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International Standard 8176

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Butadiene for industrial use — Determination of active *tert*-butyl-catechol (TBC) [4-(1,1-dimethylethyl)-1,2-benzenediol] — High performance liquid chromatographic method

Butadiène à usage industriel — Dosage du tert-*butyl-catéchol (TBC) actif [(diméthyléthyl-1,1)-4-benzènediol-1,2] — Méthode par chromatographie liquide à haute performance*

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ISO 8176-1986 (E)

Foreword

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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INTERNATIONAL STANDARD ISO 8176-1986 (E)

Butadiene for industrial use — Determination of active *tert*-butyl-catechol (TBC) [4-(1,1-dimethylethyl)-1,2-benzenediol] — High performance liquid chromatographic method

WARNING — [4-(1,1-Dimethylethyl)-1,2-benzenediol] is irritating to skin, particularly when molten or in concentrated solution. It is also toxic if swallowed or in contact with skin.

For all handling of butadiene, work in a well-ventilated hood away from flames and sparks. It is advisable to use proper personnal protection, such as gloves and goggles.

1 Scope and field of application

This International Standard specifies a high performance liquid chromatographic method for the determination of [4-(1,1-dimethylethyl)-1,2-benzenediol] (*tert*-butyl catechol or TBC) in buta-1,3-diene for industrial use.

The polymerization inhibitor TBC can also be determined by a spectrometric method (ISO 6684) but that method is not able to differentiate between the active inhibitor and its oxidized, inactive form. The present method specifically measures the concentration of the active form of TBC. The method is applicable to butadiene having TBC contents in the range 0 to 250 mg/kg.

2 References

ISO 653, *Long solid-stem thermometers for precision use.*

ISO 6684, *Butadiene, for industrial use — Determination of* tert-*butyl catechol (TBC)[4-(1,1-dimethylethyl)-1,2-benzenediol] — Spectrometric method.*

ISO 8563, *Propylene and butadiene in liquid phase — Sampling.* [1]

3 Principle

Extraction of the active TBC in a test portion by mixing with a solution containing *m*-nitrophenol (as the internal standard) and evaporating the butadiene. Separation of the TBC and *m*-nitrophenol by high-performance liquid chromatography and detection by UV. Measurement of the peak areas or peak heights and determination of the TBC content using a calibration graph.

4 Reagents and materials

During the analysis, use reagents of HPLC grade or recognized analytical grade.

4.1 Methanol.

4.2 Acetic acid.

4.3 Chloroform.

4.4 Distilled or **deionized water.**

4.5 Standards.

4.5.1 TBC [4-(1,1 dimethylethyl)-1,2-benzenediol], 25 g/l solution in chloroform.

4.5.2 *m*-**Nitrophenol** internal standard, 25 mg/l aqueous solution.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Syringes for liquids, of capacity 10, 25, 50 and 100 µl, for the preparation of calibration solutions.

5.2 Syringe for HPLC, of capacity 50 µl or more, for filling the injection loop.

5.3 Chromatograph.

Use a high-performance liquid chromatograph complying with the requirements specified below and which yields a peak

1) At present at the stage of draft.

height for TBC of at least twice the noise level for a concentration of 10 mg/l.

The apparatus below is given as an example; any apparatus which will comply with the same minimum requirements of efficiency may be used.

5.3.1 Pump, which produces a constant flow rate of 1,5 ± 0,02 ml/min.

5.3.2 Injection device, of the rotary valve type, with fixed sample loop of aproximately 20 µl.

NOTE — The exact volume of the sample loop is not critical because an internal standard procedure is used for quantitation.

5.3.3 Column, made of stainless steel, 250 mm long and internal diameter 4,6 mm.

5.3.3.1 Column packing : Reverse-phase HPLC packing, consisting of a C_{18} hydrocarbon phase, stable to hydrolysis, and chemically bonded to silica-based particles of 10 µm diameter.

5.3.3.2 Liquid phase : Mixture of methanol, water and acetic acid respectively containing the following proportion 67 + 32 + 1 by volume.

5.3.4 Detector, UV at 280 nm.

5.4 Precision thermometer STL/0,2/−55/5 (see ISO 653).

6 Sampling

Take, in a stainless steel cylinder, a liquid sample of butadiene of at least 50 ml as specified in ISO 8563.

7 Procedure

7.1 Calibration graph

7.1.1 Preparation of the calibration solutions

Into a series of six 50 ml flasks with ground stopper, introduce, by means of a pipette, 25,0 ml of the *m*-nitrophenol solution (4.5.2) and add, by means of the syringes (5.1), the volumes of the TBC standard solution (4.5.1) indicated in the table 1 :

Table 1

Volume of TBC standard solution (4.5.1)	Corresponding concentration of TBC in the calibration solution
µl	mg/l
0	0
10	10
25	25
50	50
100	100
150	150

7.1.2 Calibration

By means of the syringe (5.2), fill the sample loop of the injection valve (5.3.2) with one of the calibration solutions and inject the aliquot portion into the chromatograph (5.3). Record the areas of the peaks obtained for TBC and for *m*-nitrophenol.

NOTE — If no electronic integrator is available substitute "peak height" for "peak area". Repeat the procedure for the other calibration solutions given in table 1.

Repeat the procedure for the other calibration solutions given in table 1.

7.1.3 Plotting of the graph

Plot a graph having, for example, as abscissae, the concentrations, in milligrams per litre, of TBC and as ordinates the corresponding values of the ratio of the area of the TBC peak to the area of the *m*-nitrophenol peak.

Alternatively, substitute "peak height" for "peak area".

7.2 Test portion

Cool a 25 ml graduated glass cylinder and a coiled stainless steel tube of length 1 m, inside diameter 3 mm, to about −20 °C. Mix the sample in the steel cylinder by shaking. Attach the coiled tube to the sample cylinder and transfer 25 ml of the liquid sample through the cooled tube into the cooled graduated cylinder.

WARNING — The above operation should be performed with personal protection (gloves and goggles) in a well-ventilated hood. In order to avoid explosion risks by discharge of static electricity, the sample cylinder should be grounded during this operation.

7.3 Preparation of the test solution

Determine the temperature of the test portion (7.2) to the nearest 1,0 °C and transfer it to a 50 ml conical flask containing 25 ml of the *m*-nitrophenol solution (4.5.2).

Allow the butadiene to evaporate at ambient temperature, behind a screen under a ventilated hood, away from all sources of heat and ignition.

After complete evaporation of the butadiene, stopper the conical flask and shake for 1 min.

7.4 Determination

By means of the HPLC syringe (5.2), fill the sample loop of the injection valve (5.3.2) with the test solution (7.3) and inject the aliquot portion into the chromatograph (5.3). Record peak areas (or alternatively peak heights) obtained for TBC and *m*-nitrophenol.

Calculate the ratio of the area (or height) of the TBC peak to the area (or height) of the *m*-nitrophenol peak.

Some typical chromatograms are shown in the figures 1 and 2.

8 Expression of results

8.1 Method of calculation and formula

By means of the calibration graph (7.1.3) read the content, expressed in milligrams per litre, of active TBC in the test solution (7.3).

The active TBC content, expressed in milligrams per kilogram, is given by the formula

$$\frac{c}{\varrho}$$

where

c is the content, in milligrams per litre, of TBC in the test solution;

ϱ is the density, in grams per millilitre, of the test portion at the temperature measured in 7.3.

The density varies according to temperature as given in table 2 :

Table 2

Temperature °C	Density g/ml
−40	0,690 3
−35	0,684 8
−30	0,679 3
−25	0,673 7
−20	0,668 1
−15	0,662 5
−10	0,656 8
− 5	0,651 0
0	0,645 2

8.2 Precision

8.2.1 Repeatability

The difference between the results obtained by the same operator, with the same apparatus, under the same operating conditions on the same sample material should not exceed more than one time in twenty times 3,8 % of the mean value.

8.2.2 Reproducibility

To be determined.

9 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) reference to this International Standard;

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

— full description of the column,

— temperature of the sample in 7.3;

d) the results and the method of expression used;

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

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

10 Bibliography

OOMENS, A.C., SCHAURHUIS, F.G. and SKELLY, N.E., *J. Liquid Chromatography* **7** (11), pp. 2143-2149 (1984).

Annex

Typical chromatograms

(This annex does not form an integral part of the Standard.)

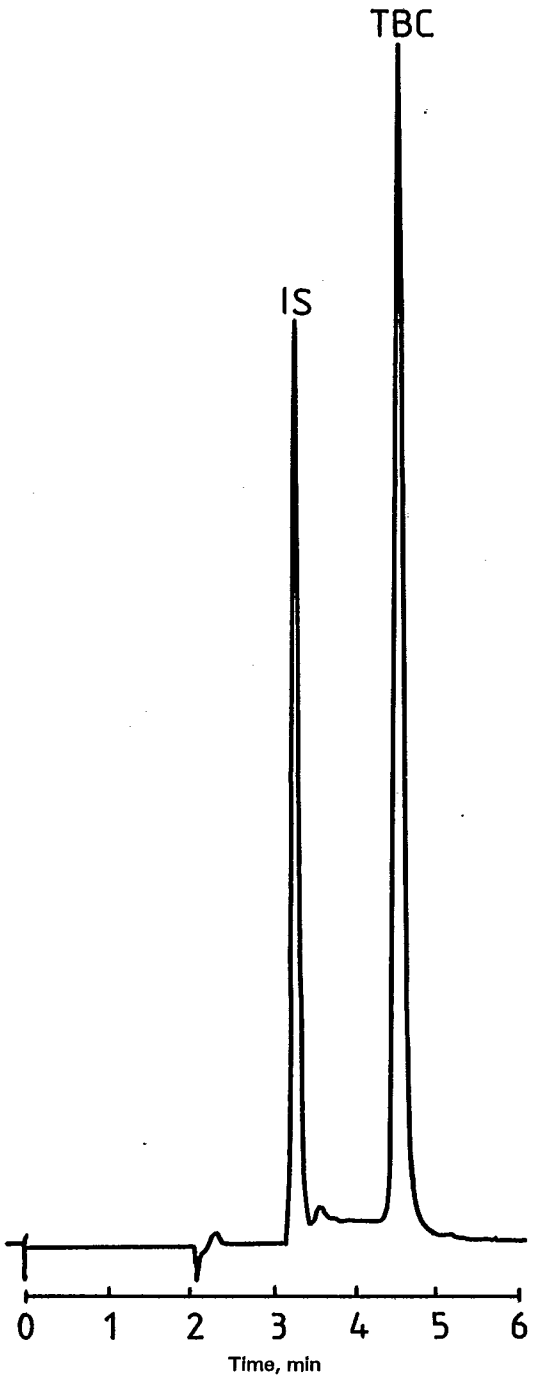

Figure 1 — Standard solution, containing 200 mg of TBC per litre and 28 mg of *m*-nitrophenol (IS) per litre

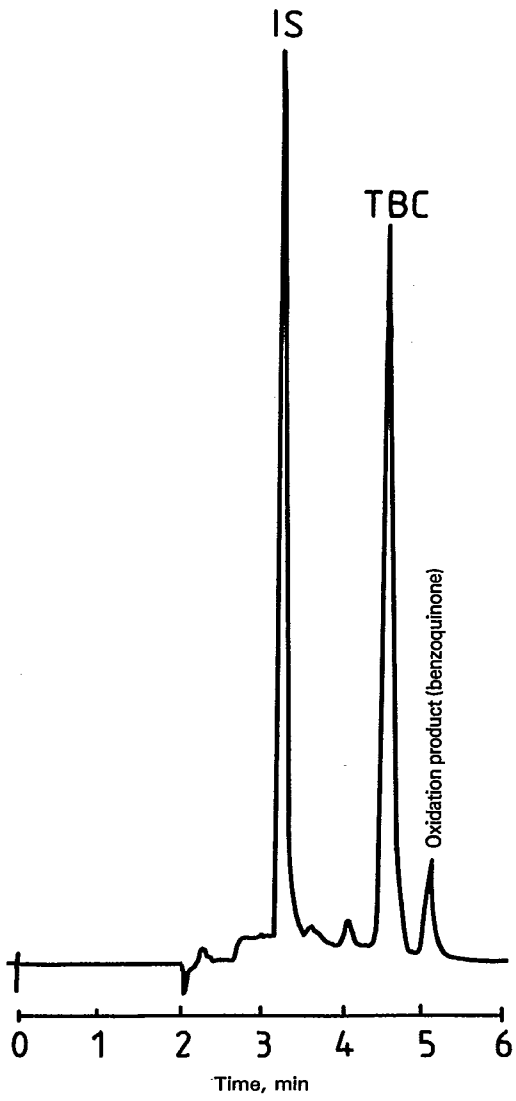

Figure 2 — Test solution, containing 120 mg of TBC per litre

[Note the presence of the oxidation product benzoquinone.)