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International Standard ISO 7106

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Liquefied anhydrous ammonia for industrial use — Determination of oil content — Gravimetric and infra-red spectrometric methods

Ammoniac anhydre liquéfié à usage industriel — Dosage de l'huile — Méthode gravimétrique et méthode spectrométrique dans l'infrarouge

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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.

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Liquefied anhydrous ammonia for industrial use — Determination of oil content — Gravimetric and infra-red spectrometric methods

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.

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.

The operations described shall be carried out only in 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 two methods for the determination of the oil content non volatile at about 105 °C, of liquefied anhydrous ammonia for industrial use, namely:

- a gravimetric method;
- an infra-red spectrometric method.

The gravimetric method is applicable to products having an oil content equal to or greater than 10 mg/kg.

The infra-red spectrometric method, being more sensitive, is applicable to products having an oil content greater than 1 mg/kg.

2 References

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

Evaporation at ambient temperature of a test portion of liquefied anhydrous ammonia, extraction, using carbon tetrachloride, of the oil contained in the residue and determination of the oil content by method 3.1 or 3.2.

3.1 Gravimetric method

Evaporation of the organic solvent and weighing of the residue.

3.2 Infra-red spectrometric method

Spectrometric measurement of the absorbance of the organic phase at a wavelength of approximately 3,42 µm, that is, the most intense absorption band corresponding to the asymmetric vibration of the CH radicals.

4 Reagents and materials

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Carbon tetrachloride, giving no absorbance at a wavelength of approximately 3,42 µm.

WARNING — Carbon tetrachloride is toxic. Avoid breathing vapour. Avoid contact with skin and eyes.

4.2 Hydrochloric acid (ϱ approximately 1,19 g/ml), approximately 4 % (*m*/*m*) solution.

4.3 Sulfuric acid (ϱ approximately 1,84 g/ml), approximately 10 % (*m*/*m*) solution.

4.4 Freezing mixture, consisting of a mixture of solid carbon dioxide and technical grade methanol in such proportions as to be capable of reaching a temperature between − 35 and − 40 °C.

NOTE — As an alternative to methanol, technical grade acetone may be used.

4.5 Paraffin oil, standard solution in carbon tetrachloride, corresponding to 0,500 g of oil per litre.

Weigh, to the nearest 0,000 1 g, 0,050 g of paraffin oil of spectrometric grade (*n*-hexadecane is suitable), place in a beaker of suitable capacity (100 ml is suitable) and dissolve in approximately 50 ml of the carbon tetrachloride (4.1). Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, dilute to the mark with the same carbon tetrachloride and mix.

1 ml of this standard solution contains 0,50 mg of oil.

4.6 Methyl red, 1 g/l solution in 95 % (*V*/*V*) ethanol.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Apparatus for taking the test portion.

A typical example of this apparatus is shown in the figure and consists of the following items:

5.1.1 Glass test tube, of total capacity 250 ml, having a 200 ml reference mark, fitted with a 24/29 ground glass stopper to an arm with a three-way stopcock (3) and a side arm for connecting it in series to two conical flasks (A and B), each of 1 000 ml capacity.

In the assembled apparatus, the test tube is thus linked to two three-way stopcocks (3 and 4) permitting it to be connected either to the cylinder containing the liquefied anhydrous ammonia or to the two conical flasks (A and B).

The stopcocks are lubricated either with silicone grease or made of polytetrafluoroethylene (PTFE).

5.1.2 Dewar vessel, capable of containing the test tube (5.1.1), leaving the reference mark visible.

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

5.3 Platinum dish, capacity approximately 70 ml.

5.4 Spectrometer, for measuring in the infra-red range (IR), equipped with silica cells of 1 cm optical path length capable of being closed.

6 Sampling

Use the procedure specified in ISO 7103.

7 Procedure

WARNING — Carry out all operations in a well-ventilated fume cupboard.

7.1 Test portion

Weigh, to the nearest 0,1 g, the assembly comprising the two conical flasks (A and B), each containing approximately 500 ml of the sulfuric acid solution (4.3) and several drops of the methyl red solution (4.6), together with the connecting tubes shown in the figure, starting at point 5.

Immerse the stoppered test tube (5.1.1) in the Dewar vessel (5.1.2), three-quarters filled with the freezing mixture (4.4), and connect it to the conical flasks.

Adjust stopcock 3 so as to isolate the test tube and to connect arms 1 and 2 to the atmosphere.

Connect arm 1 to the cylinder containing the laboratory sample, using rubber tubing. Carefully open the valve of the cylinder and allow the ammonia to escape slowly into the atmosphere, until arms 1 and 2 are well cooled and the ammonia emerges in the form of droplets.

Immediately adjust stopcock 3 so as to isolate arm 2, at the same time connecting arm 1 with the test tube and leaving arm 6 open by means of stopcock 4.

Quickly adjust stopcock 4 so as to connect the two conical flasks to the rest of the apparatus, taking care to isolate arm 6. The liquid anhydrous ammonia in thus collected in the test tube, while any ammonia gas is absorbed by the sulfuric acid solution (4.3) contained in the two conical flasks.

As soon as the liquefied ammonia in the test tube reaches the 200 ml mark, adjust stopcock 4 so as to connect the test tube to the atmosphere and to isolate the two conical flasks.

Immediately adjust stopcock 3 so as to isolate the test tube and allow the ammonia gas to escape into the atmosphere through arm 2.

Then close the valve of the cylinder containing the laboratory sample and disconnect it from the apparatus.

As soon as the test portion has been obtained, disconnect the assembly comprising the two conical flasks and the connecting tubes shown in the figure, starting at point 5. Allow it to attain ambient temperature and weigh it to the nearest 0,1 g.

7.2 Isolation of the oil

Heat the platinum dish (5.3) for 1 h in the electric oven (5.2), controlled at 105 ± 1 °C. Allow to cool in a desiccator, preferably containing activated silica gel or activated alumina, and weigh to the nearest 0,000 1 g.

Remove the test tube (5.1.1) containing the test portion from the Dewar vessel (5.1.2) and allow the ammonia to evaporate slowly at ambient temperature through arm 2 (see the figure) until a residue consisting of an aqueous ammonia solution, oil and other substances, not volatile at ambient temperature, is obtained at the bottom of the test tube.

Add a little water and several drops of the hydrochloric acid solution (4.2) to the test tube until the mixture is slightly acid, checking by means of the indicator (4.6).

Then add 10 ml of the carbon tetrachloride (4.1), stir and transfer to a separating funnel. Wash the test tube with two or three 10 ml portions of the carbon tetrachloride in order to remove quantitatively all traces of oil, collecting the washings in the separating funnel.

Shake the separating funnel vigorously, allow the organic phase to settle, filter slowly through a dry filter paper and collect the filtrate in the tared platinum dish (5.3). Wash the filter with 10 ml of the carbon tetrachloride, adding the washings to the filtrate.

Add to the separating funnel, 10 ml of the carbon tetrachloride, shake vigorously, allow the organic phase to settle, filter through the filter paper and collect the filtrate in the platinum dish.

7.3 Determination

7.3.1 Gravimetric method

7.3.1.1 Removal of the solvent and weighing

Evaporate the carbon tetrachloride over a boiling water bath in a well-ventilated fume cupboard. Place the dish, with its contents, for 15 to 20 min in the electric oven (5.2), controlled at 105 ± 2 °C.

Allow the dish to cool to ambient temperature in a desiccator, preferably containing activated silica gel or activated alumina, and weigh to the nearest 0,000 1 g.

7.3.1.2 Expression of results

The oil content, non-volatile at about 105 °C, expressed in milligrams per kilogram, is given by the formula

$$\frac{m_2 - m_1}{m_0} \times 10^6$$

where

m_0 is the mass, in grams, of the test portion (7.1). This is the sum of the volume, in millilitres, of the liquefied anhydrous ammonia collected in the test tube, multiplied by 0,68 (0,68 g/ml being the density of the liquefied anhydrous ammonia), and the increase in mass, in grams, of the assembly comprising the two conical flasks and the connecting tubes shown in the figure, starting at point 5;

m_1 is the mass, in grams, of the empty tared platinum dish (5.3);

m_2 is the mass, in grams, of the platinum dish (5.3) and the oil.

Carry out two determinations and give the mean of the two results.

7.3.2 Infra-red spectrometric method

7.3.2.1 Preparation of the test solution

After having removed the dish and its contents as obtained in 7.3.1.1, from the desiccator, add to the dish 10 ml of the carbon tetrachloride (4.1) to dissolve the oil. Transfer the solution to a 50 ml one-mark volumetric flask. Wash the dish with two or three 10 ml portions of the carbon tetrachloride, collecting, in order to remove quantitatively all traces of oil, the washings in the same volumetric flask. Dilute to the mark with the same carbon tetrachloride and mix.

NOTE — This operation is necessary to obtain the same conditions in the infra-red method as in the gravimetric method, i.e. elimination of any light hydrocarbons present capable of altering the result of the determination.

7.3.2.2 Preparation of the calibration graph

7.3.2.2.1 Preparation of reference solutions relating to spectrometric measurements carried out with silica cells of 1 cm optical path length

Place, in a series of six 50 ml one-mark volumetric flasks, the volumes of the oil standard solution (4.5) shown in the following table:

Standard oil solution (4.5)	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

Dilute the contents of each flask to the mark with the carbon tetrachloride (4.1) and mix.

7.3.2.2.2 Spectrometric measurements

Using the IR spectrometer (5.4), equipped with 1 cm silica cells and adjusted to a wavelength of approximately 3,42 µm, carry out the spectrometric measurements, after having adjusted the apparatus to zero absorbance against the carbon tetrachloride (4.1).

7.3.2.2.3 Plotting the graph

Plot a graph having, for example, the masses, in milligrams, of oil contained in 50 ml of reference solution, as abscissae and the corresponding values of the absorbance as ordinates.

NOTE — Prepare a new calibration graph for each determination.

7.3.2.3 Spectrometric measurement of the test solution

Carry out the spectrometric measurement of the test solution (7.3.2.1) as specified in 7.3.2.2.2.

7.3.2.4 Expression of results

Using the calibration graph (7.3.2.2.3), determine the mass of oil corresponding to the absorbance of the test solution.

The oil content, non-volatile at about 105 °C, expressed as milligrams per kilogram, is given by the formula

$$\frac{m_3 \times 1\,000}{m_0}$$

where

m_0 has the same meaning as in 7.3.1.2;

m_3 is the mass, in milligrams, of oil in the test solution (7.3.2.1).

The oil content is conventionally given as a function of the calibration. In the present International Standard the determined oil content is expressed as linear paraffin, for example *n*-hexadecane.

NOTE — Because of the sensitivity of the method, avoid contaminating the apparatus with oil or fats.

Carry out two determinations and give the mean of the two results.

8 Test report

The test report shall include the following particulars:

a) an identification of the sample;

b) name of the method used and a reference to this International Standard;

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.

Dimensions in millimetres

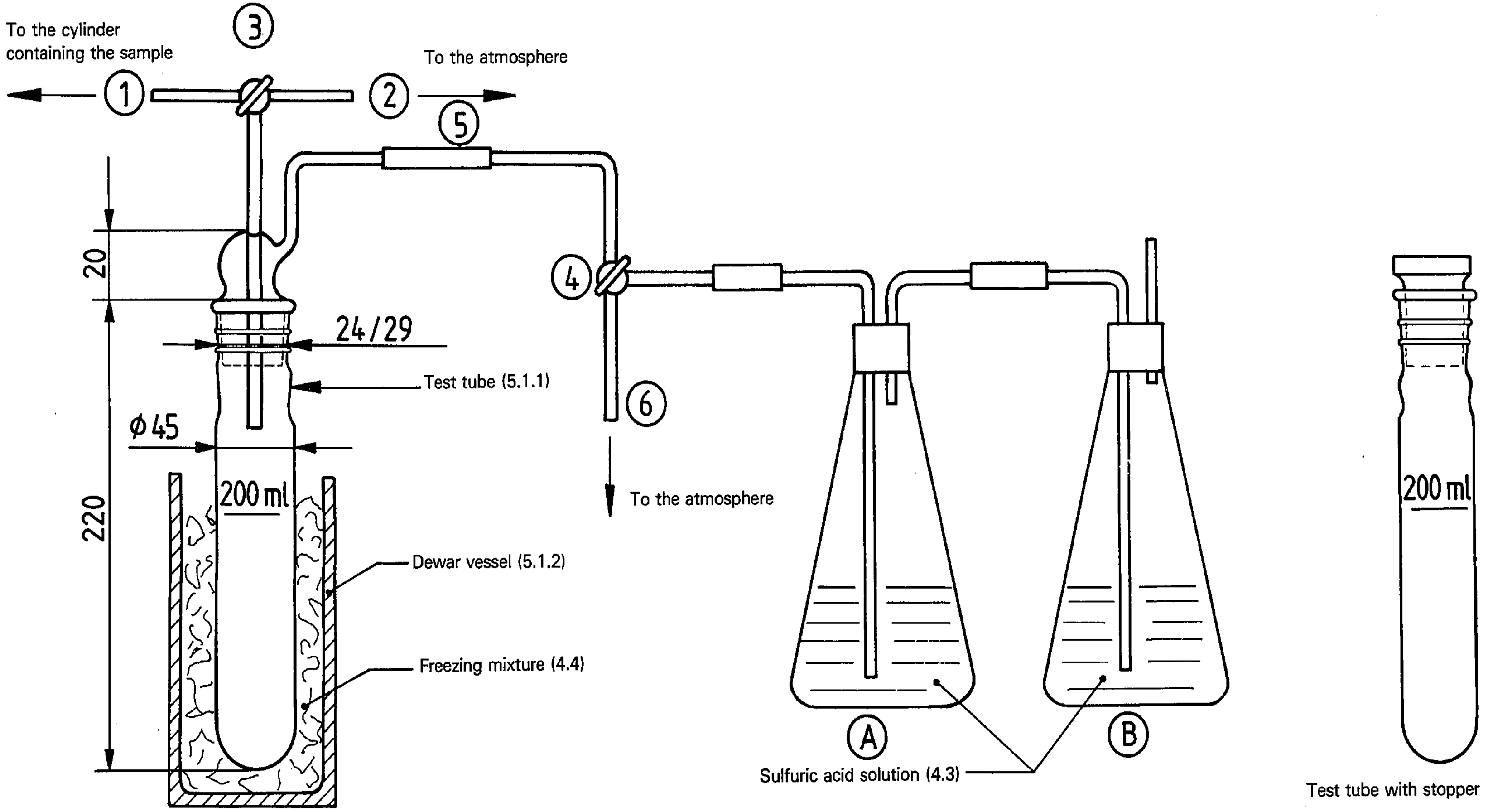

Figure — Typical apparatus for the sampling of the test portion