International Standard ISO 6377

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Light olefins for industrial use — Determination of hydrocarbon impurities by gas chromatography — General considerations

Oléfines légères à usage industriel — Dosage des impuretés hydrocarbonées par chromatographie en phase gazeuse — Considérations générales

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

International Standard ISO 6377 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in October 1979.

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

Australia
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The member body of the following country expressed disapproval of the document on technical grounds :

Switzerland

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Light olefins for industrial use — Determination of hydrocarbon impurities by gas chromatography — General considerations

1 Scope and field of application

This International Standard describes general considerations relating to the determination, by gas chromatography, of hydrocarbon impurities in light olefins for industrial use, and, in particular, in ethylene (ethene), propylene (propene) and butadiene (1,3-butadiene).

2 Materials

Refer to the specific International Standard for the product to be analysed.

3 Apparatus for chromatography

3.1 Type of apparatus

Refer to the specific International Standard for the product to be analysed.

3.2 Injection device

If the test portions are introduced in the gaseous phase into the chromatograph, the latter shall be fitted with an injection device comprising a stainless steel gas sampling valve and a sample loop. It is desirable that the valve should be able, as far as possible, to be used with loops of different volume, as the quantity to be injected is a function of the geometry of the olefins, of the valve and of the loop.

The device shall permit the injection of gas volumes constant to within ± 1 %.

3.3 Columns

Specific International Standards for the products to be analysed will give examples of columns which are suitable for the determinations concerned.

The column selected as suitable for the determination to be carried out shall permit the separation of adjacent peaks of the impurities to be determined. The resolution of the adjacent peaks is given by the formula

$$R = \frac{d_R(B) - d_R(A)}{\delta(B) + \delta(A)}$$

where

d_R is the retention distance;

δ is the peak width at half height measured half way between the base line and the top of the peak;

(B) indicates one of the impurities;

(A) indicates another impurity giving an adjacent peak.

The condition for complete resolution is expressed by :

$$R \geqslant 1$$

3.4 Detector

A flame ionization detector is suitable in the majority of cases, but other types of detector may be necessary for some determinations.

3.5 Recorder and/or integrator

Refer to the specific International Standard for the product to be analysed.

4 Sampling

The sampling of light olefins for industrial use will form the subject of ISO 7382.

4.1 Taking of the sample

Samples of olefins are usually contained in sampling bombs, and may be either in the gaseous or liquefied condition. In the latter case, it is advisable to vaporize them before introducing them into the injection device (3.2).

4.2 Vaporization of liquid samples

It is recommended to use for this purpose a device made up of a coiled, stainless steel, capillary tube (2 to 4 m in length and with an internal diameter of 0,2 mm) placed in a water bath at a temperature in the range 50 to 70 °C.

This coil is connected to the exit valve of the sampling bomb placed in position as shown in the figure. When the valve is completely open, the drop in pressure causes the vaporization of the product inside the capillary tube.

The free end of the capillary tube may be connected either directly to the injection device, or to a sample chamber.

In both cases, it is advisable to ensure a suitable purge.

The amount of gas necessary to purge the sample chamber, may be reduced, if necessary, by making use of a vacuum pump fitted with a mercury manometer, as shown in the figure.

5 Procedure

5.1 Setting up the apparatus

Refer to the specific International Standard for the product to be analysed and, in particular, prepare the column in conformity with the descriptions given therein and condition it by maintaining it for at least 12 h at a temperature 20 °C above the operating temperature.

If chromatography is carried out under isothermal conditions, the temperature should be constant to within ± 1 °C.

The flow rate of the carrier gas shall be constant, controllable and measurable.

Before carrying out a determination, make the necessary adjustments in order to obtain optimum operating conditions and response from the detector. Wait until the conditions become stabilized, i.e. a stable base line is obtained.

Check the linearity of the response of the detector by injecting standard mixtures of different concentrations.

5.2 Calibration

Calibration, carried out before and after each analysis, is, most often, an external calibration effected by means of standard mixtures. These standard mixtures may be commercial products, manufactured by specialist firms, or they may be prepared in the laboratory. In the latter case, proceed in conformity with the International Standards for gas analysis.

If a standard mixture for an impurity is not readily available or not available at all, it is possible to use another product having the same number of carbon atoms as the impurity and to work by calculation.

5.3 Test

5.3.1 Preparation of the test portion

Refer to the specific International Standard for the product to be analysed.

5.3.2 Introduction of the test portion

Connect, as appropriate, either the sampling bomb, the free end of the coil or the sample chamber to the sample inlet port. Interpose a fritted stainless steel filter in order to avoid carrying solids forward into the gas sampling valve and a transparent tube in order to check that no liquid is present. Purge the loop of the injection device by passing a volume of gas equal to about ten times the volume of the loop/valve connection. Close the valve of the sampling bomb and allow, if necessary, the pressure of the gas contained in the loop to reach equilibrium with the atmospheric pressure; then open the sampling valve to allow injection of the test portion contained in the loop.

NOTE — The pressure of the gas in the sampling bomb or in the sample chamber will generally be sufficient to ensure the flow of the product. If this pressure is insufficient, for example because previous determinations have almost emptied the sample chamber, it can be raised by heating the sample chamber by means of a hot air blower. Do not heat the valves. In cases when this operation does not suffice, as a last resort and if another identical sample is not available, a suitable liquid may be introduced into the sample chamber.

This last operation should be carried out with care and the liquid used should neither change the characteristics of the sample, nor contaminate the sample chamber. Mercury may be suitable, provided that the usual precautions are taken.

5.4 Examination of the chromatograms

Refer to the specific International Standard for the product to be analysed.

6 Expression of results

Quantitative analysis is based on the measurement (A_i) of the height or of the area of the peak, by a method chosen by the user or from the reading of an integrater.

The concentration C_i of the constituent i is given, in millilitres per cubic metre or in milligrams per kilogram, by the formula

$$C_i = C_E \times \frac{A_i}{A_E} \times \frac{E_i}{E_E} \times K_{E,\,i}$$

where

C_E is the concentration, in millilitres per cubic metre or in milligrams per kilogram, of the standard material;

A_i is the measurement corresponding to the peak for constituent i;

A_E is the measurement corresponding to the peak for the standard material;

E_i is the position of the attenuator during the measurement;

E_E is the position of the attenuator during calibration;

$K_{E,i}$ is the coefficient of proportionality between the impurity i in relation to the standard material.

NOTE — If the standard substance is identical with the impurity i, $K_{E,i} = 1$.

If this is not the case, and if the detector is a flame ionization detector and the results are expressed in millilitres per cubic metre :

$$K_{E,i} \approx \frac{F_E}{F_i}$$

where

F_i is the number of carbon atoms in the molecule of the impurity i;

F_E is the number of carbon atoms in the molecule of the standard material.

7 Test report

The test report shall include the following information :

a) all information necessary for the complete identification of the sample (lot, date, time and duration of each sampling, etc.);

b) a reference to this International Standard;

c) the concentration of each impurity as required;

d) the nature of the hydrocarbon and its concentration in the gaseous standard mixture;

e) a statement of any experimental conditions which are regarded as optional :

- a description of the column or combination of columns used, or reference to the column or combination of columns specified in the International Standard,
- the nature of the carrier gas,
- the pressure, in bars[1], of the carrier gas at the entrance to the column or in the first part of the column,
- the flow rate of the carrier gas, in litres per hour, measured at standard atmospheric pressure,
- the volume, in millilitres measured at standard atmospheric pressure, of gas injected for each test,
- the duration of recording;

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

g) details of any operations not included in this International Standard, or in the International Standard to which reference is made, or regarded as optional.

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[1] 1 bar = 10^5 Pa

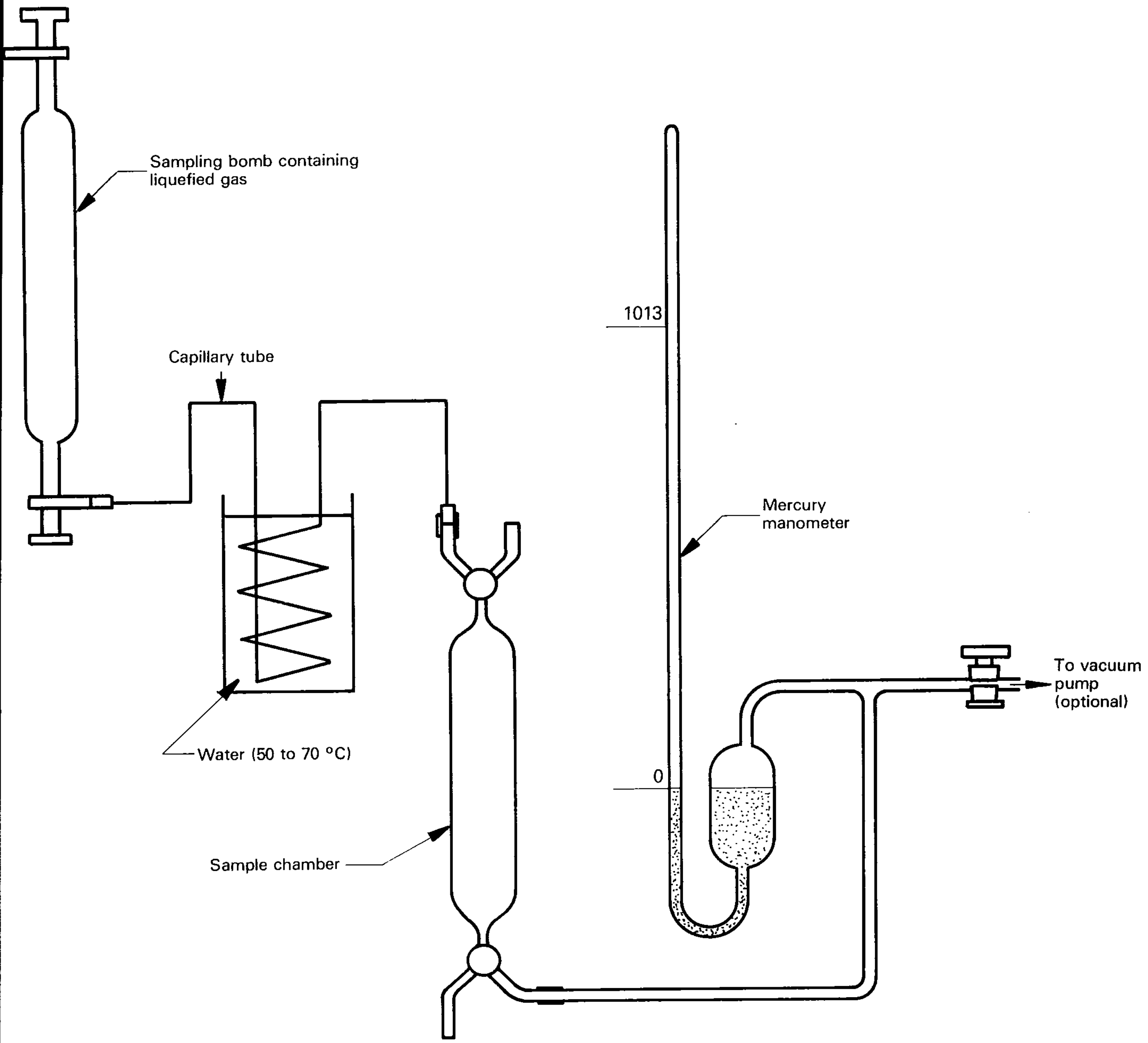

Figure — Apparatus for the volatilization of liquid samples