BRITISH STANDARD

BS 4431:1989

Methods of sampling and test for

Liquefied anhydrous ammonia

UDC 661.518:543

Committees responsible for this British Standard

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Contents

Foreword

This British Standard has been prepared under the direction of the Chemicals Standards Committee. It supersedes BS 4431:1969, which is withdrawn.

The principal differences between this revision and the previous edition are as follows:

a) a general procedure for taking the test portion has been introduced, based on international test methods;

b) a method of sampling for the determination of oxygen is described;

c) a general test report clause has been introduced.

For many years the UK has participated in the work of Sub-committee 4, of Technical Committee 47, Chemistry, of the International Organization for Standardization (ISO). However, ISO 7103-1982 "*Liquefied anhydrous ammonia for industrial use — Sampling — Taking a laboratory sample*", which was produced by Technical Committee 47, was disapproved by the UK as the procedure is not used in the UK. ISO test methods applicable to anhydrous ammonia will not be implemented as Parts of BS 4431 as they refer to ISO 7103.

This revision retains the guidance on sampling given in the previous edition and therefore the use of the evaporation factor has been retained for the calculation of results. Where appropriate, the methods have been based on international test methods, and the International Standards that are related to the methods described in the clauses are as follows.

Clause	**Related International Standard**
2 **3**	ISO 4276
4 **5**	ISO 7106
6	ISO 7105

The method for determination of water content, described in clause **6**, refers frequently to BS 2511:1970, possession of which is essential.

It was assumed in the drafting of this British Standard that the methods described would be carried out by fully trained and supervised personnel.

WARNING. Liquefied anhydrous ammonia is a highly corrosive, toxic substance, which boils at – 33.3 °C at standard atmospheric pressure. Its action on the skin is strongly corrosive, producing severe and painful burns. Contact with the eyes can cause permanent blindness. Its vapour is strongly irritant to the mucous membrane and eyes, and produces a suffocating effect on the respiratory tract. Obtain advice for the safe storage and handling of liquefied anhydrous ammonia from manufacturers and suppliers. Prohibit smoking and sources of ignition during the sampling of ammonia.

NOTE Mixtures of ammonia gas and air can explode, if ignited, when the proportion of ammonia gas is within the limits of 16 % to 27 % by volume.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 12, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This British Standard describes methods of test and sampling for liquefied anhydrous ammonia suitable for general industrial purposes.

NOTE 1 In the methods described the ammonia is sampled by volume but the calculations are by mass. The density has been taken as 0.68 g/mL, at about – 33 °C, at which temperature liquid ammonia has a vapour pressure of 10^5 Pa[1]. A corrective evaporation factor is applied in each case to allow for loss through sampling at atmospheric pressure.

Clause **2** describes a general method for collecting the test portion with minor variations given for particular methods.

Clause **3** describes a method for the determination of residue on evaporation, which applies to products giving a residue value greater than or equal to 100 mg/kg.

Clause **4** describes a gravimetric method for the determination of the oil content (non-volatile at about 105 °C), which applies to products having an oil content greater than or equal to 10 mg/kg.

Clause **5** describes a method for the determination of the oil content (non-volatile at about 105 °C) in which the method used for the isolation of the oil content is as described in clause **4**, but the determination is made using infra-red spectrometry. This is more sensitive than the gravimetric method and applies to products with an oil content less than 10 mg/kg.

Clause **6** describes a method for the determination of the water content by the Karl Fischer method, which applies to products with a water content greater than or equal to 25 mg/kg.

Clause **7** describes the determination of carbon dioxide by a titrimetric method, which applies to products with a carbon dioxide content greater than or equal to 15 mg/kg.

Clause **9** describes a method of sampling for the subsequent determination of oxygen by gas chromatography.

In Appendix A guidance is given on the sampling of anhydrous ammonia and in Appendix B a method for the determination of the evaporation factor, *F*, is described.

NOTE 2 The titles of the publications referred to in this standard are listed on the inside back cover.

2 Method for collecting the test portion

2.1 Principle

A known volume of anhydrous ammonia is collected in a graduated, chilled (– 35 °C to – 40 °C) glass tube fitted with a modified Drechsel head and is allowed to begin to evaporate at ambient temperature and pressure.

2.2 Reagents

2.2.1 *General*. During the collection of the test portion, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

2.2.2 *Ethanediol (ethylene glycol)*, of water content not greater than 0.1 % (*m*/*m*).

NOTE Care should be taken to avoid absorption of atmospheric moisture as ethanediol is very hygroscopic.

2.2.3 *Barium hydroxide, standard volumetric solution*, $c(\mathrm{Ba(OH)_2}) = 0.05$ mol/L. Weigh, to the nearest 0.0005 g, 15.774 g of barium hydroxide octahydrate ($\mathrm{Ba(OH)_2.8H_2O}$), dissolve in a little water, transfer quantitatively the solution to the one-mark volumetric flask (**2.3.2**), dilute to the mark and mix.

2.2.4 *Freezing mixture*, consisting of solid carbon dioxide and methanol (technical grade is suitable), capable of reaching a temperature of between – 35 °C and – 40 °C.

2.3 Apparatus

2.3.1 *General*. Use ordinary laboratory apparatus and the following.

2.3.2 *One-mark volumetric flask*, 1 000 mL, complying with BS 1792.

2.3.3 *Apparatus for collecting the test portion* (see Figure 1).

2.3.3.1 *Glass test tube of total capacity* 250 mL, having a reference mark at 200 mL, fitted via a 24/29 ground glass modified Drechsel head to an arm with a three-way stopcock, with a key made from polytetrafluoroethylene (PTFE), and a side arm (3).

2.3.3.2 *Dewar vessel*, capable of containing the test tube (**2.3.3.1**) and the freezing mixture (**2.2.4**) while leaving the graduation mark visible.

2.4 Procedure

2.4.1 *General*. Carry out the procedure in accordance with **2.4.2**, if appropriate, and **2.4.3**. Do not attempt to subdivide the test portion.

2.4.2 *Additional details for test portions to be used in the methods described in clauses **3**, **6** and **7**.*

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[1] 10^5 Pa = 10^5 N/m^2 = 1 bar.

2.4.2.1 *Clause 3*. Initially weigh the test tube assembly (**2.3.3.1**) to the nearest 0.0001 g.

2.4.2.2 *Clause 6*. Introduce 2 mL of the ethanediol (**2.2.2**) into the test tube immediately before assembling the apparatus (**2.3.3**).

2.4.2.3 *Clause 7*. Add 10.0 mL of the standard barium hydroxide solution (**2.2.3**) to the test tube before assembling the apparatus (**2.3.3**).

NOTE When sampling direct from a cylinder or other pressurized vessel (see Appendix A), note the gauge pressure at that time in order to determine the evaporation factor, *F* (see Appendix B).

2.4.3 *Common details*. Three-quarters fill the Dewar vessel (**2.3.3.2**) with the freezing mixture (**2.2.4**), immerse the test tube (**2.3.3.1**) in the Dewar vessel (**2.3.3.2**) and insert the modified Drechsel head (see **2.3.3.1**). Connect the inlet arm (1) to the ammonia sample point and attach to the outlet arms (2) and (3) pieces of tubing of sufficient length to lead away the escaping ammonia safely.

Ensure that the liquid anhydrous ammonia flow is controlled by means of a by-pass so that the apparatus is not subjected to high pressures.

Quickly turn the stopcock to introduce the liquid anhydrous ammonia into the test tube. As soon as the liquid anhydrous ammonia has reached the 200 mL graduation mark, turn the stopcock to isolate the branch into the test tube and to open the outlet arm (2).

Close the liquid anhydrous ammonia sample point valve to allow the liquid ammonia in the inlet and outlet arms (1 and 2 respectively) to evaporate before disconnecting the apparatus.

Remove the test tube containing the test portion from the Dewar flask and place it in a bath of cold running water. Allow the ammonia to evaporate slowly through arm (3). Turn the stopcock to the open position to ensure that no liquid anhydrous ammonia is trapped within the valve.

NOTE Numbers in parentheses in medium type refer to Figure 1.

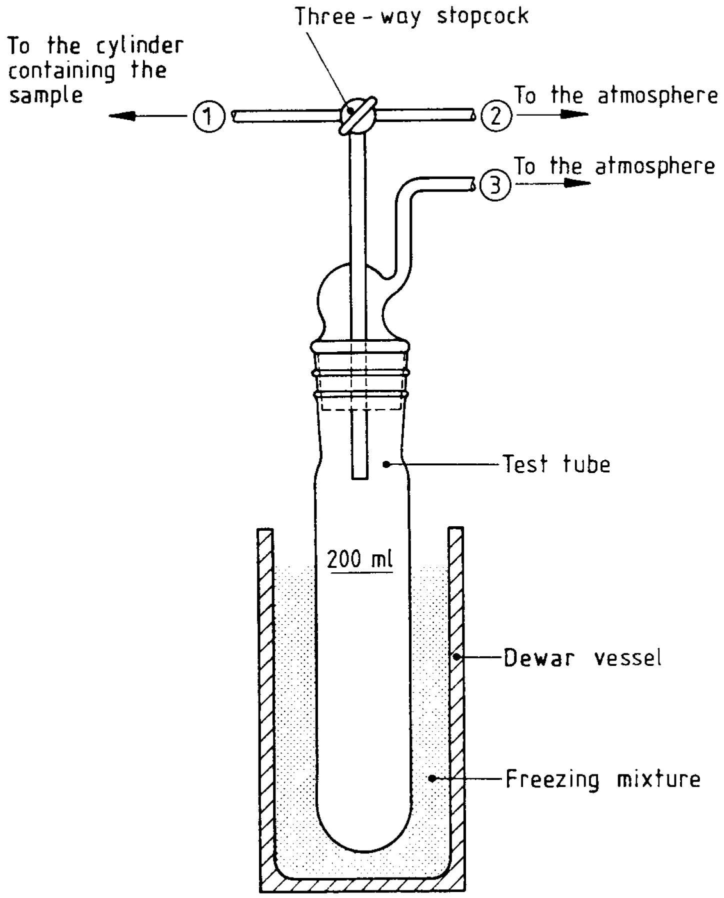

Figure 1 — Apparatus for collecting the test portion

3 Determination of residue on evaporation

3.1 Principle

A test portion is evaporated at ambient temperature, the residue is weighed and the residual ammonia is titrated with standard sulphuric acid solution and the residue is calculated by difference.

3.2 Reagents

3.2.1 *General*. During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

3.2.2 *Sulphuric acid, standard volumetric solution*, $c(H_2\ SO_4) = 0.050$ mol/L.

3.2.3 *Methyl red indicator solution*, 1 g/L in 95 % (*V*/*V*) ethanol.

NOTE The ethanol may be replaced by industrial methylated spirits 95 % (*V*/*V*) complying with BS 3591, or such spirits diluted as required. It should be noted that the use of industrial methylated spirits is governed by the Methylated Spirits Regulations, 1983 (SI 1983 No. 252). It is not permissible to use duty-free ethanol, received under the provisions of the Alcoholic Liquors Duties Act 1972, Section 10, for purposes for which industrial methylated spirits is an acceptable alternative.

3.3 Apparatus

Use ordinary laboratory apparatus.

3.4 Procedure

Collect the test portion in accordance with clause **2**. When the evaporation of ammonia is complete, apply gentle suction to the outlet to remove residual ammonia. Allow the test tube assembly to reach ambient temperature, wipe with a clean, dry cloth and weigh to the nearest 0.0001 g. Remove the modified Drechsel head (see **2.3.3.1**) and add about 50 mL of water to the test tube. Add one or two drops of the methyl red indicator solution (**3.2.3**) and titrate with the sulphuric acid solution (**3.2.2**) until the indicator changes from yellow to red.

3.5 Expression of results

The residue on evaporation, expressed as a percentage by mass, is given by the expression

$$\frac{(M_2 - M_1 - M_3) \times 100 \times F}{200 \times \rho}$$

where

M_1 is the mass of the test tube assembly (in g);

M_2 is the mass of the test tube assembly containing the residue after evaporation (in g),

M_3 is the mass of ammonia in the residue after evaporation (in g) and is given by the expression
$V_1 \times 0.0017$

where

V_1 is the number of millilitres of the sulphuric acid solution used for the titration (in mL);

0.0017 is the mass of ammonia (NH_3) equivalent to 1 mL of the standard volumetric sulphuric acid solution (in g);

F is the evaporation factor (see Appendix B);

200 is the volume of liquid ammonia collected in the test tube (in mL);

ρ is the density of liquid ammonia, i.e. 0.68 (in g/mL).

4 Determination of oil content by the gravimetric method

4.1 Principle

A test portion is evaporated at ambient temperature, the oil in the residue is extracted with 1,1,2-trichlorotrifluoroethane, the organic solvent is evaporated and the resulting residue is weighed.

4.2 Reagents

4.2.1 *General*. During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

4.2.2 *Solvent*, 1, 1, 2-trichlorotrifluoroethane.

4.2.3 *Hydrochloric acid solution*, c (HCl) = 40 g/L, (made up by diluting hydrochloric acid of density approximately 1.19 g/mL).

4.2.4 *Methyl red indicator solution*, as described in **3.2.3**.

4.2.5 *Silica gel*, complying with BS 3523.

4.3 Apparatus

4.3.1 *General*. Use ordinary laboratory apparatus and the following.

4.3.2 *Electric oven*, capable of being controlled at 105 ± 2 °C.

4.3.3 *Platinum dish*, capacity approximately 70 mL.

4.4 Procedure

4.4.1 *Test portion*. Collect the test portion in accordance with clause **2**.

4.4.2 *Isolation of the oil*. When the evaporation of ammonia is complete, apply gentle suction to the outlet tube to remove residual ammonia.

Heat the platinum dish (**4.3.3**) for 30 min in the electric oven (**4.3.2**) controlled at 105 ± 2 °C. Allow to cool to ambient temperature in a desiccator containing the activated silica gel (**4.2.5**) and weigh to the nearest 0.0001 g.

Add a little water and several drops of the hydrochloric acid solution (**4.2.3**) to the test tube until the mixture is slightly acidic, checking by means of the methyl red indicator solution (**4.2.4**).

Add 10 mL of the solvent (**4.2.2**) and transfer the mixture to a separating funnel. Wash the test tube again with three further 10 mL portions of the solvent (**4.2.2**) to remove all traces of oil. Collect all the washings in the separating funnel.

Shake the separating funnel vigorously, allow the organic phase to settle, separate it and filter it slowly through a dry filter paper and collect the filtrate in the tared platinum dish (**4.3.3**). Wash the filter with 10 mL of the solvent (**4.2.2**) adding the washing to the filtrate.

4.4.3 *Removal of solvent and weighing*. Evaporate the solvent (**4.2.2**) over a boiling water bath in a well ventilated fume cupboard. Heat the dish for 30 min in the electric oven (**4.3.2**) controlled at 105 ± 2 °C. Allow the dish to cool to ambient temperature in a desiccator containing the activated silica gel (**4.2.5**) and reweigh to the nearest 0.0001 g.

4.5 Expression of results

The oil content (non volatile at 105 °C), expressed in mg/kg, is given by the expression

$$\frac{(M_4 - M_5) \times F \times 10^6}{\rho \times V_2}$$

where

M_4 is the mass of dish and residue (in g);

M_5 is the mass of the dish alone (in g);

F is the evaporation factor (see Appendix B);

ρ is the density of liquid ammonia, i.e. 0.68 (in g/mL);

V_2 is the volume of sample taken (in mL).

5 Determination of oil content by the infra-red spectrometric method

5.1 Principle

The oil content is isolated and then spectrometric measurement of the absorbance of the organic phase at a wavelength of 3.42 μm (which is the most intense absorption band corresponding to the asymmetric vibration of the CH radicals) is carried out.

5.2 Reagents

5.2.1 *General*. During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

5.2.2 *Solvent*, 1,1,2-trichlorotrifluoroethane, spectrometric grade.

5.2.3 *Standard oil stock solution*, 0.50 g/L of the solvent (**5.2.2**). Weigh 0.0500 g of *n*-hexadecane, place it in a 100 mL beaker and dissolve it in approximately 50 mL of the solvent (**5.2.2**). Transfer the solution quantitatively to the 100 mL one-mark volumetric flask (**5.3.3**), dilute to the mark with the solvent (**5.2.2**) and mix. 1 mL of this solution contains 0.50 mg of oil.

5.2.4 *Hydrochloric acid solution* as described in **4.2.3**.

5.2.5 *Methyl red indicator solution* as described in **3.2.3**.

5.2.6 *Silica gel* complying with BS 3523.

5.3 Apparatus

5.3.1 *General*. Use the apparatus described in **4.3** and that described in **5.3.2** to **5.3.4**.

5.3.2 *Spectrometer*, capable of measuring in the infra-red range and equipped with silica cells that are of 10 mm optical path length which are capable of being closed.

5.3.3 *One-mark volumetric flask, 100 mL*, complying with BS 1792.

5.3.4 *Seven one-mark volumetric flasks*, 50 mL, complying with BS 1792.

5.4 Procedure

5.4.1 *Test portion*. Collect the test portion in accordance with clause **2**.

5.4.2 *Isolation of the oil*. Isolate the oil in accordance with **4.4.2**.

5.4.3 *Determination*

5.4.3.1 *Preparation of the test solution*. Follow the procedure described in **4.4.3**, but do not carry out the final weighing. Remove the dish (**4.3.3**) from the desiccator and add to the dish 10 mL of the solvent (**5.2.2**) to dissolve the oil. Transfer the solution to a one-mark volumetric flask (**5.3.4**). Wash the dish with three further 10 mL portions of the solvent (**5.2.2**). Collect all the washings in the same volumetric flask. Dilute to the mark with the solvent (**5.2.2**) and mix.

NOTE Heating the residue at 105 °C removes light hydrocarbons and thus the same conditions are obtained for both the gravimetric and infra-red methods.

5.4.3.2 *Preparation of the standard solutions*. Place in the 50 mL one-mark volumetric flasks (**5.3.4**) the portions of the oil standard stock solution (**5.2.3**) given in Table 1. Dilute the contents of each flask to the mark with the solvent (**5.2.2**) and mix.

5.4.3.3 *Absorbance measurements*. Using the spectrometer (**5.3.2**), measure the absorbance at 3.42 µm of each of the standard solutions (see **5.4.3.2**) and of the test solution (see **5.4.3.1**), with the solvent (**5.2.2**) as the reference.

5.4.3.4 *Calibration graph*. Plot a graph of the masses of oil in the standard solutions in milligrams against the corresponding absorbance values.

5.5 Expression of results

Using the calibration graph, determine the mass of oil corresponding to the absorbance value for each test solution.

The oil content (non volatile at 105 °C), expressed in mg/kg, is given by the expression

$$\frac{M_6 \times 1000 \times F}{\rho \times V_3}$$

where

M_6 is the mass of oil in the total volume of the test solution (in mg);

F is the evaporation factor (see Appendix B);

ρ is the density of liquid ammonia, i.e. 0.68 (in g/mL);

V_3 is the volume of the sample taken (in mL).

Table 1 — Standard oil solutions for calibration graph

Standard oil solution	Corresponding mass of oil
mL	mg
0.50	0.25
1.00	0.50
2.00	1.00
3.00	1.50
4.00	2.00
5.00	2.50

6 Determination of water content by the Karl Fischer method

6.1 Principle

A test portion is evaporated at ambient temperature in the presence of ethanediol, any residual ammonia is neutralized with acetic acid and the water content is determined by the Karl Fischer direct electrometric method described in BS 2511:1970.

6.2 Reagents

6.2.1 *General*. During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978.

Use the reagents described in **2.3** of BS 2511:1970 and the reagent described in **6.2.2**.

6.2.2 *Methanol-acetic acid mixture*. Mix 100 mL of glacial acetic acid, density approximately 1.05 g/mL, with 900 mL of methanol having a water content not greater than 0.03 % (*m*/*m*).

NOTE Take precautions to exclude all atmospheric moisture during the preparation, storage and use of this mixture.

6.3 Apparatus

Use ordinary laboratory apparatus and the apparatus described in **3.2** of BS 2511:1970.

6.4 Procedure

6.4.1 *Test portion*. Collect the test portion in accordance with clause **2**.

6.4.2 *Determination*. When the evaporation of ammonia is complete, remove the modified Drechsel head (see **2.3.3.1**) from the test tube and add 10.0 mL of the methanol-acetic acid mixture (**6.2.2**), ensuring that it runs slowly down the walls of the test tube.

Stir carefully and transfer the solution quantitatively into the reaction vessel described in **3.2** of BS 2511:1970. Rinse the test tube using 10.0 mL portions of the methanolacetic acid mixture (**6.2.2**), using a maximum of 50.0 mL and collecting the washings quantitatively in the reaction vessel.

Proceed in accordance with **3.4.3** of BS 2511:1970.

6.4.3 *Blank test*. Carry out a blank test at the same time as the determination, using the same procedure and the same quantities of all the reagents (except the Karl Fischer reagent) as used in **6.4.2**, but omitting the test portion.

6.5 Expression of results

The water content, expressed in mg/kg, is given by the expression

$$\frac{f \times (V_4 - V_5) \times 1000}{M_7}$$

where

f is the water equivalent of the Karl Fischer reagent calculated in accordance with **3.4.2** of BS 2511:1970 (in mg/mL);

NOTE This symbol should not be confused with the symbol used for the evaporation factor. In BS 2511 the symbol "*F*" is used for the water equivalent of the Karl Fischer reagent.

V_4 is the volume of the Karl Fischer reagent used for the titration (in mL);

V_5 is the volume of the Karl Fischer reagent used for the blank test (in mL);

M_7 is the mass of the test portion (in g) and is given by the expression

$$\frac{V_6 \times \rho}{F}$$

where

V_6 is the volume of the liquid ammonia collected in the test tube, i.e. 198 (200 mL less 2.0 mL of ethanediol) (in mL);

ρ is the density of liquid ammonia, i.e. 0.68 (in g/mL);

F is the evaporation factor (see Appendix B).

7 Determination of carbon dioxide content

7.1 Principle

A test portion is evaporated at ambient temperature in the presence of an excess volume of a standard barium hydroxide solution and the excess barium hydroxide is then back-titrated with standard hydrochloric acid solution using thymolphthalein indicator solution.

7.2 Reagents

7.2.1 *General*. During the analysis, use only reagents of recognized analytical grade and water complying with grade 3 of BS 3978, freshly boiled to be free from carbon dioxide.

7.2.2 *Hydrochloric acid, standard volumetric solution*, *c* (HCl) = 0.100 mol/L.

7.2.3 *Thymolphthalein indicator solution*, 5 g/L in 95 % (*V*/*V*) ethanol.

7.2.4 *Barium hydroxide, standard volumetric solution* as described in **2.2.3**.

7.3 Apparatus

Use ordinary laboratory apparatus.

7.4 Procedure

7.4.1 *Test portion*. Collect the test portion in accordance with clause **2**.

7.4.2 *Determination*. When the evaporation of ammonia is complete, add 10 mL of carbon dioxide free water to the test tube and gently heat using a boiling water bath to eliminate the last traces of ammonia (check using pH indicator paper).

Close the test tube with a rubber stopper fitted with a soda-lime tube and allow to cool.

Add three drops of the thymolphthalein indicator solution (**7.2.3**) and back-titrate the excess of the standard volumetric barium hydroxide solution (**7.2.4**) with the standard volumetric hydrochloric acid solution (**7.2.2**) until the blue colour of the solution disappears.

7.4.3 *Blank test*. Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents [except the standard volumetric hydrochloric acid solution (**7.2.2**)] as used in **7.4.2**, but omitting the test portion.

7.5 Expression of results

The carbon dioxide content, expressed as CO_2 (in mg/kg), is given by the expression

$$\frac{(V_7 - V_8) \times D \times 1000 \times F}{G}$$

where

V_7 is the volume of the hydrochloric acid solution (**7.2.2**) used for the blank test (**7.4.3**) (in mL);

V_8 is the volume of the hydrochloric acid solution (**7.2.2**) used for the determination (**7.4.2**) (in mL);

D is the mass of carbon dioxide corresponding to 1.00 mL of the volumetric hydrochloric acid solution (**7.2.2**), i.e. 2.2 (in mg);

F is the evaporation factor (see Appendix B);

G is the mass of the test portion, i.e. 129.2 (in g).

NOTE This is the volume of liquid anhydrous ammonia collected in the test tube [i.e. 200 mL minus the volume of standard volumetric barium hydroxide solution added to the test tube (10.0 mL)] multiplied by 0.68 [which is the density of the liquid anhydrous ammonia (in g/mL)].

8 Test report

The test report shall include the following information:

a) a reference to this British Standard, i.e. BS 4431:1989;

b) a reference to the method used, e.g. clause **3**;

c) a complete identification of the sample;

d) details of any unusual features noted during the determination;

e) the results and the method of expression used;

f) any operation not included in this British Standard or in a British Standard to which reference is made, or regarded as optional.

9 Method of sampling for the subsequent determination of oxygen by gas chromatography

9.1 Principle

The anhydrous ammonia is sampled according to Hunt[2] by the evaporation of a small amount into a larger vessel.

9.2 Apparatus

Sampling apparatus, made from stainless steel, complying with grade 316 of BS 3605 throughout and using needle or ball valves, as illustrated in Figure 2. Connect a 500 mL cylinder fitted with two needle valves (2 and 3) to a 3 mL tube that has one valve fitted (1).

9.3 Procedure

Connect the sampling apparatus (**9.2**) vertically to the sample point from below (see **A.2**). Connect a vent line to the lowest valve (3) and fix this to vent safely down wind.

Successively open the valves 1 and 2 on the apparatus and then slowly open the valve A and allow the apparatus to fill with liquid. Close valve 1 and open valve 3 to vent the apparatus to atmosphere. When venting is seen to have finished, close valves 2 and 3 and reopen valve 1, to allow the upper part of the apparatus to fill with liquid. Close valve 1 and open valve 2 to allow the liquid to vaporize into the large cylinder. Close valve 2 and open valve 3 to allow the contents to vent to atmosphere and when this is complete, close valve 3.

Repeat the filling and emptying of the sampling apparatus five times to ensure complete purging of the apparatus. On the final occasion leave valve 3 unopened so that the sample is contained in the apparatus. Close valves A and 1, to leave valve 2 open to ensure complete evaporation into the large cylinder.

Close all the valves on the sample line and carefully remove the sampling apparatus from the sample point.

NOTE This method provides a laboratory sample that should be at enough pressure to allow direct connection to the sample loop of the chromatography apparatus. This laboratory sample should be capable of providing several test portions for replicate analysis.

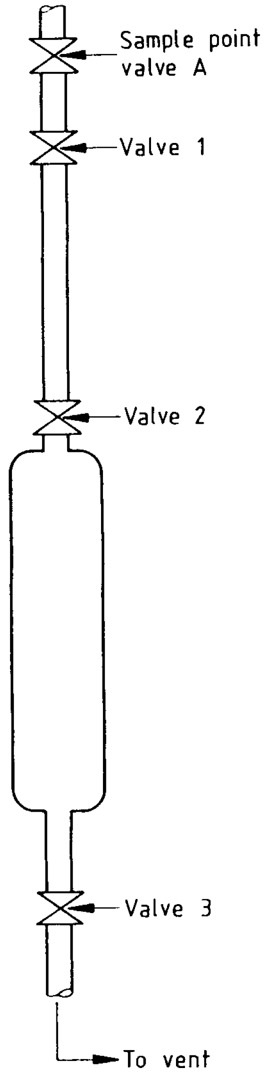

Figure 2 — Diagram of sampling apparatus for the subsequent determination of oxygen by gas chromatography

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[2] Hunt, A.D. Vessel for sampling liquefied anhydrous ammonia for subsequent trace oxygen determination. *Analyst*, 1977, **102**, 846–851.

Appendix A Guidance on the sampling of liquefied anhydrous ammonia

NOTE Attention is drawn to the warning about the handling of this product given in the foreword.

A.1 General

Anhydrous ammonia is stored and transported as a liquefied gas, either without cooling, under a gauge pressure that at 20 °C is approximately 7.6×10^5 Pa[3], or with refrigeration, at lower temperatures and pressures.

When sampling from a storage or process point it is essential that all the valves and couplings are checked for satisfactory operation and that there are adequate access and egress facilities. Furthermore, the system should be capable of being purged adequately and safely and there should be no operations nearby that could be deleteriously affected by the sampling.

Appropriate protective clothing, PVC gloves, goggles and self-contained breathing equipment should be worn. Other safety equipment (including an eye-wash bottle) should be provided.

The supplier of the ammonia should be consulted regarding the need for other safety equipment.

After sampling, care should be taken to avoid trapping significant quantities of liquefied anhydrous ammonia between closed valves, as subsequent exposure to direct heat could cause unacceptably high increases in pressure in the pipework.

A.2 Sampling from cylinders

It is essential that the contents of a cylinder or other small transport container at or near ambient temperature is sampled in an adequately ventilated fume cupboard or in the open air, by means of a short, solid-drawn steel tube attached by a steel union nut to the cylinder outlet valve. Low carbon steel complying with CFS, Category 2 of BS 3602-1 is recommended for all sampling components.

In the event of corrosion and wear it may be necessary to use a suitable washer to ensure a good seal between the cylinder and the sampling apparatus; steel compression fittings should be used for small pipes (up to 12.5 mm nominal bore) and compressed fibre washers for larger pipes.

The cylinder should be securely supported in the position for liquid anhydrous ammonia discharge, the open end of the steel tube pointing downwards.

Since the technique used will be dependent upon the design of the tank, it should be agreed between the owner of the tank and the supplier of the ammonia. The gauge pressure of the barrel/tank should be noted at the time of sampling in order to determine the evaporation factor (see Appendix B).

A.3 Sampling from tanks into cylinders

It will be necessary to sample into a cylinder only if the sample has to be sent to a distant testing station or if it is necessary to store the sample for some time.

However, a special sampling cylinder should be used to obtain a sample of anhydrous ammonia for the determination of its oxygen content (see clause **9**).

Unless carried out very carefully, this procedure may increase the possibility of contamination of the sample and it may involve danger to personnel.

If it is necessary to use cylinders to take ammonia samples, an appropriate, permanent cylinder-filling installation should be used as a temporary arrangement is likely to be unsafe.

NOTE 1 The design and operation of such installations demand special care and detailed consideration, specific recommendations for which are not made by this British Standard.

For sampling liquid anhydrous ammonia stored at or near ambient temperature, steel cylinders complying with BS 5045-1 may be used, but equivalent cylinders specially made for the purpose from austenitic stainless steel complying with grade 316 of BS 3605 are to be preferred because of their freedom from rust.

NOTE 2 Ammonia at sub-zero temperatures should never be sampled into an ordinary steel cylinder since the steel may be fragile under such conditions. Any cylinder used (and its valves) should be constructed from a special steel suitable for use at low temperatures.

Special cylinders should be kept for sampling ammonia and, before they are used, they should be cleaned thoroughly and dried. This will involve removal of the whole valve and the repeated washing with oil-free (redistilled) 1,1,2-trichlorotrifluoroethane, both of the interior of the cylinder and of the valve components. After cleaning, any residual moisture or solvent should be removed by blowing hot filtered air into the cylinder.

To avoid contamination of the sample, the valve should be reassembled without greasing and any jointing material used in connecting it to the cylinder should be unaffected by ammonia (PTFE is suitable).

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[3] $10^5 = 10^5 = 1$ bar.

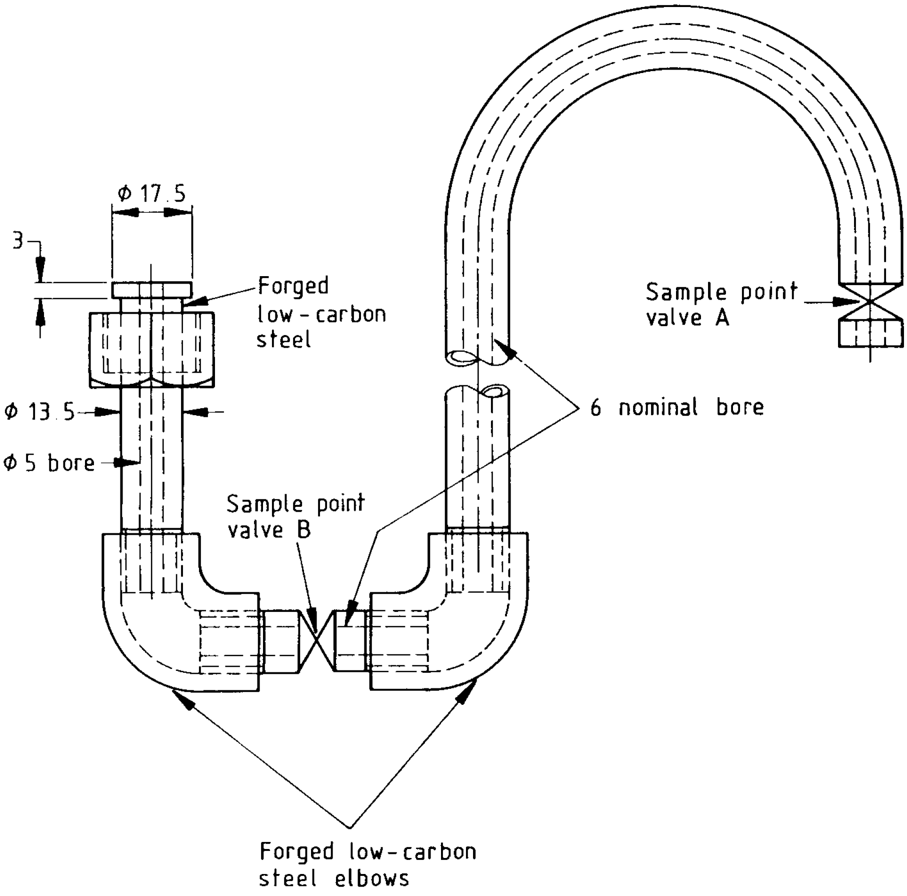
Wearing goggles or self-contained breathing apparatus, PVC gloves and standing up-wind of the cylinder, the operator should then open the cylinder sample valve for a few seconds to remove any foreign matter and to ensure its free working. Any purge liquor should be collected in a container and disposed of in a suitable open site.

The end of the steel tube should be wiped dry, the sample collection apparatus (Figure 1) positioned firmly under the tube and connected to it and the required volume of sample collected in the test tube.

During sampling, the cooling produced by the evaporation of the liquid anhydrous ammonia may cause condensation of atmospheric moisture and frost on the steel sampling tube; care should be taken to prevent subsequent contamination of the sample.

NOTE 3 Frost or ice on the outside of the stoppered test tube is not significant, although it can cause the test tube to stick to certain surfaces (gloves etc.) so additional care should be taken during subsequent handling.

The gauge pressure of the cylinder should be noted at the time of sampling in order to determine the evaporation factor (see Appendix B).



All dimensions are in millimetres.

Figure 3 — Illustration of equipment for sampling from tank wagons and storage tanks

A.4 Sampling from tanker barrels and storage tanks

It is recommended, for maximum safety, to avoid taking samples directly from a road or rail wagon barrel, but to take them instead from a sampling point specifically designed for the purpose in the fixed pipeline through which the ammonia is discharged from the mobile barrel to the storage tank. The sampling should then follow the same procedure as for sampling from cylinders (see **A.3**).

The sampling of the contents of a fixed storage tank should be carried out in a similar way during discharge of the tank. A suitable apparatus for sampling from tank wagons and storage tanks is shown in Figure 3.

In the event of corrosion and wear it may be necessary to use a suitable washer to ensure a good seal between the tank valve and the sampling apparatus; steel compression fittings should be used for small pipes (up to 12.5 mm nominal bore) and compressed fibre washers for larger pipes.

Although it is recommended that mobile transport tanks are not sampled directly, there may be occasions when it is unavoidable. In this case, it is essential that a clear, readily understood sampling procedure is available and that the operatives are properly briefed.

Liquid anhydrous ammonia has a high coefficient of thermal expansion and, to avoid any risks from overfilling, it is most important to comply with the filling ratio requirements specified in BS 5355, which are summarized as follows.

a) The maximum filling ratio (i.e. the ratio of the mass of liquefiable gas passed into a container to the mass of water required to fill the container at 15 °C) shall not exceed the following values:

1) 0.54 in a temperate climate (i.e. a climate in which the temperature of the contents of a container may exceed 45 °C but is not likely to exceed 45 °C);

2) 0.51 in a tropical climate (i.e. a climate in which the temperature of the contents of a container may exceed 45 °C but is not likely to exceed 65 °C).

Therefore it is important that the water capacity of any cylinder used for sampling is accurately known and that the quantity of liquid anhydrous ammonia put into it is strictly controlled by weighing. If, by accident, a sampling cylinder is overfilled, the excess ammonia in it should be discharged without delay. The liquid ammonia should be purged into an empty line that either leads to a recovery system or is vented safely to atmosphere.

b) If a sample is transferred from a container to a cylinder, there should be no loss by evaporation and therefore it is not necessary to use an evaporation factor (see Appendix B).

Appendix B Determination of the evaporation factor, *F*

B.1 General

If a sample of liquid anhydrous ammonia is transferred to an open flask from a container in which the pressure is higher than atmospheric, that sample quickly reaches thermodynamic equilibrium with its new environment.

Some of the liquid ammonia will evaporate and, since the ammonia so lost as vapour contains none of the non-volatile constituents present in the original product, the concentration of those constituents will increase in the liquid sample taken.

This may be significant in subsequent analysis, but it is possible to calculate an appropriate correction from the known thermodynamic properties of ammonia.

This correction is usually known as the "evaporation factor" (or "flash factor") and is that fraction by mass of the original liquid anhydrous ammonia that remains as liquid in the sample.

B.2 Determination

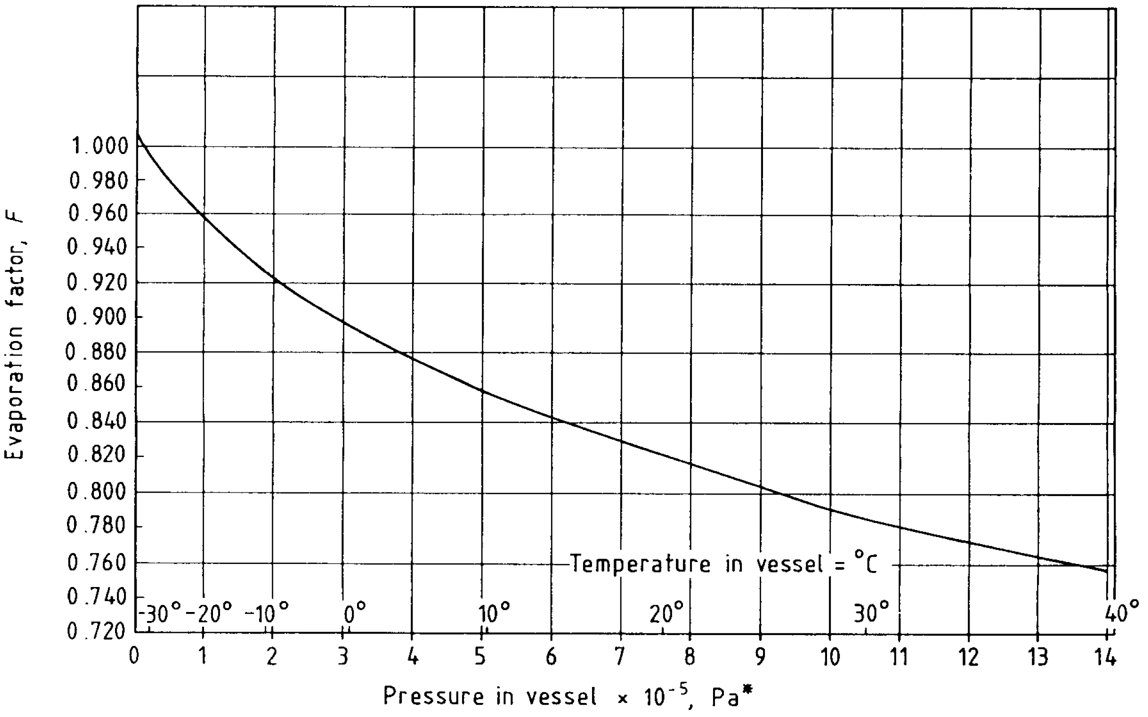
Determine the value of F that corresponds to the gauge pressure recorded from the pressure vessel from the graph in Figure 4.

B.3 Treatment of results

Multiply the determined quantity of the non-volatile constituent (oil, water, dissolved or suspended solids etc.) by the value of F.

Example. A sample was taken from a cylinder at a gauge pressure of 8.3×10^5 Pa and collected in an open flask at atmospheric pressure. In the actual determination of the oil content of this sample, a direct figure of 40 mg/kg was obtained; reference to Figure 4 gave an evaporation factor of 0.812, thus giving a true oil content of the material of $40 \times 0.812 = 32$ mg/kg.

NOTE If a sample is transferred (e.g. by gravity) from a container to a cylinder at the same pressure, there should be no loss by evaporation and it is therefore not necessary to use an evaporation factor.



*10^5 Pa = 10^5 N/m^2 = 1 bar.

Figure 4 — Graph of evaporation factor against pressure in vessel

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Publications referred to

BS 1792, *Specification for one-mark volumetric flasks.*

BS 2511, *Methods for the determination of water (Karl Fischer method).*

BS 3523, *Specification for silica gel, cobalt chloride impregnated.*

BS 3591, *Specification for industrial methylated spirits.*

BS 3602, *Specification for steel pipes and tubes for pressure purposes: carbon and carbon manganese steel with specified elevated temperature properties.*

BS 3602-1, *Seamless, electric resistance welded and induction welded tubes.*

BS 3605, *Specification for seamless and welded austenitic stainless steel pipes and tubes for pressure purposes.*

BS 3978, *Specification for water for laboratory use.*

BS 5045, *Transportable gas containers.*

BS 5045-1, *Specification for seamless steel gas containers above 0.5 litre water capacity.*

BS 5355, *Specification for filling ratios and developed pressures for liquefiable and permanent gases.*

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