2.4 Oxygen flask method

The oxygen flask method for the determination of halogens and sulfur in organic compounds consists of a combustion procedure followed by appropriate titrimetric determination. Combustion of the organic material in oxygen yields water-soluble inorganic products, which are determined as directed for the individual element.

Apparatus

The combustion is carried out in a suitable conical flask into the stopper of which is fused one end of a piece of platinum wire. A flask of 500 mL is used, unless otherwise specified in the monograph. Towards the other end of the wire, a piece of platinum gauze is attached to provide a means of holding the substance clear of the absorbing liquid during combustion.

Recommended procedure

CAUTION: The analyst should wear safety glasses and use a suitable safety shield between himself and the apparatus. The flask must be scrupulously clean and free from all traces of organic solvents.

Wrap the test substance in a piece of halide-free filter-paper about 5 cm long and 3 cm wide, secure the package in the platinum gauze, and insert one end of a narrow strip of filter-paper into it. Moisten the neck of the flask with water, place the specified absorbing liquid in the flask, fill the flask with oxygen, light the free end of the narrow strip of filter-paper and immediately insert the stopper. Hold the stopper firmly in place. When vigorous burning has begun, tilt the flask to prevent incompletely burned material falling into the liquid. Immediately after combustion is completed, shake the flask intermittently for 10 minutes, place a little water around the rim of the flask, carefully withdraw the stopper, and rinse the stopper, platinum wire, platinum gauze, and sides of the flask with water. Complete the analysis of this solution as specified in the monograph.

Pulverizable substances should be finely ground and thoroughly mixed before the specified quantity is weighed.

For liquids, use capsules of suitable material (e.g. methylcellulose). Place the specified quantity on about 15 mg of ashless filter-paper flock contained in one part of a capsule of suitable size, close the capsule, inserting one end of a narrow strip of filter-paper between the two parts, and secure the capsule in the platinum gauze.

Determination of bromine and chlorine

Using the oxygen flask method described above, burn the quantity of the substance specified in the monograph. The absorbing liquid consists of 17 mL of hydrogen peroxide (~60 g/l) TS and 3 mL of water. When the process is complete, rinse the stopper, platinum wire, platinum gauze, and sides of the flask with 40 mL of water.

Add 5 drops of bromophenol blue/ethanol TS and then, by drops, sodium hydroxide (0.1 mol/l) VS until the colour changes from yellow to blue. Then add 1 mL of nitric acid (3 g/l) TS and 5 drops of diphenylcarbazone/ethanol TS as indicator, and titrate with mercuric nitrate (0.01 mol/l) VS until the solution turns light violet.

Each mL of mercuric nitrate (0.01 mol/l) VS is equivalent to 1.598 mg of Br or 0.709 mg of Cl.

Determination of fluorine

Using the oxygen flask method described, burn the quantity of the substance specified in the monograph. The absorbing liquid consists of 15 mL of water. When the process is complete, rinse the stopper, platinum wire, platinum gauze, and sides of the flask with 40 mL of water.

Add 0.6 mL of sodium alizarinsulfonate (1 g/l) TS and then, by drops, sodium hydroxide (0.1 mol/l) VS until the colour changes from pink to yellow. Add 5 mL of acetate buffer, pH 3.0, TS and titrate with thorium nitrate (0.005 mol/l) VS until the yellow colour changes to pinkish yellow.

Each mL of thorium nitrate (0.005 mol/l) VS is equivalent to 0.380 mg of F.

If a difficulty arises in observing the colour change of the indicator, a preliminary test with a solution containing known quantities of inorganic fluoride should be performed.

Determination of iodine

Using the oxygen flask method described, burn the quantity of the substance specified in the monograph. The absorbing liquid consists of 10 mL of sodium hydroxide (0.2 mol/l) VS. When the process is complete, rinse the stopper, platinum wire, platinum gauze, and sides of the flask with 25 mL of potassium acetate TS to which 15 drops of bromine TS1 are added. Then rinse with 40 mL of water and add, by drops, formic acid (~1080 g/l) TS until discoloration, 20 mL of sulfuric acid (0.05 mol/l) VS, 0.5 g of potassium iodide R, and allow to stand for 5 minutes. Titrate the liberated iodine with sodium thiosulfate (0.05 mol/l) VS, adding starch TS as indicator towards the end of the titration.

Each mL of sodium thiosulfate (0.05 mol/l) VS is equivalent to 1.06 mg of I.

Determination of sulfur

Using the oxygen flask method described, burn the quantity of the substance specified in the monograph. The absorbing liquid consists of 12.5 mL of hydrogen peroxide (~60 g/l) TS. When the process is complete, rinse the stopper, platinum wire, platinum gauze, and sides of the flask with 40 mL of water. Boil the solution for 10 minutes, cool, add 2 mL of acetic acid (~300 g/l) TS, and 20 mL of ethanol (~750 g/l) TS. Titrate with barium nitrate (0.01 mol/l) VS using 2 drops of thorin (2 g/l) TS and 2 drops of methylthioninium chloride (0.2 g/l) TS as indicator until the yellow colour changes to pink.

Each mL of barium nitrate (0.01 mol/l) VS is equivalent to 0.321 mg of S.