International Standard 6192

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Light olefins for industrial use — Determination of ammonia — Photometric method

Oléfines légères à usage industriel — Dosage de l'ammoniac — Méthode photométrique

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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.

International Standard ISO 6192 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in August 1979.

It has been approved by the member bodies of the following countries :

Australia	France	Poland
Austria	Germany, F.R.	Portugal
Belgium	Hungary	Romania
Brazil	India	South Africa, Rep. of
Chile	Italy	Switzerland
China	Libyan Arab Jamahiriya	Thailand
Czechoslovakia	Netherlands	United Kingdom
Egypt, Arab Rep. of	Philippines	

No member body expressed disapproval of the document.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

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Light olefins for industrial use — Determination of ammonia — Photometric method

WARNING — The operations specified in this International Standard must be carried out under a well ventilated hood and in a completely flame-free environment (handling of flammable gas).

1 Scope and field of application

This International Standard specifies a photometric method for the determination of ammonia in light olefins for industrial use, especially in ethylene (ethene), propylene (propene) and butadiene (1,3-butadiene).

The method is applicable to products having ammonia (NH_3) contents greater than 0,25 mg/kg.

It is not applicable to butadiene inhibited by TBC (*tert*-butylcatechol), the red coloration of which interferes with the blue coloration of indophenol.

2 Principle

Absorption of the ammonia from a gaseous sample in sulphuric acid medium with the formation of ammonium sulphate.

Passing a current of nitrogen into the absorption liquid to remove hydrogen sulphide which would interfere.

Formation in an alkaline medium of the indophenol complex by reaction of the ammonium ions with phenol and hypochlorite ions in the presence of sodium pentacyanonitrosoferrate(III) as catalyst. Photometric measurement of the blue coloration obtained at a wavelength of about 625 nm.

3 Reagents and materials

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

3.1 Nitrogen.

3.2 Sulphuric acid, approximately 0,05 g/l solution.

3.3 Sodium hydroxide, approximately 40 g/l solution.

3.4 Sodium hypochlorite, alkaline solution.

Dissolve 2,5 g of sodium hydroxide in water, add 4,2 ml of a sodium hypochlorite (NaOCl) solution containing 5 % active chlorine and dilute to 500 ml with water.

Store this solution in a dark glass flask. It is stable for 2 months.

3.5 Phenol and sodium pentacyanonitrosoferrate(III) solution.

Dissolve 5,0 g of phenol (C_6H_5OH) and 0,050 g of sodium pentacyanonitrosoferrate(III) dihydrate (sodium nitroprusside) $[Na_2Fe(CN)_5(NO).2H_2O]$ in 500 ml of water.

Store this solution in a coloured flask made of plastics material. It is stable for 2 months.

3.6 Ammonia, standard solution corresponding to 50 mg of NH_3 per litre.

Weigh, to the nearest 0,000 1 g, 0,157 0 g of ammonium chloride (NH_4Cl), transfer quantitatively into a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark and mix.

1 ml of this standard solution contains 50 µg of NH_3.

3.7 Ammonia, standard solution corresponding to 2,0 mg of NH_3 per litre.

Place 20,0 ml of the standard ammonia solution (3.6) in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 2,0 µg of NH_3.

Prepare this solution at the time of use.

4 Apparatus

Ordinary laboratory apparatus and :

4.1 Spectrophotometer, fitted with cells of thickness 20 mm, or

4.2 Photoelectric absorptiometer, fitted with filters giving maximum transmission between 600 and 660 nm, and cells of thickness 20 mm.

If necessary, cells of different thickness can be used and the mass of the test portion changed accordingly.

4.3 Two absorption flasks, assembled in series (see the figure) of capacity 100 ml, with sintered glass discs of porosity P 100 (pore size index between 40 and 100 µm).

4.4 Gas meter, 1 litre per revolution.

4.5 Water bath, capable of being controlled at 37 ± 1 °C.

5 Sampling

The sampling of ethylene, propylene and butadiene will form the subject of a future International Standard.

Take samples of 10 to 50 g in sample bottles of an appropriate stainless steel and analyse the contents as soon as possible.

6 Procedure

6.1 Preparation of the calibration graph

The calibration graph should be prepared each time a new solution of phenol and sodium nitroprusside (3.5) and/or a new sodium hypochlorite solution (3.4) is prepared.

6.1.1 Preparation of standard colorimetric solutions related to photometric measurements carried out in cells of thickness 20 mm

Into a series of six 50 ml one-mark volumetric flasks, place 1 ml of the sodium hydroxide solution (3.3) and the volumes of the standard ammonia solution (3.7) indicated in the following table.

Standard ammonia solution (3.7)	Corresponding mass of ammonia
ml	µg
0*	0
0,50	1,0
1,00	2,0
2,00	4,0
5,00	10,0
10,00	20,0

* Compensation solution.

Into each flask, place 5,0 ml of the phenol and sodium nitroprusside solution (3.5) and shake. Add 5,0 ml of the sodium hypochlorite solution (3.4) and again shake. Dilute to the mark and mix.

Place the flasks in the water bath (4.5) controlled at 37 ± 1 °C for 20 min. Allow to cool to room temperature for about 40 min.

6.1.2 Photometric measurements

Measure the absorbances of the standard colorimetric solutions (6.1.1) in cells of thickness 20 mm using the spectrophotometer (4.1) set at the wavelength of maximum absorption (about 625 nm) or using the photoelectric absorptiometer (4.2) fitted with appropriate filters, after having adjusted the instrument, in each case, to zero absorbance against the compensation solution.

6.1.3 Plotting the calibration graph

Plot a graph having, for example, the masses of ammonia, in micrograms per 50 ml of standard colorimetric solution, as abscissae and the corresponding values of absorbance as ordinates.

6.2 Determination

6.2.1 Absorption

Place 30 ml of the sulphuric acid solution (3.2) in each of the two absorption flasks (4.3) and connect the different components of the apparatus in the following order :

a) absorption flasks;

b) gas meter.

Determine, to the nearest 0,1 g, the mass of the sample bottle and its contents and fit the gas outlet of the bottle to the first absorption flask. Pass the gas into the apparatus at a rate of 30 to 40 l/h until the sample bottle is empty. Re-weigh the empty bottle to the nearest 0,1 g.

Pass a current of nitrogen (3.1) into the absorption liquid in the two absorption flasks to remove any dissolved hydrogen sulphide.

6.2.2 Preparation of the test solution

Transfer quantitatively the contents of the two absorption flasks into a 100 ml one-mark volumetric flask, add 2 ml of the sodium hydroxide solution (3.3), dilute to the mark and mix. Take an aliquot portion (between 1 and 40 ml) of this solution, containing between 1 and 20 µg of NH_3, and place it in another 50 ml one-mark volumetric flask.

Add to this flask 5,0 ml of the phenol and sodium nitroprusside solution (3.5) and shake. Add 5,0 ml of the sodium hypochlorite solution (3.4) and shake again. Dilute to the mark and mix.

Place the flask in the water bath (4.5), controlled at 37 ± 1 °C, for 20 min. Allow to cool to room temperature.

6.2.3 Photometric measurement

Carry out the photometric measurement on the test solution (6.2.2) by the procedure described in 6.1.2, after having adjusted the instrument to zero absorbance against the blank test solution (6.3).

6.3 Blank test

Place 60 ml of the sulphuric acid solution (3.2) in a 100 ml one-mark volumetric flask and dilute to the mark.

Take a volume of this solution equal to that of the aliquot portion taken for the preparation of the test solution and place it in a 50 ml one-mark volumetric flask. Proceed as specified in 6.2.2, starting from "Add to this flask...".

7 Expression of results

By means of the calibration graph (6.1.3), determine the mass m_1, in micrograms, of ammonia (NH_3) corresponding to the absorbance of the test solution.

The ammonia content, expressed in milligrams of NH_3 per kilogram, is given by the formula

$$\frac{m_1 \times 100}{V \times m_0}$$

where

m_0 is the mass, in grams, of sample (6.2.1) taken for absorption;

m_1 is the mass, in micrograms, of ammonia in 50 ml of the test solution;

V is the volume, in millilitres, of the aliquot portion of the liquid treated (6.2.2).

8 Test report

The test report shall contain 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 regarded as optional.

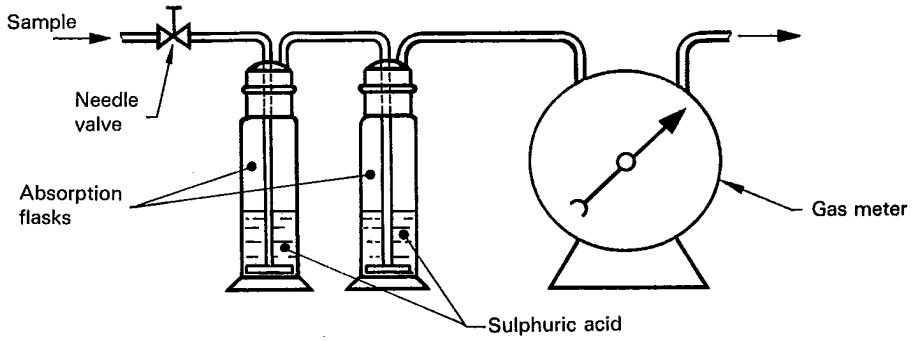

Figure — Absorption apparatus