H-25-11

International Standard 7104

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Liquefied anhydrous ammonia for industrial use — Determination of water content — Gas chromatographic method

Ammoniac anhydre liquéfié à usage industriel — Dosage de l'eau — Méthode par chromatographie en phase gazeuse

First edition — 1985-08-15

UDC 661.51 : 543.544 : 543.712 **Ref. No. ISO 7104-1985 (E)**

Descriptors : industrial products, inorganic compounds, nitrogen inorganic compounds, liquid ammonia, chemical analysis, determination of content, water, gas chromatography.

Price based on 4 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7104 was prepared by Technical Committee ISO/TC 47, *Chemistry*.

Printed in Switzerland

INTERNATIONAL STANDARD ISO 7104-1985 (E)

Liquefied anhydrous ammonia for industrial use — Determination of water content — Gas chromatographic method

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 produces a suffocating effect on the respiratory tract.

In concentrations of 16 to 25 % (*V*/*V*), gaseous anhydrous ammonia forms explosive mixtures with air.

Personnel responsible for handling the product shall be fully informed as to its dangerous character and the precautions to be taken.

Operators shall wear thick rubber gloves, a rubber apron and full face and head protection, and shall be provided with a protective gas-mask fitted with a filter for ammonia.

All operations shall be carried out only inside a well-ventilated fume-cupboard.

For further information, see the appropriate sections of ISO 3165.

1 Scope and field of application

This International Standard specifies a gas chromatographic method for the determination of the water content of liquefied anhydrous ammonia for industrial use.

The method is applicable to products having water contents between 5 mg/kg and 3 000 mg/kg.

2 References

ISO 565, *Test sieves — Woven metal wire cloth, perforated plate and electroformed sheet — Nominal sizes of openings.*

ISO 683/13, *Heat-treated steels, alloy steels and free-cutting steels — Part 13: Wrought stainless steels.*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling.*

ISO 7103, *Liquefied anhydrous ammonia for industrial use — Sampling — Taking a laboratory sample.*

3 Principle

Transformation of the water present into acetylene by reaction with calcium carbide. Determination of the acetylene formed by gas chromatography using an external standard.

4 Reagents

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

4.1 Calcium carbide granular, particle size 200 µm to 1 mm diameter.

WARNING — Calcium carbide gives a violent reaction with water, liberating acetylene. The acetylene released is likely to explode on heating and in contact with the atmosphere, and is highly flammable. Calcium carbide should be stored in the absence of moisture, and should always be handled in a well-ventilated fume cupboard.

Crush the calcium carbide in a porcelain mortar to a particle size of 200 µm to 1 mm. During the operation, maintain a dry atmosphere above the mortar by slowly passing a continuous stream of dry nitrogen. Sieve the product obtained and collect the amount remaining between the two sieves of 200 µm and 1 mm aperture (see ISO 565). Store the calcium carbide obtained in this way in a tightly sealed container and, before use, clean with dry nitrogen so that any acetylene which may be present is removed, checking by means of a chromatographic test.

4.2 Carrier gas and **auxiliary gases,** pure, for gas chromatography.

4.2.1 Carrier gas

4.2.1.1 Nitrogen.

4.2.2 Auxiliary gases

4.2.2.1 Hydrogen.

4.2.2.2 Air.

4.3 Products for preparation of the standards

4.3.1 Acetylene, standard gas mixture with an inert gas, containing a known amount of acetylene (see 7.3.2).

5 Apparatus

5.1 Reaction tube, to hold the calcium carbide (4.1), consisting of an austenitic stainless steel (ISO 683/13, type 11) container closed at the ends, with two valves (see the figure) resistant to a test pressure of 2 MPa.

5.2 Inflatable balloon, made of polyethylene, capacity 30 to 50 l.

5.3 Chromatographic system

5.3.1 Characteristics of assembly

The chromatograph shall have a suitable oven, capable of being controlled to within ±0,1 °C in the range 45 to 55 °C (see 7.2.2).

5.3.2 Control valves for adjusting the flow of carrier gas and auxiliary gases

The flow of the carrier gas through the column shall be adjusted accurately by means of a needle control valve.

The flow of the auxiliary gas used across the detector is adjusted by means of a normal diaphragm valve.

5.4 Injection device

The valve for sampling the gases is made of austenitic stainless steel (ISO 683/13, type 11) and polytetrafluoroethylene (PTFE) and is fitted with interchangeable sampling loops of 1 ml, 3 ml and 5 ml capacity. The capacity of the loop to be used will depend on the water content of the ammonia. For very low water contents (about 10 mg/kg) use a 5 ml loop.

5.5 Chromatographic column

5.5.1 General

A single column is sufficient (assembled in accordance with the manufacturer's instructions).

5.5.2 Construction

The column shall be constructed of austenitic stainless steel (ISO 683/13, type 11) tubing having the following characteristics:

- length 2 m;
- internal diameter 2,2 mm;
- external diameter 3,2 mm;
- in the form of a helix.

5.5.3 Packing

5.5.3.1 Support

Silica gel, particle size 150 to 180 µm.

5.5.3.2 Stationary phase

Dissolve 2 g of di(2-ethylhexyl) sebacate in about 10 ml of diethyl ether and add 100 g of the silica gel (5.5.3.1) to form a slurry. Stir carefully in a well-ventilated fume cupboard until the diethyl ether is completely evaporated. Remove the final traces of diethyl ether by heating for several hours in an oven controlled at about 60 °C.

NOTE — About 10 ml of diethyl ether may be sufficient. This solvent is further eliminated by evaporation and therefore its quantity may be increased if necessary.

5.5.3.3 Method of filling

With the aid of a mechanical shaker.

5.5.4 Efficiency and resolution

A column with the characteristics described should give well-defined and separate peaks for acetylene and for impurities (such as methane) which might be present in the anhydrous ammonia, when used under the conditions specified in 7.2.

5.6 Detector

Flame ionization type.

5.7 Recorder and integrator

Electronic type, automatically balanced, with a full scale response at 2,5 mV and a response time of 1 s. The peak areas may also be measured with a planimeter.

6 Sampling

Take the laboratory sample from the liquid phase in a sampling cylinder in accordance with the procedure described in ISO 7103.

7 Procedure

7.1 Preparation of reaction tube

Fill the reaction tube (5.1) completely with the calcium carbide (4.1) and purge with a stream of the nitrogen (4.2.1.1) which has previously been dried by passing through two U-tubes filled with a mixture of phosphorus(V) oxide and pumice stone.

If care has been taken to minimize contact between the calcium carbide and the atmosphere when filling the reaction tube, 2 h purging is usually sufficient to prepare the tube for the determination.

Before taking a sample of ammonia for analysis, ensure that the nitrogen entering the tube is free from appreciable quantities of acetylene.

If the anhydrous ammonia contains appreciable quantities of water, change the calcium carbide frequently; for water contents between 0,2 % and 0,3 % (m/m), change the calcium carbide after three determinations.

CAUTION — Do not wash the reaction tube with water.

7.2 Setting up the apparatus

7.2.1 Injector

Regulate the temperature of the injector at approximately 50 °C.

7.2.2 Oven and column

The test shall be carried out under isothermal conditions, controlled to ±0,1 °C in the temperature range 45 to 55 °C.

7.2.3 Gas flow rates

7.2.3.1 Carrier gas : nitrogen (4.2.1.1) at 3 l/h.

7.2.3.2 Auxiliary gases : for feeding the burner; adjust the hydrogen (4.2.2.1) or air (4.2.2.2) flow rate to obtain the best response of the flame ionization detector (5.6) (to be previously established by experiment).

7.2.4 Detector

When the flow of the auxiliary gas used (4.2.2) has been adjusted, ignite the flame of the flame ionization detector (5.6) ensuring that the recorder (5.7) responds adequately.

7.2.5 Recorder

Adjust the chart speed to about 40 mm/min.

7.3 Calibration

7.3.1 External calibration

A suitable quantity of the sample to be analysed and an equal quantity of a synthetic mixture of known acetylene content are subjected in turn to chromatography. The dimensions of the peaks obtained are compared.

7.3.2 Standard mixture

Use a mixture containing known proportions of acetylene and an inert gas (4.3). Such mixtures are available commercially with a certificate of guarantee.

7.4 Introduction of the sample and reaction

Connect the prepared reaction tube (see 7.1) to the sampling cylinder containing the anhydrous ammonia (see clause 6).

Mount the cylinder so that only liquid ammonia may be withdrawn.

Open, in the order given, the sampling cylinder valve, the reaction tube entry valve and then the other reaction tube valve. Allow the liquefied ammonia to flow for about 2 min and close the valves in reverse order.

Allow to stand for 20 to 30 min. Connect the outlet valve of the reaction tube (7.1) to the polyethylene balloon (5.2) which has previously been purged with the nitrogen (4.2.1.1) and emptied by means of a vacuum pump set at a pressure of about 100 Pa. Open the outlet valve of the tube and allow the ammonia to flow slowly, in the gaseous state, into the balloon. Heat the reaction tube on a boiling water bath for 10 to 15 min.

Allow the balloon to stand for 15 to 30 min, agitating it periodically so as to homogenize the gas mixture.

7.5 Determination

Introduce the gas mixture for analysis contained in the balloon into the chromatograph (5.3) by means of the sampling valve of the injection device (5.4). Then connect the recorder (5.7) at the specified chart speed (see 7.2.5). Usually two peaks will be obtained, one corresponding to the methane dissolved in the ammonia and the other to the acetylene evolved by the water present in the ammonia.

Immediately afterwards, carry out the chromatographic analysis of the standard mixture (7.3.2).

8 Expression of results

Determine the areas of the peaks corresponding to the evolved acetylene obtained for the anhydrous ammonia (7.4) and for the standard mixture (7.3.2).

As 1 mol of acetylene is produced from 1 mol of water, the water content of the anhydrous ammonia, expressed as a percentage by mass, is given by the formula

$$\frac{A \times c}{A_0} \times 1{,}052$$

where

A is the area of peak obtained for the anhydrous ammonia;

A_0 is the area of peak obtained for the standard mixture;

c is the concentration of acetylene in the standard mixture, expressed as a percentage by volume;

1,052 is the factor converting "percentage by volume" to "percentage by mass".

Carry out a duplicate analysis and take the mean of the two results.

9 Test report

The test report shall include the following information:

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.

10 Bibliography

ISO 2718, *Standard layout for a method of chemical analysis by gas chromatography.*

GUERRANT, G.O. Gas chromatographic determination of traces of water in anhydrous ammonia. *Analytical Chemistry,* Vol. 39, No. 1, January 1967, pp. 143-144.

Dimensions in millimetres

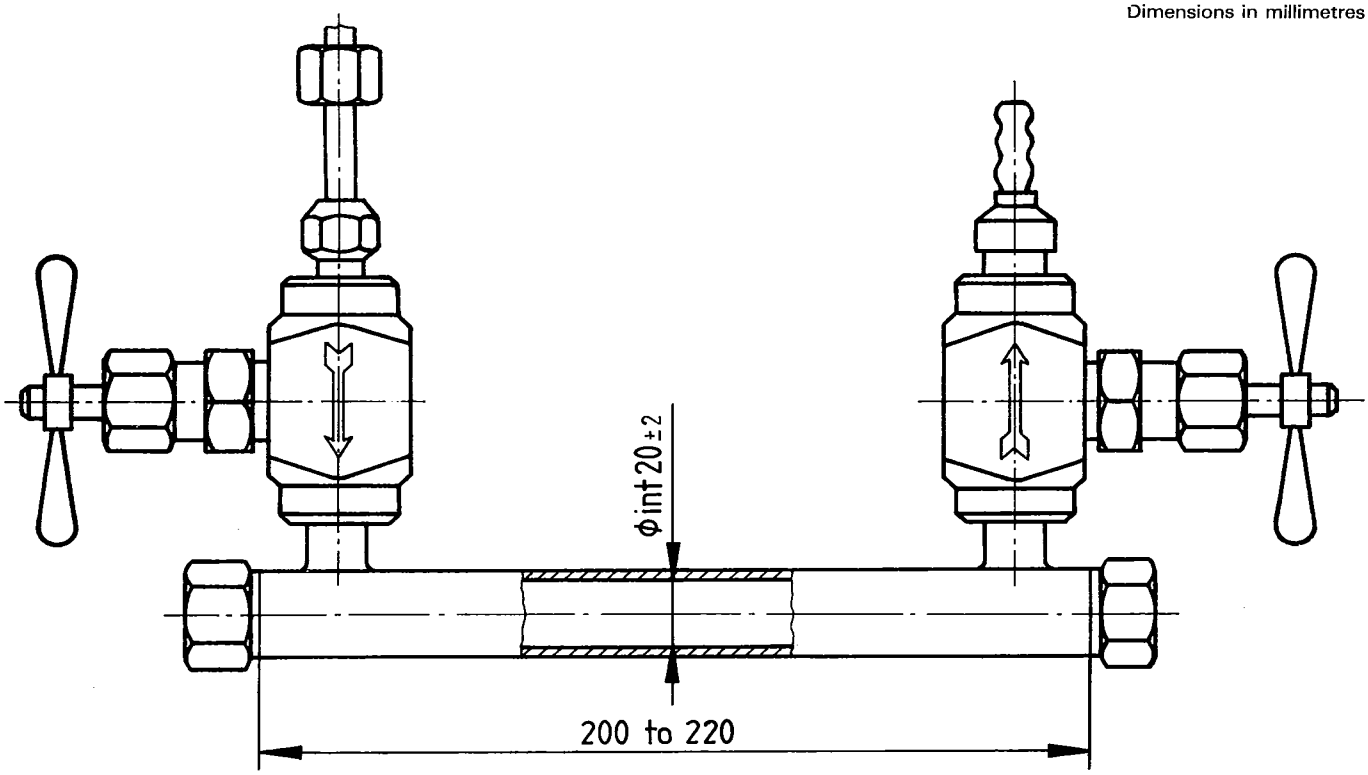

Figure — Reaction tube (5.1)