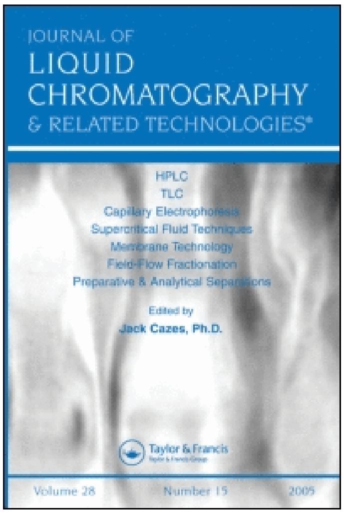

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Hlavačková, E. , Mlejnek, O. and Berek, D.(1990) 'Analysis of 4-Tert-Butylpyrocatechol in Styrene by Solid Phase Extraction and High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 13: 15, 3053 — 3060

To link to this Article: DOI: 10.1080/01483919008049087

URL: http://dx.doi.org/10.1080/01483919008049087

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(15), 3053-3060 (1990)

ANALYSIS OF 4-TERT-BUTYLPYROCATECHOL IN STYRENE BY SOLID PHASE EXTRACTION AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A solid phase extraction procedure has been developed to isolate and preconcentrate 4-tert-butylpyrocatechol and its oxidation products from styrene. The eluted amount of 4-tert-butylpyrocatechol from the cartridges was determined by reversed phase HPLC. External calibration method was used in the concentration range between 3 and 80 ppm of 4-tert--butylpyrocatechol and mean recovery was found to be 97 % with a relative standard deviation of 3.4 %.

INTRODUCTION

Monomeric styrene is an important material for manufacturing many polymer products including electrical insulations. However, this monomer is sensitive to heat, light and various impuritied that can lead to undesirable polymerization during shipping, storage and technological processes. Consequently, inhibitors must be added to styrene. One of the most common inhibitors is 4-tert-butylpyrocatechol (TBC). The concentration of TBC in styrene is an important criterion of its stability. Colorimetric methods (1,2) determine the total amount of both TBC and its oxidation products (3).

The knowledge of the amount of the original unchanged TBC is therefore important for practice. Domens et al. (4) have proposed the reversed phase liquid chromatography for the determination of TBC in butadiene. However, the direct injection of the styrene samples into an HPLC column is problematic owing to the low concentration of TBC and the undesirable effects of the high excess of styrene alone. Solid phase extraction (SPE) technique was applied to solve this problem. A method for determining TBC in styrene based on the combination of SPE and reversed phase HPLC is described in the present paper.

MATERIALS AND METHOD

HPLC

The chromatographic system included the HPLC pump, model 364.00, the Spectrophotometric detector with the Lambda selector, model 87.00 all from KNAUER, FRG, the valve-loop injector with a twenty microliter fixed loop RHEODYNE, USA, model 1125 and the integrator SHIMADZU, JAPAN, model C-R6A. The UV detector was set at a wavelength of 280 nm. A silica gel based reversed phase glass column (150 mm x 3.3 mm

Separon SGX C 18, 5 µm TESSEK, Czechoslovakia) was used. The mobile phase consisted of a mixture of methanol, water and acetic acid, 67:32:1 by volume. External calibration method was used as a quantitation method. Calibration was done by injection of the solutions of a TBC standard in the mobile phase, concentration ranging from 3 to 80 ppm. Chromatography was carried out at ambient temperature at a mobile phase flow rate of 0.5 ml/min.

Reagents

Styrene, technical grade, with TBC in the concentration range from 10 to 40 ppm, determined by the colorimetric method (2) was obtained from the Company KAUČUK KRALUPY, CZECHOSLOVAKIA. Inhibitor-free styrene samples were prepared in two steps. First, technical styrene was extracted with 1 M sodium hydroxide of analytical grade from LACHEMA, CZECHOSLOVAKIA (2:1), then it was vacuum distilled in an inert atmosphere. Analytical grade TBC was obtained from FLUKA, SWITZERLAND. Solvents for HPLC and SPE, analytical grade, were obtained from LACHEMA; acetic acid was used as received without any purification; methanol, chloroform and heptane were glass distilled; water was distilled twice.

SPE

Disposable cartridges Separcol were supplied by Polymer Institute CCR, Slovak Academy of Sciences, Bratislava. Separcol minicolumns containing 400 mg of bare silica gel were conditioned by passing 30 ml of chloroform with 300 µl acetic acid. Then 5 ml of the sample was added and the

TABLE 1

Recovery Data for TBC added to Styrene

Sample No.	TBC-added [ppm]	TBC-found [ppm]	S.D. [%]	Recovery [%]
1	3.0	3.0	2.65	99
2	5.0	5.1	4.30	102
3	10.1	10.0	3.51	99
4	20.0	18.6	1.81	93
5	30.5	29.3	2.28	97
6	39.9	37.6	2.34	95
7	76.9	71.8	1.89	93

column was flushed with 15 ml of heptane to wash out interfering substances. The retained compounds were eluted with 10 ml of chloroform containing 100 μl of acetic acid. Finally, this effluent was evaporated under a stream of inert gas and the residue was redissolved in 2 ml of the mobile phase.

RESULTS AND DISCUSSION

Table 1 shows the results of the analyses of various concentrations of TBC performed in 9 parallel determinations together with absolute recoveries and relative standard deviations. Satisfactory repeatability was confirmed by the sample analysis containing 39.9 ppm TBC in 9 parallel

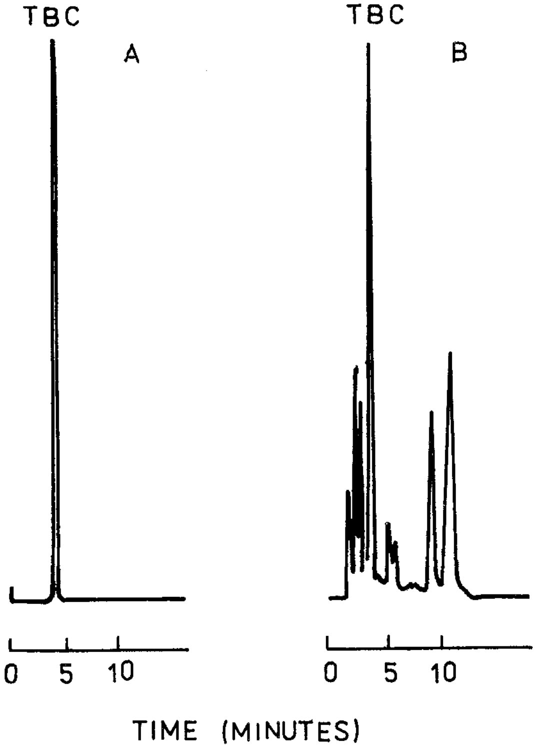

FIG. 1. Chromatograms of TBC in styrene. Chromatographic conditions: Reversed phase glass column Separon SGX C 18, 5 /um, 150 x 3.3 mm. Mobile phase-methanol: water:acetic acid (67:32:1), flow rate 0.5 ml/min, UV detector: 280 nm, injection 20 /ul with fixed loop.
A. TBC added to inhibitor-free styrene
B. TBC in technical grade styrene.

determinations the following days; the relative standard deviation and recovery found were 2.34 % and 95 % respectively. Fig. 1A shows the chromatogram of the inhibitor-free styrene with 76.9 ppm TBC added. The calibration graph was constructed by plotting the peak area

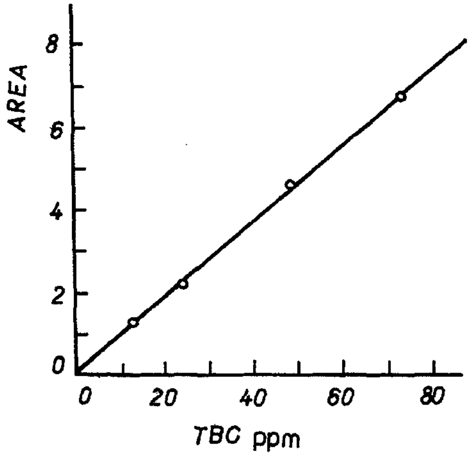

FIG. 2. Calibration graph. Y = 0.9245X + 0.0593 Reasonable response linearity is indicated by correlation coefficient of 0.9998.

of TBC versus its concentration in ppm as demonstrated in Fig. 2.

The above method was applied to the determination of TBC in technical styrene. Fig. 1B shows an example of this separation. The amount of TBC in technical styrene was analysed by the described HPLC and colorimetric methods (2). Results are summarized in Table 2. Apparent differences can be noticed between the results of the two methods used that can be explained by the different principles of the methods. By the colorimetric method, not only the amount of TBC alone is determined, but also its oxidation products i.e. quinone mixture. On the other hand, SPE/HPLC method presented here gives only the amount of unchanged TBC.

TABLE 2

Determination of TBC in Technical Styrene

Sample No.	TBC HPLC [ppm] average	S.D. [%]	TBC colorimetry [ppm]
1	18.3	4.75	25.3
2	18.2	3.81	24.9
3	18.2	5.91	24.7
4	23.0	4.92	40
5	24.2	2.89	40
6	25.3	5.93	40
7	25.6	2.30	40
8	25.4	1.14	40

TBC is known to undergo chemical reactions in the presence of air and alkalis to form various oxidation products (4,5). A different situation may arise when TBC in styrene enters the inhibition reactions (6,7). Fig. 1B shows, in comparison with the chromatogram in Fig. 1A a number of new peaks which may correspond to the transformation products of TBC.

ACKNOWLEDGEMENTS

The authors would like to thank T. MACKO for valuable discussions and I. BARKOVÁ for colorimetric analyses.

REFERENCES

1. ANSI/ASTM D 1157-59 (Reapproved 1978), "Total Inhibitor Content (TBC) of Light Hydrocarbons", ASTM, Philadelphia, PA, USA.
2. ANSI/ASTM D 2120-82 "Inhibitor p-tert-butylpyrocatechol in Styrene Monomer". ASTM, Philadelphia, USA.
3. Kline, N., Analytical Chemistry of Polymers I. Monomers and Polymeric Materials Part I, Interscience publishers, INC., New York, 1959, p. 421.
4. Domens, A.C., Schuurhuis, F.G., and Skelly, N.E., Active TBC in Butadiene by HPLC, J. Liq. Chromatogr., 7, 2143, 1984.
5. Pilař, J., Buben, I., Pospíšil, J., Oxidation of Pyrocatechol VIII. EPR Study of the Mechanism of Autooxidation of 2-Tert-Alkylhydroquinones and 4-Tert--Alkylpyrocatechols Collection Czechoslov. Chem. Commun., 35, 489, 1970.
6. Levy, M., Louvain-Neuve, The Activity of Phenollic Antioxidants in Rubber Applications - Theory and Practice. Kautschuk, Gummi, Kuntstoffe, 40, 1043, 1987.
7. Pospíšil, J., Transformation Products of Antioxidants: The Role in Stabilization Mechanisms, Angew. Makromol. Chem., 158/159, 209, 1988.