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Methyl chloride and ethyl chloride for industrial use — Methods of test

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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No member body expressed disapproval of the document.

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Methyl chloride and ethyl chloride for industrial use — Methods of test

WARNING — Methyl chloride and ethyl chloride are flammable and form explosive mixtures with air. In the presence of aluminium, they may react vigorously to produce methyl- or ethyl-aluminium compounds. Their vapours have toxic and narcotic properties and care should be taken to avoid inhaling them. The liquids can generate very low temperatures by rapid evaporation, thereby causing severe burns if spilled on the skin. These products should be handled in a well ventilated area, away from naked flames and using a protective mask and gloves. Fires should be tackled with carbon dioxide, chemical powders, foam or commercially available extinguishing agents using suitable halogenated hydrocarbon derivatives. In no event should water be used.

1 Scope and field of application

This International Standard specifies the following methods of test for methyl chloride (chloromethane) and ethyl chloride (chloroethane) for industrial use :

a) determination of acidity;

b) determination of residue on evaporation;

c) determination of water content by the Karl Fischer method.

2 References

ISO 760, *Determination of water — Karl Fischer method (General method).*

ISO 2210, *Liquid halogenated hydrocarbons — Determination of residue on evaporation.*

ISO 3427, *Gaseous halogenated hydrocarbons (liquefied gases) — Taking of a sample.*

3 Determination of acidity

3.1 Field of application

The method is applicable to products having acidities, expressed as hydrochloric acid, between 1 and 50 mg/kg.

3.2 Principle

Evaporation of a test portion and absorption of its acidity in water. Titration of this acidity using standard volumetric sodium hydroxide solution in the presence of bromocresol green as indicator.

3.3 Reagents

During the analysis, use only reagents of recognized analytical grade.

3.3.1 Distilled water, neutral to bromocresol green.

Add to distilled water, in a flask fitted with a ground glass stopper, 1 % *(V/V)* of the bromocresol green solution (3.3.3) and neutralize with the standard volumetric sodium hydroxide solution (3.3.2) until the colour turns to light blue.

3.3.2 Sodium hydroxide, standard volumetric solution , of concentration $c(\text{NaOH}) \approx 0{,}01$ mol/l[1], freshly prepared.

3.3.3 Bromocresol green, 1 g/l solution in 95 % *(V/V)* ethanol.

3.4 Apparatus

Ordinary laboratory apparatus and the apparatus shown in figure 1, comprising :

3.4.1 Conical flask (F), 500 ml capacity, with ground glass neck.

3.4.2 Ground glass stopper, fitting the conical flask (3.4.1) and having two side tubes including a dip-tube.

3.4.3 Gas washing bottles (L), 350 ml capacity, with sintered borosilicate glass discs, each containing 100 ml of the water (3.3.1).

3.4.4 Three way stopcock (R).

3.5 Procedure

3.5.1 Test portion

Weigh, to the nearest 1 g, a type (a) or (b) sample cylinder (see ISO 3427) containing the test sample (see figure 1). Connect to the apparatus, slowly introduce at least 100 g of the liquefied product into the conical flask (3.4.1), which shall be clean and dry, and reweigh the cylinder to the nearest 1 g.

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[1] Hitherto expressed as approximately 0,01 N standard volumetric solution.

3.5.2 Determination

Allow the product to evaporate into the two gas washing bottles (3.4.3) containing the water (3.3.1), first at room temperature, then by heating the conical flask in a hot water bath. When evaporation is complete, pass a stream of dry air via the third outlet of the stopcock (**R**) (3.4.4) in order to eliminate any residual vapour of the product from the apparatus. Transfer the water from both gas washing bottles quantitatively to the conical flask and titrate with the standard volumetric sodium hydroxide solution (3.3.2) until the colour turns to light blue [compare with the water (3.3.1)].

3.6 Expression of results

The acidity, expressed as a percentage by mass of hydrochloric acid (HCl), is given by the formula

$$\frac{V \times 0{,}000\,365}{m} \times 100$$

$$= \frac{0{,}036\,5\,V}{m}$$

where

m is the mass, in grams, of the test portion (4.4.1);

V is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (3.3.2) used for the titration;

0,000 365 is the mass, in grams, of hydrochloric acid corresponding to 1 ml of sodium hydroxide solution of concentration $c(\text{NaOH}) = 0{,}01$ mol/l.

NOTE — If the standard volumetric solution used does not have the exact concentration specified in the list of reagents, an appropriate correction shall be applied.

4 Determination of residue on evaporation

Use the method specified in ISO 2210.

NOTE — The method is applicable to products leaving a residue on evaporation equal to or greater than 5 mg/kg.

5 Determination of water content — Karl Fischer method

Use the method specified in ISO 760 subject to the following modifications appropriate for methyl chloride and ethyl chloride.

5.1 Field of application

The method is applicable to products having water contents between 5 and 200 mg/kg.

5.2 Principle

Introduction of a test portion, in the liquid phase, directly into a titration vessel containing a small amount of methanol, previously saturated with the methyl chloride or ethyl chloride, the low water content of which has been neutralized with the necessary amount of Karl Fischer reagent.

Heating the solution to room temperature to achieve complete evaporation of the product. Measurement of the test portion either volumetrically by a gas meter connected to the outlet, or by weighing the sample cylinder before and after taking the test portion.

Electrometric titration using the Karl Fischer reagent according to ISO 760, clause 7, "Direct electrometric titration", or clause 8, "Electrometric back titration".

5.3 Reagents and materials

During the analysis use only reagents of recognized analytical grade.

Use the reagents specified in clause 4 of ISO 760 with exception of those specified in 4.2 (ethylene glycol monomethyl ether) and 4.4 (sample solvent).

5.4 Apparatus

Replace the apparatus specified in ISO 760, sub-clause 5.1 and annex B, by that shown in figure 2 of this International Standard. This apparatus incorporates the following modifications appropriate for methyl chloride and ethyl chloride.

5.4.1 Type (a) or (b) cylinder (see ISO 3427) containing the sample, in inverted position. The cylinder shall be connected to the apparatus by a flexible tube allowing it to be weighed without being disconnected when the test portions taken are measured by mass.

5.4.2 Needle valve (P).

5.4.3 Titration vessel (**V**), working capacity about 200 ml, connected to the automatic microburette containing the Karl Fischer reagent by means of a ground glass joint, and having in addition four side tubes : one for admitting the liquid sample, another for introducing the platinum electrodes, the third, closed with a ground glass stopper (**A**), for introducing certain reagents, and the last one for leading the gas out to the gas meter (**C**) through a safety flask (**G**) and a Drechsel bottle (**R**) containing some Karl Fischer reagent in order to prevent penetration of water into the apparatus.

5.4.4 Water bath, containing the titration vessel (**V**), the water temperature of which is capable of being controlled at 20 ± 0,5 °C by means of a thermostat.

5.5 Procedure

NOTE — This International Standard describes only the direct titration method. However, the determination may also be carried out by back titration if the required apparatus is available. This will include, in addition to the microburette containing the Karl Fischer reagent, a second microburette containing methanol of known water content for the back titration of the excess of Karl Fischer reagent. A sequence of operations similar to that described in this International Standard are carried out, but all direct titrations are replaced by additions of Karl Fischer reagent the excess of which is back titrated using the methanol solution of known water content, following the instructions in clause 8, "Electrometric back titration", of the general method described in ISO 760.

5.5.1 Test portion

Take a test portion of about 100 g of liquid sample, corresponding to approximately 50 litres of gaseous product. Measure this test portion either by mass, by weighing the sample cylinder (5.4.1) before and after taking the test portion, or by volume, measured at room temperature by means of the gas meter (**C**).

5.5.2 Standardization of the Karl Fischer reagent

5.5.2.1 Assembly of the apparatus

With the apparatus assembled as shown in figure 2, switch on the thermostat set at 20 ± 0,5 °C (see 5.4.4). Open the valve of the sample cylinder (5.4.1) and the needle valve (**P**) in order to purge the apparatus by allowing a sufficient amount (about 50 litres) of the sample, measured using the gas meter (**C**), to flow through.

Close the valve of the cylinder but not the needle valve. Remove the stopper (**A**) for a few seconds in order to introduce the volume (approximately 50ml) of methanol required to immerse the electrodes and the tip of the sample inlet dip-tube. Open the valve of the cylinder to allow the sample to flow through the methanol until the latter is saturated. Switch on the electromagnetic stirrer and close the circuit of the device for the electrometric detection of the end point. Adjust the device so that a potential difference of about 1 to 2 V is applied to the electrodes and the galvanometer indicates a weak current, generally of the order of a few microamperes.

Add the Karl Fischer reagent until the galvanometer indicates a sudden increase in current of about 10 to 20 µA, persisting for at least 1 min.

5.5.2.2 Standardization

Standardize the Karl Fischer reagent according to ISO 760, sub-clause 7.2.1.2 or 8.2.1.2. In the latter case, the solution of known water content used for the back titration shall be saturated with methyl chloride or ethyl chloride, as described in 5.5.2.1.

The water equivalent of the Karl Fischer reagent shall be about 1 mg of water per millilitre.

5.5.3 Determination

5.5.3.1 Preparation of the apparatus

Drain the titration vessel (**V**) by removing the stopper (**A**) and introducing a tube connected to a water jet pump. Introduce through the same opening the volume (about 50 ml) of methanol required to immerse the electrodes and the tip of the sample inlet dip-tube. Replace the stopper immediately. Open the valve of the cylinder to allow the sample to flow through the methanol until the latter is saturated. Switch on the electromagnetic stirrer and close the circuit of the device for the electrometric detection of the end point. Adjust the device so that a potential difference of about 1 to 2 V is applied to the electrodes and the galvanometer indicates a weak current, generally of the order of a few microamperes.

Add the Karl Fischer reagent until the galvanometer indicates a sudden increase in current of about 10 to 20 µA, persisting for at least 1 min.

5.5.3.2 Taking the test portion

Set the gas meter (**C**) to zero and open the valve of the cylinder in order to take approximately 100 g of the liquid sample, corresponding to about 50 litres of the gaseous product [read on the meter (**C**)]. Close the valve of the cylinder but not the needle valve.

In the absence of a gas meter, measure the test portion by weighing the cylinder before and after taking the test portion, without disconnecting it, as provided for by the flexible tube connecting it to the apparatus.

5.5.3.3 Titration

When the meter (**C**) has stopped completely or, in the absence of a meter, when bubbling has ceased in the Drechsel bottle (**R**), close the needle valve (**P**). Measure the volume, in litres, of gas used, its temperature, in degrees Celsius, and the atmospheric pressure, in millibars, at the time of testing.

When the test portion has completely evaporated and the mixture in the titration vessel has reached room temperature, titrate the water from the test portion with the standardized Karl Fischer reagent contained in the microburette until the galvanometer indicates the same deflection as previously, persisting for at least 1 min.

Record the volume of Karl Fischer reagent used.

Carry out a second titration, the result of which should not differ from the first by more than 10 mg/kg if the apparatus has been properly purged.

5.6 Expression of results

5.6.1 Water equivalent of Karl Fischer reagent

The water equivalent, T, of the Karl Fischer reagent, expressed in milligrams of water per millilitre, is given by the formula

$$\frac{m_0}{V_0} \times 0{,}156\,6$$

where

m_0 is the mass, in milligrams, of *di*sodium tartrate dihydrate used for standardizing the reagent;

V_0 is the volume, in millilitres, of the standardized Karl Fischer reagent used;

0,156 6 is the mass, in milligrams, of water contained in 1 mg of *di*sodium tartrate dihydrate.

5.6.2 Water content of the sample

5.6.2.1 Gaseous products

The volume V_1 of gaseous sample introduced, corrected to 20 °C and 1 013 mbar, is given, in litres, by the formulae below.

a) **For samples measured by volume,** using a gas meter :

$$V_1 = V_t \times \frac{293}{273 + t} \times \frac{p_1 - p_2}{1\,013}$$

where

V_t is the volume, in litres, of the gaseous test portion, read from the meter (**C**);

t is the temperature of the gas, in degrees Celsius;

p_1 is the atmospheric pressure at the time of testing, in millibars;

p_2 is the vapour pressure, in millibars, of water at temperature t; the corresponding value given in the table below for temperatures ranging from 10 to 30 °C shall be deducted from p_1 when a water operated meter is used.

b) **For samples measured by mass,** by weighing the cylinder :

$$V_1 = \frac{m_1}{2{,}15} \text{ for methyl chloride}$$

$$V_1 = \frac{m_1}{2{,}68} \text{ for ethyl chloride}$$

where

m_1 is the mass, in grams, of product taken;

2,15 is the density at 20 °C, in grams per litre, of gaseous methyl chloride;

2,68 is the density at 20 °C, in grams per litre, of gaseous ethyl chloride.

The water content of the sample, in milligrams per cubic metre of gas, corrected to 20 °C and 1 013 mbar, is given by the formula

$$V \times T \times \frac{1\,000}{V_1}$$

where

T is the water equivalent, expressed in milligrams of water per millilitre, of the Karl Fischer reagent;

V is the volume, in millilitres, of Karl Fisher reagent used for the determination.

Calculate the average of two results agreeing within 10 mg/kg.

5.6.2.2 Liquid products

The mass m_1, in grams, of liquid sample introduced is given either directly by the difference between the weighings of the cylinder before and after taking the test portion, or by the formula

$$m_1 = V_1 \times 2{,}15 \text{ for methyl chloride}$$

$$m_1 = V_1 \times 2{,}68 \text{ for ethyl chloride}$$

where

V_1 is the volume, in litres, of gaseous sample introduced, corrected to 20 °C and 1 013 mbar (see table below);

2,15 is the density at 20 °C, in grams per litre, of gaseous methyl chloride;

2,68 is the density at 20 °C, in grams per litre, of gaseous ethyl chloride.

The water content, of the sample, in milligrams per kilogram, is given by the formula

$$V \times T \times \frac{1\,000}{m_1}$$

Calculate the average of two results agreeing within 10 mg/kg.

6 Gas chromatographic analysis

Under study.

7 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

Table

Temperature, t, °C	10	12	14	16	18	20	22	24	26	28	30
Vapour pressure, p_2, mbar	12,2	13,3	16,0	18,1	20,7	23,1	26,5	30,0	33,6	37,4	40,0

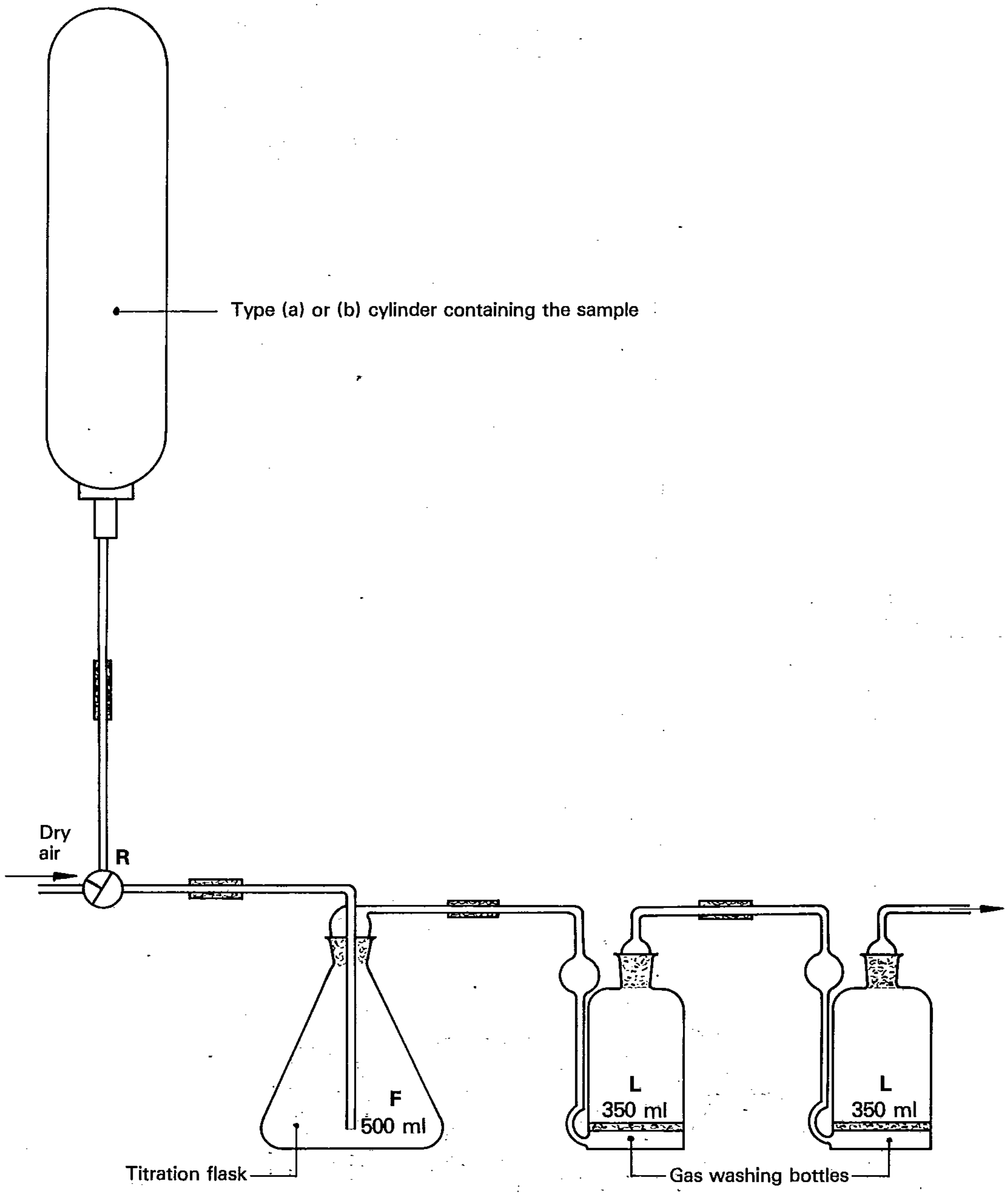

Figure 1 — Apparatus for determination of acidity of gaseous halogenated hydrocarbons

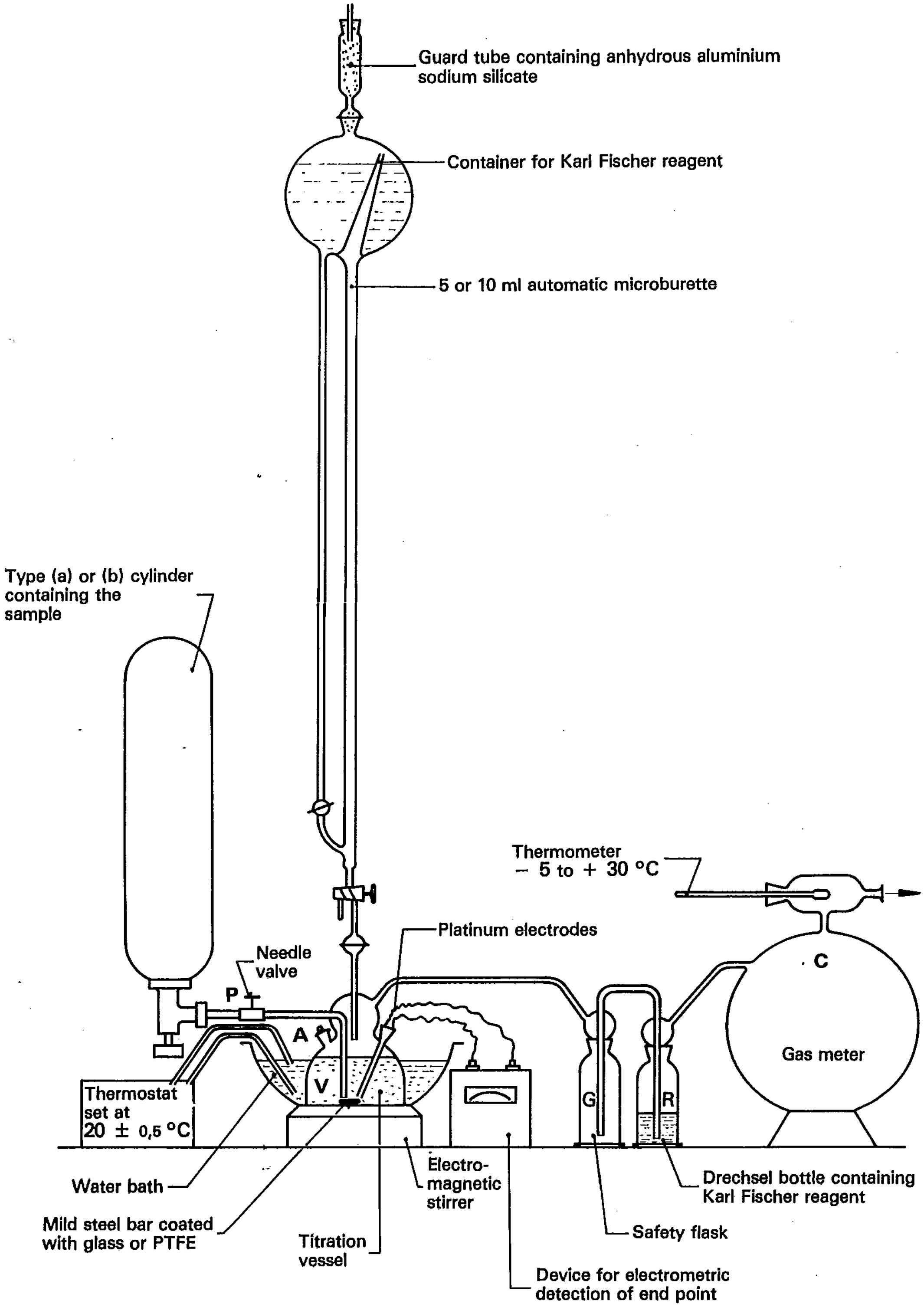

Figure 2 — Determination of water content of methyl chloride and ethyl chloride — Karl Fischer method