International Standard 6684

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Butadiene for industrial use — Determination of *tert*-butylcatechol (TBC) [4-(1,1-dimethylethyl)-1,2 benzenediol] — Spectrometric method

Butadiène à usage industriel — Dosage du tert-*butyl-catéchol (TBC) [(diméthyléthyl-1,1)-4 benzènediol-1,2] — Méthode spectrométrique*

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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 6684 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in November 1980.

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

Australia	Hungary	Poland
Austria	India	Portugal
Belgium	Ireland	Romania
Brazil	Italy	South Africa, Rep. of
Czechoslovakia	Korea, Rep. of	Switzerland
Egypt, Arab Rep. of	Mexico	Thailand
France	Netherlands	USSR
Germany, F. R.	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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Butadiene for industrial use — Determination of *tert*-butylcatechol (TBC) [4-(1,1-dimethylethyl)-1,2 benzenediol] — Spectrometric 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.

1 Scope and field of application

This International Standard specifies a spectrometric method for the determination of 4-(1,1-dimethylethyl)-1,2 benzenediol (*tert* Butyl Catechol or TBC) added as an oxidation inhibitor to 1,3-butadiene for industrial use.

The method is applicable to butadiene (and to all mixtures of C_4 hydrocarbons) containing no phenolic component other than TBC, and no oxidized phenolic component other than those derived from the oxidation of TBC. If present, all phenols and their quinone oxidation products are determined as TBC. Small amounts of non-volatile residue do not interfere. The method is applicable to butadiene containing more than 50 mg of TBC per kilogram.

2 Reference

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

3 Principle

Separation of the inhibitor from the butadiene by evaporation. Dissolution of the residue in water and addition of an excess of iron(III) chloride. Spectrometric measurement of the absorbance of the yellow-coloured complex at a wavelength of about 425 nm.

4 Reagents

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

4.1. Iron(III) chloride, 20 g/l acid solution in ethanol.

Dissolve 20,0 g of iron(III) chloride hexahydrate ($FeCl_3.6H_2O$) in 95 % (*V/V*) ethanol. Add 9,2 ml of hydrochloric acid solution, ϱ 1,19 g/ml, dilute to 1 000 ml with the same ethanol and mix.

4.2 TBC [$(CH_3)_3—C—C_6H_3(OH)_2$], standard solution 6,7 g/l.

Weigh, to the nearest 0,000 1 g, 0,670 g of 4-(1,1-dimethylethyl)-1,2 benzenediol and dissolve in 10 ml of 95 % (*V/V*) ethanol. Complete the volume to 100 ml with water in a volumetric flask and mix.

1 ml of this standard solution contains 6,7 mg of TBC.

Prepare this solution immediately before use.

NOTE — If a test portion of 100 ml (67 g) is used at −20 °C, 1,00 ml of this standard solution corresponds to 100 mg of TBC per kilogram of butadiene.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrometer or **filter spectrometer.**

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

6 Sampling

A liquid sample of at least 100 ml taken from the original source in a stainless steel container is required for this test.

7 Procedure

7.1 Plotting of the calibration graph

7.1.1 Preparation of the standard colorimetric solutions, for spectrometric measurements carried out in a cell of thickness 1 cm

Into a series of six 100 ml one-mark volumetric flasks, introduce the volumes of the TBC standard solution (4.2) indicated in table 1.

Table 1

TBC Standard solution (4.2)	Corresponding mass of TBC	Corresponding concentration of TBC in a 100 ml test portion at −20 °C
ml	mg	mg/kg
0	0	0
0,50	3,35	50
1,00	6,70	100
1,50	10,05	150
2,00	13,40	200
2,50	16,75	250

Complete the volume of each flask to 100 ml and mix.

Introduce 5,0 ml of each of these solutions into six separate optical cells to be used as reference solutions.

7.1.2 Colour development

Add to each flask 5,0 ml of the iron(III) chloride solution (4.1), mix and allow to stand for 5 min.

The colour of the solution is stable for 5 to 15 min after the addition of the iron(III) chloride solution and the spectrometric measurements shall be carried out within this period.

7.1.3 Spectrometric measurement

Carry out the absorbance measurement of each standard colorimetric solution (7.1.2) by means of a spectrometer (5.1) at a wavelength of about 425 nm, after having adjusted the instrument to zero absorbance against each reference solution (7.1.1).

7.1.4 Plotting of the calibration graph

Deduct the absorbance of the reference solution (7.1.1) from those of the standard colorimetric solutions (7.1.2).

Plot a graph having, for example, as abscissae, the number of milligrams of TBC contained in 100 ml of standard colorimetric solution and as ordinates the corresponding values of the absorbances.

7.2 Blank test

Carry out a blank test at the same time as the determination, using the same procedure and the same quantities of all the reagents as used for the determination, but omitting the test portion.

7.3 Test portion

Cool a 100 ml graduated cylinder and a coiled stainless steel tube fitting the sample container to about −20 °C. In running through the cooled tube, measure 100 ml of liquid sample into the cooled graduated cylinder.

7.4 Determination

7.4.1 Preparation of the test solution

After mixing the contents of the stainless steel container by stirring, determine the temperature of the test portion (7.3) to the nearest 1,0 °C and transfer the sample into a 250 ml conical flask. Allow the liquid to evaporate at ambient temperature, behind a screen under a ventilated hood away from all sources of heat. A steam bath may be used to complete the evaporation.

After evaporation of the test portion, add 30 ml of water to the flask, stopper, shake and filter into a 100 ml one-mark volumetric flask through a rapid, low-ash filter paper which has previously been moistened. Repeat the operation with two more 30 ml portions of water, collecting the washing water in the same volumetric flask. Complete the volume with water and mix. Transfer 5,0 ml of this solution into an optical cell to be used as a reference solution.

Add 5,0 ml of the iron(III) chloride solution (4.1) to the volumetric flask, mix and allow to stand for 5 min.

7.4.2 Spectrometric measurement

Five to fifteen minutes after addition of the iron(III) chloride solution, carry out the absorbance measurement of the test solution (7.4.1) and of the blank test solution, using a spectrometer (5.1) at a wavelength of about 425 nm, after having adjusted the instrument to zero absorbance against the reference solution.

Deduct the absorbance of the blank test solution (7.2) from that of the test solution.

8 Expression of results

8.1 Method of calculation and formula

By means of the calibration graph (7.1.4), determine the mass of TBC, expressed in milligrams, of the test portion, corresponding to the absorbance obtained. The TBC content, expressed in milligrams per kilogram, is given by the formula

$$\frac{m \times 1\,000}{V \times \varrho}$$

where

m is the mass, in milligrams, of TBC found in 100 ml of the test solution (7.4.1);

V is the volume, in millilitres, of the test portion of liquid butadiene (7.3);

ϱ is the density, in grams per millilitre, of the sample as a function of its temperature at the time of sampling carried out in (7.3). This density varies according to table 2.

Table 2

Temperature	Density
°C	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 Repeatability and reproducibility

8.2.1 Repeatability

Duplicate results obtained by the same operator should be considered suspect if they differ by more than 12 mg/kg.

8.2.2 Reproducibility

Results submitted by each of two laboratories should be considered suspect if they differ by more than 47 mg/kg.

9 Test report

The test report shall include the following particulars :

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 the International Standard to which reference is made, or regarded as optional.