists of a 25-mL round-bottomed boiling flask into which is sealed a capillary side-arm, 1 mm in diameter, to provide an inlet for a stream of carbon dioxide. The flask is also fitted with an air condenser, approximately 25 cm in height and about 9 mm in internal diameter. A suitable scrubber device containing about 2 mL of water is placed over the condenser. Add 5 mL of antimony sodium tartrate (50 g/l) TS to the scrubber. The outlet from the scrubber terminates in a tube that dips below the surface of the absorbing liquid in the first of two receivers connected in series. For greater convenience in use and cleaning, separate parts of the apparatus are connected by means of ground glass conical or ball joints.

Recommended procedure

Place a quantity of the substance being tested, accurately weighed, as specified in the monograph, in the boiling flask with a boiling rod. Add 2.5 mL of melted phenol R and 5 mL of hydriodic acid (~970 g/l) TS, and connect the flask to the condenser. Add potassium acetate TS to each of the two receivers, about 6 mL to the first one and about 4 mL to the second, and to each receiver 6 drops of bromine R. Pass a slow uniform stream of carbon dioxide R through the capillary side-arm of the boiling flask, and heat the liquid gently by means of a mantled microburner or another suitable device, at such a rate that the vapours of the boiling liquid rise halfway up the condenser. For most substances 30 minutes are sufficient to complete the reaction and sweep out the apparatus. Wash the contents of both receivers into a 250-mL conical flask containing 5 mL of sodium acetate (150 g/l) TS.

Adjust the volume of the liquid to approximately 125 mL, and add 6 drops of formic acid (~1080 g/l) TS. Rotate the flask until the colour due to the bromine is discharged, then add 12 drops of formic acid (~1080 g/l) TS, stopper the flask and mix the contents thoroughly so as to remove any free bromine including the vapour above the liquid, and allow the solution to stand for 1-2 minutes; add 1 g of potassium iodide R and 5 mL of sulfuric acid (~100 g/l) TS, and titrate the liberated iodine with sodium thiosulfate (0.1 mol/l) VS using starch TS as indicator. Repeat the operation without the substance being tested, and deduct the volume of sodium thiosulfate (0.1 mol/l) VS used from the volume required in the determination of methoxyl.

Each mL of sodium thiosulfate (0.1 mol/l) VS is equivalent to 0.5172 mg of methoxyl (CH_3O).