TERTIARY BUTYLHYDROQUINONE

Prepared at the 49th JECFA (1997) , published in FNP 52 Add 5 (1997) superseding specifications prepared at the 44th JECFA (1995), published in FNP 52 Add 3 (1995). Metals and arsenic specifications revised at the 61st JECFA (2003). An ADI of 0-0.7 mg/kg bw was established at the 49th JECFA (1997).

SYNONYMS   TBHQ, INS No 319

DEFINITION

Chemical names   Mono-tert-butylhydroquinone, *t*-butylhydroquinone, 2-(1,1-dimethylethyl)-1,4-benzenediol
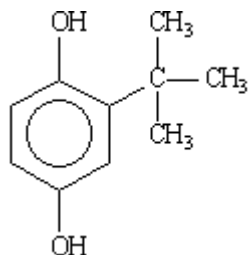
C.A.S. number   1948-33-0

Chemical formula $C_{10}H_{14}O_2$

Structural formula

Formula weight   166.22

Assay   Not less than 99.0% of $C_{10}H_{14}O_2$

DESCRIPTION   White, crystalline solid having a characteristic odour.

FUNCTIONAL USES   Antioxidant

CHARACTERISTICS

IDENTIFICATION

Solubility (Vol. 4)   Practically insoluble in water; soluble in ethanol

Melting point (Vol. 4)   Not less than 126.5^o

Phenolics   Dissolve about 5 mg of the sample in 10 ml of methanol, and add 10.5 ml of dimethylamine solution (1 in 4). A red to pink colour is produced.

PURITY

t-Butyl-p-benzoquinone   Not more than 0.2%
          See description under TESTS

2,5-Di-t-butyl hydroquinone	Not more than 0.2% See description under TESTS
Hydroxyquinone	Not more than 0.1% See description under TESTS
Toluene	Not more than 25 mg/kg See description under TESTS
Lead (Vol. 4)	Not more than 2 mg/kg Determine using an atomic absorption technique appropriate to the specified level. The selection of sample size and method of sample preparation may be based on the principles of the method described in Volume 4, "Instrumental Methods."

TESTS

PURITY TESTS

t-Butyl-p-benzoquinone

Apparatus:
Use a suitable double-beam infrared spectrophotometer and matched 0.4 mm liquid sample cells with calcium fluoride windows.

Reagents and Solutions:
Standard preparation: Transfer about 10 mg of mono-tertiary-butyl-p-benzoquinone Reference Standard (available from US Pharmacopeial Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852, USA), accurately weighed, into a 10-ml volumetric flask, dissolve in chloroform, dilute to volume with the same solvent and mix.
Sample preparation: Transfer about 1 g of the sample, previously ground to a fine powder in a high-speed blender and accurately weighed, into a 10-ml volumetric flask, dissolve in chloroform, dilute to volume with the same solvent, and mix. Filter through a Millipore filter (UHWPO1300), or equivalent, before use in the Procedure below.

Procedure:
Fill the reference cell with chloroform and the sample cell with the Standard preparation. Place the cells in the respective reference and sample beam of the spectrophotometer, and record the infrared spectrum from 1600 to 1775 cm^{-1}. On the spectrum draw a background line from 1612 to 1750 cm^{-1}, and determine the net absorbence (A_S) of the Standard preparation at 1659 cm^{-1}.
Similarly, obtain the spectrum of the sample preparation, and determine its net absorbence (A_U) at 1659 cm^{-1}.

Calculation:
Calculate the percent of t-butyl-p-benzoquinone in the sample by the formula:

$$100 \times A_U/A_S \times W_S/W_U$$

where
W_S = the exact weight, in mg, of the mono-tertiary-butyl-p-benzoquinone Reference Standard taken
W_U = the exact weight, in mg, of the sample taken.

2,5-Di-t-butylhydroquinone and hydroquinone

Apparatus:
Use a suitable gas chromatograph equipped with a thermal conductivity detector (F and M Model 810 or equivalent), containing a 0.61-m (2 ft) × 6.35-mm (outside diameter) stainless steel column packed with 20% Silicone SE-30, by weight and 80% Diatoport S (60/80-mesh), or equivalent materials.

Operating conditions:
The operating parameters may vary, depending upon the particular instrument used, but a suitable chromatogram may be obtained using the following conditions:
- Column temperature: programmed from 100 to 270°, at 15° per min
- Injection port temperature: 300°
- Carrier gas: helium, flowing at a rate of 100 ml per min
- Bridge current: 140 mA
- Sensitivity: 1 × for integrator (Infotronics CRS 100), 2 × for recorder

Reagents and Solutions:
Stock solution: Weigh accurately about 50 mg each of hydroquinone (HQ), 2,5-di-t-butylhydroquinone (DTBHQ), and methyl benzoate (internal standard), transfer into separate 50-ml volumetric flasks, dilute to volume with pyridine, and mix.
Calibration standards: Into separate 10-ml volumetric flasks add 0.50, 1.0, 2.0 and 3.0 ml of the HQ stock solution, then to each flask add 2 ml of the methyl benzoate (internal standard) stock solution, dilute each to volume with pyridine, and mix. In the same manner prepare four DTBHQ calibrating solutions. Prepare the trimethylsilyl derivative of each solution as follows. Add 9 drops of calibration solution to a 2-ml gas syringe, add 250 µl of N,O-bistrimethylsilylacetamide, and heat at about 80° for 10 min. Chromatograph 10-µl portions of each standard in duplicate, and plot the concentration ratio of HQ to internal standard (X-axis) against the response ratio of HQ to internal standard (Y-axis). Plot the same relationships between DTBHQ and the internal standard.

Procedure:
Transfer about 1 g of the sample, accurately weighed, into a 10-ml volumetric flask, add 2 ml of the methyl benzoate internal standard stock solution, dilute to volume with pyridine, and mix. Prepare the trimethylsilyl derivative as described above under Calibration standards, and then chromatograph duplicate 10-µl portions to obtain the chromatogram. The approximate peak times, in minutes, are: methyl benzoate, 2.5; TMS derivative of HQ, 5.5; TMS derivative of tert-butylhydroquinone, 7.3; TMS derivative of DTBHQ, 8.4.

Calculation:
Determine the peak areas (response) of interest by automatic integration or manual triangulation. Calculate the response ratio of HQ and DTBHQ

to internal standard. From the calibration curves determine the concentration ratio of HQ and DTBHQ to internal standard, and calculate the % HQ and % DTBHQ in the sample by the formula:

$$A = Y \times I \times 10/S$$

where
A = the % HQ or % DTBHQ in the sample
Y = the concentration ratio (X-axis on calibration curve)
I = the percentage (w/v) of internal standard in the Sample preparation
S = the weight of sample taken, in g.

Toluene

Apparatus:
Use a suitable gas chromatograph equipped with a flame ionization detector (F and M Model 810 or equivalent), containing a 3.66-m (12-ft) × 3.18-mm (outside diameter) stainless steel column packed with 10% Silicone SE-30, by weight, and 90% Diatoport S (60/80 mesh), or equivalent materials.

Operating conditions:
The operating parameters may vary, depending upon the particular instrument used, but a suitable chromatogram may be obtained using the following conditions:
- Column temperature: programmed from 70 to 280° at 15° per minute and held
- Injection port temperature: 275°
- Cell temperature: 300°
- H_2 and O_2 (or air) settings: 1.4 atm (20 psi) each

Reagents and solutions:
Standard solution: Prepare a solution of toluene in octanol containing approximately 50 µg per ml, and calculate the exact concentration (C_R) in percent (w/v).
Sample solution: Transfer about 2 g of the sample, accurately weighed, into a 10-ml volumetric flask, dissolve in octanol, dilute to volume with the same solvent, and mix. Calculate the exact concentration of the solution (C_S) in percent (w/v).

Procedure:
Inject a 5-µl portion of the Standard solution into the chromatograph, and measure the height of the toluene peak (H_R) on the chromatogram. The toluene retention time is 3.3 min; other peaks are of no interest in this analysis. Similarly, obtain the chromatogram on a 5-µl portion of the Sample solution and of a blank consisting of octanol, and measure the height of the toluene peak (H_S).

Calculation:
Calculate the mg/kg of toluene in the sample by the formula:

$$H_S / C_R \times C_R / C_S \times 10^6$$

METHOD OF

Transfer about 170 mg of the sample, previously ground to a fine powder

ASSAY

and accurately weighed, into a 250-ml wide-mouth conical flask, and dissolve in 10 ml of methanol. Add 150 ml of water, 1 ml of N sulfuric acid, and 4 drops of diphenylamine indicator (3 mg of p-diphenylaminesulfonic acid, sodium salt, per ml of 0.1 N sulfuric acid), and titrate with 0.1 N ceric sulfate to the first complete colour change from yellow to red-violet. Record the volume, in ml, of 0.1 N ceric sulfate required as V.

Calculate the percent of $C_{10}H_{14}O_2$ in the sample, uncorrected for hydroquinone (HQ) and 2,5-di-tert-butylhydro- quinone (DTBHQ), by the formula:

$$(V - 0.1 \text{ ml}) \times N \times 8.311/W$$

where
0.1 ml = the volume of ceric sulfate consumed by the primary oxidation products of tert-butylhydroquinone ordinarily present in the sample
N = the normality of the standard ceric sulfate solution
W = the weight of the sample taken, in g.

Record the uncorrected percentage thus calculated as A. If HQ and DTBHQ are present in the sample, they will be included in the titration.

Calculate the corrected percentage of $C_{10}H_{14}O_2$ in the sample by the formula:

A - (%HQ x 1.51) - (%DTBHQ x 0.75)

using the respective values for % HQ and % DTBHQ as determined by the gas chromatographic procedures given above.