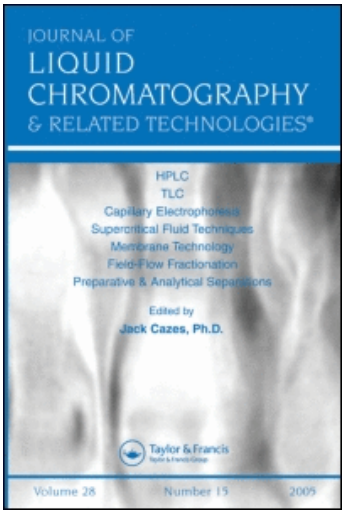

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Active TBC in Butadiene by HPLC

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ACTIVE TBC IN BUTADIENE BY HPLC

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ABSTRACT

A high performance liquid chromatographic method has been developed for the determination of active 4-tert-butylcatechol (TBC) in 1,3-butadiene. Following evaporation of the butadiene from an aqueous m-nitrophenol internal standard solution, a 20-microliter aliquot is injected onto a reversed-phase liquid chromatographic column. Recovery of TBC was found to be quantitative over a 17-242 ppm range with a relative standard deviation of 3.8%.

INTRODUCTION

The polymerization inhibitor 4-tert-butylcatechol (TBC) or 4-(1,1-dimethylethyl)-1,2-benzenediol in 1,3-butadiene has been historically determined by colorimetric methods such as ASTM method D1157 (ref 1). In these methods the catechol

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is deliberately oxidized to the colored quinone which is measured by a suitable photometer. This means, however, that these methods are not able to differentiate between the active inhibitor and its oxidized, inactive, form. Therefore, a method that specifically measures the concentration of the active inhibitor would be of considerable importance for industry with respect to butadiene stability during shipping, storage and immediately prior to polymerization. We have developed an analytical method for the determination of the active TBC in liquid butadiene.

MATERIALS

Apparatus :

A modular HPLC has been used throughout this investigation. A Waters M6000A pump or a Spectra-Physics SP8700 pump were applied as a solvent delivery system. Reversed-phase columns included LiChrosorb®RP-18 10 micron or Hypersil ODS packings. A LDC model 1203 UV detector was used with wavelength set at 280 nm. In all cases, a Valco injection valve with a twenty-microliter fixed loop was applied. The unit was interfaced with a Hewlett-Packard 3354 Laboratory Data System.

Reagents :

All reagents were of recognized analytical grades such as TBC (BDH 27520), m-nitrophenol (Baker 1357), methanol (Baker 8045), acetic acid (Baker 6052) and chloroform (Baker 7386). Deionized water from a Milli-Q® system (Millipore Corporation) was used as the extraction liquid. Inhibitor-free butadiene samples in stainless steel containers equipped with an inlet and an outlet valve came directly from our production plant.

Chromatographic conditions :

Column : 250 x 4.6 mm, reversed-phase packing
Eluent : methanol/water/acetic acid, 67/32/1 by volume
Flow rate : 1.5 mL/min.
Detector : 280 nm
Injection : 20 microliter via fixed loop

METHOD

Cool sample container and a 25-mL graduated cylinder to about -20 degC. Measure 25 mL of liquid sample into the graduated glass cylinder. Pour the sample into a 50-mL vial containing 25 mL of internal standard solution (25 mg m-nitrophenol per liter of water) and allow the butadiene to evaporate at room temperature in a fume hood. After the upper organic layer has completely evaporated, close the vial and shake the contents for one minute. Inject the resulting extract into the chromatograph and obtain peak areas for TBC and the internal standard (IS). The ratio of peak areas TBC/IS is used for quantitation. A calibration graph is prepared by analyzing solutions of TBC in water with a concentration range of 0-150 mg/L. These solutions are prepared by adding 0-150 microliter aliquots of a solution containing 2.50 g TBC in 100 mL chloroform to 25-mL aliquots of the internal standard solution.

RESULTS AND DISCUSSION

Figure 1a depicts a typical chromatogram for a sample containing 134 mg TBC per liter liquid butadiene sampled at - 20 degrees C. This corresponds to (134/0.6681=) 200 mg TBC per kg liquid butadiene (ppm by weight).
Linearity of response is excellent as shown in figure 2.

The repeatability of the prescribed analytical method was determined by analyzing an actual sample 10 times, 5 ti-

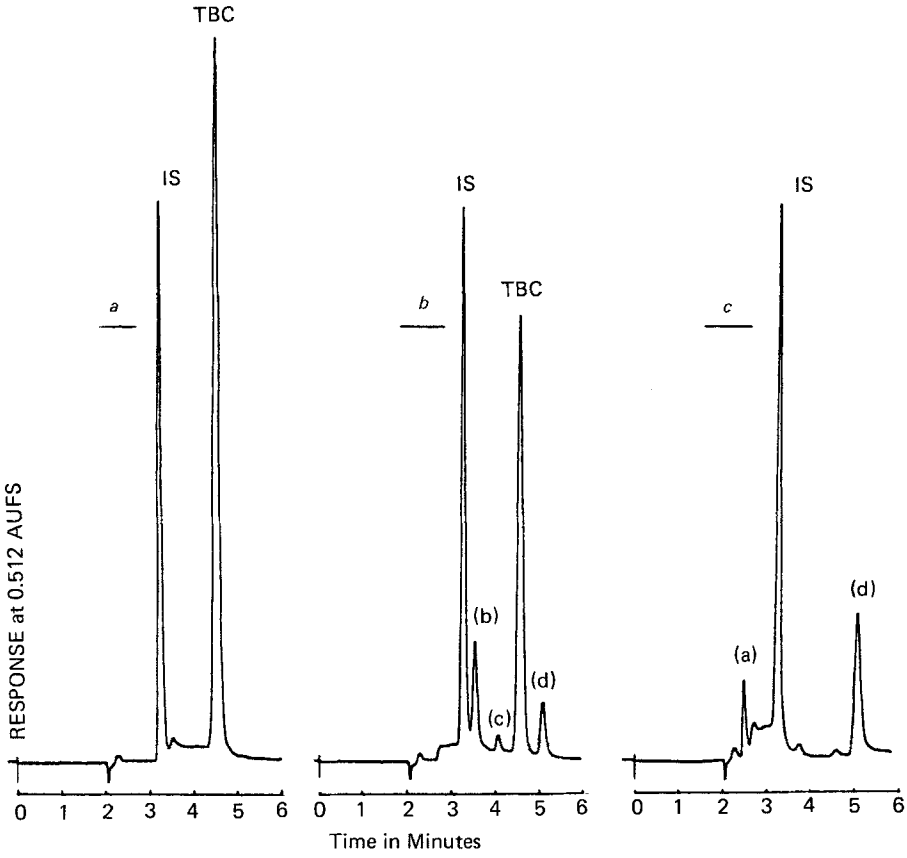


Figure 1: Chromatograms.

1a Normal sample extract (IS = m-nitrophenol),

1b Same solution with addition of NaOH, after 1 minute.

1c Same as 1b, except after 10 minutes.

mes on two successive days. A mean concentration of 95 mg/kg was obtained with a relative standard deviation of 1.9%.

The absolute recoveries of the inhibitor were determined by adding known amounts of TBC from a chloroform solution to inhibitor-free butadiene in stainless steel containers. These spiked samples were then extracted and measured in the normal manner. Recovery was quantitative within the experimental error of the method as shown in Table I.

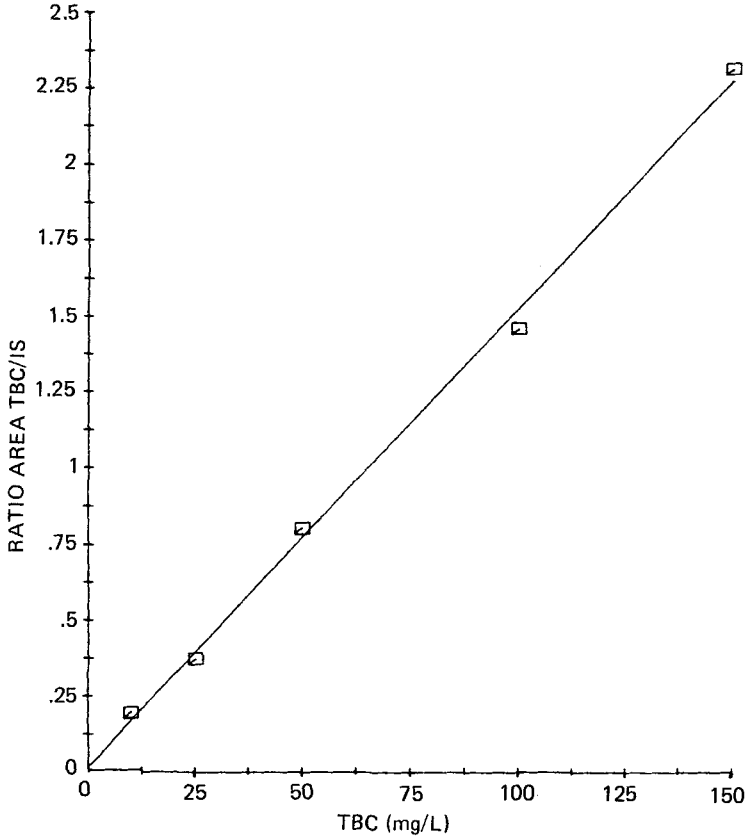


Figure 2: Calibration graph.
Regression data: slope 1.5118E-02, intercept 1.5079E-02, correlation coefficient 0.9987.

TABLE I : Recovery data for TBC added to butadiene.

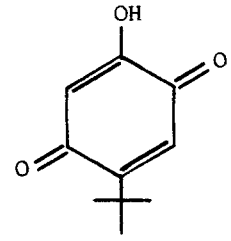
TBC added	TBC found	Recovery
16 mg/kg	17 mg/kg	106 %
40	39	98
79	79	100
159	153	96
238	242	102
Mean recovery		100 %
Relative standard deviation		3.8 %

In order to demonstrate that with this method only the active form of TBC is measured, the following experiment was performed. To 25 mL of an aqueous extract (figure 1a) 200 microliters of sodium hydroxide solution (4N) was added, shaken for 1 minute and immediately chromatographed. Figure 1b shows the decrease of the TBC peak while oxidation products, labeled (b), (c) and (d), are appearing. After another 9 minutes the mixture was injected again with the results vizualized in figure 1c. Now the TBC peak has almost completely disappeared and another reaction product, (a), has appeared.

An experiment was undertaken to isolate and identify the aqueous-caustic oxidation product of TBC. A 25-mg sample of TBC was dissolved in 0.5N sodium hydroxide. Air was bubbled through the solution at a rate of approximately five bubbles per second for ten minutes. The solution was placed in a separatory funnel, acidified with dilute sulfuric acid, and extracted with 5 mL of chloroform. The chloroform extract was washed with an equal volume of water and evaporated under a stream of nitrogen.

Examination of the residue by IR, NMR and MS, together with elemental analysis, proved the oxidation product to be:

2-tert-butyl-5-hydroxy-p-benzoquinone



Injection of this compound into the liquid chromatograph under the conditions used for the TBC analysis gave a peak that had an identical retention time as peak (d) in figure 1c. However, since this peak was generated by alkaline oxidation of TBC, in the butadiene it may be different than oxidation products that result from normal storage of the product. Pilar et al (ref 2) made an electron paramagnetic resonance (EPR) study on the mechanism of the autoxidation of 4-tert-butylcatechol and showed 2-tert-butyl-5-hydroxy-p-benzoquinone to be the final product. The mechanism was in agreement with that of Stone and Waters (ref 3).

Since the mobile phase in the described procedure is acidic, there was some concern as to the durability of the HPLC packing. Using a pneumatically-operated injection valve, a solution of inhibitor with internal standard was automatically injected 36 times a day for 6 weeks, over 1500 injections in all. There was no loss in column efficiency over the period of the test.

It is concluded that a reliable and an accurate analytical method has been developed that enables the specific measurement of active TBC in liquid butadiene.

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