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Comparison of colorimetric and chromatographic determination of *tert.*-butylpyrocatechol

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ABSTRACT

A high-performance liquid chromatographic method for the determination of 4-*tert.*-butylpyrocatechol (TBC) in styrene after its preconcentration by a solid-phase extraction technique is compared with a colorimetric method based on absorbance measurement of TBC products formed with alkaline hydroxide. The differences between the results obtained with both methods when applied to technical samples and samples enriched with prepared TBC oxidation products are discussed. It is assumed that in the high-performance liquid chromatographic method only unchanged TBC is determined, while in the colorimetric method its transformation products are also included. Apparently, oxidation products contribute to a measurement which represents neither the concentration of remaining TBC nor the total concentration of TBC and its oxidation products in the sample.

INTRODUCTION

Technical styrene undergoes undesirable polymerization during shipping, storage and technological processes and it is therefore stabilized with 4-*tert*-butylpyrocatechol (TBC) in the concentration range 10–50 ppm. For industrial applications, the content of TBC in the monomer is an important criterion. Colorimetric methods have been frequently used for its determination. The total amount of TBC is currently determined by an alkaline method [1] utilizing the formation of coloured oxidation products with sodium hydroxide. A similar principle is applied in the test method of the American Society for Testing and Materials (ASTM) [2] for determination of total TBC content in light hydrocarbons. In another method the intensity of the yellow-coloured complex of TBC with ferric chloride is measured by a suitable photoelectric photometer.

The above-mentioned methods are not capable of distinguishing between original TBC and its transformation products formed during inhibition processes. Another colorimetric method is based on the reduction of Fe^{3+} with inhibitor to Fe^{2+} and on the measurement of the absorbance of its complex with 1,10-phenanthroline. The above method is limited to the non-oxidized form of phenolic and the total amount of aminic inhibitors and has been applied to the quantitative analysis of the following inhibitors: TBC, hydroquinone, 2,6-*tert.*-butyl-4-methylphenol and *n*-phenyl-*n*′-izopropyl-*n*-phenylendiamine [3]. Later the same authors [4] published a paper dealing with the comparison of photocolorimetric methods for determination of the total content and unchanged portion of inhibitors.

High-performance liquid chromatography (HPLC) has also been shown to be a useful method for determination of phenolic inhibitors, antioxidants and light stabilizers [5–9]. An HPLC method was developed for the determination of 4-*tert*-butylphenol and TBC by Gaguardi *et al.* [10]. For the determination of only the active form of TBC in butadiene an HPLC method was published by Oomens *et al.* [11].

In a recent paper we have reported an HPLC method [12] for determination of TBC in styrene. The separation conditions were similar to those in the above-mentioned method [11], but a solid-phase extraction (SPE) technique for preconcentration and preseparation of TBC from styrene was used. In the present study the results of a comparison of HPLC and an alkali colorimetric method for the determination of TBC in styrene are presented and discussed.

EXPERIMENTAL

Reagents and chemicals

TBC of analytical grade was obtained from Fluka (Switzerland) and styrene of technical grade stabilized with TBC was obtained from Kautshuk (Czechoslovakia) as well as from Prochema (Austria).

The oxidized form of TBC was prepared from TBC by reaction with sodium hydroxide [11] in various modifications. For TBC_{OX}, each solution of TBC in 1 *M* sodium hydroxide was mixed for 30 min; moreover TBC_{OXI} was mixed and saturated with oxygen for 30 min; TBC_{OXII} was saturated with oxygen for only 15 min; TBC_{OXIII} was saturated with oxygen for only 10 min; TBC_{OXIV} was saturated with oxygen for 5 min, and TBC_{OXV} was prepared without saturation. In Table I the concentrations of TBC in such prepared samples are shown.

Solvents and reagents for both HPLC and colorimetric determination, all analytical grade, were from Lachema (Czechoslovakia); acetic acid was used as received without purification; methanol, chloroform and *n*-heptane were glass-distilled; water was doubly distilled.

Calibration standards and standard samples were prepared by addition of 2–32 ml of TBC stock solution (0.113 g of TBC in 1000 ml of inhibitor-free styrene) to inhibitor-free styrene.

TABLE I

HPLC ANALYSIS OF TBC_{OX} IN THE MOBILE PHASE

Sample	TBC found (mean ± R.S.D.) (%)
TBC_{OXI}	0
TBC_{OXII}	6.74 ± 4.66
TBC_{OXIII}	16.72 ± 5.03
TBC_{OXIV}	66.36 ± 4.85
TBC_{OXV}	105.06 ± 5.93

Inhibitor-free styrene was prepared by washing the monomer three times with an equal volume of a 1 *M* solution of sodium hydroxide in water followed by washing with water until neutral to litmus.

Methods

For chromatographic determination of TBC in styrene, an HPLC [12] method was used.

For colorimetric determinations of TBC in styrene the ASTM test method [1] was applied using a Model 559 UV–VIS spectrophotometer from Perkin Elmer (USA), wavelength 700–800 nm, with PTFE-covered glass rectangular cells: *d* (optical path length of cell) = 10 mm, scan speed = 480 nm/min, slit = 2 nm.

RESULTS AND DISCUSSION

The calibration graph in Fig. 1, in which curve A shows the dependence of absorbance on TBC concentration, was constructed on the basis of spectrophotometric measurements at a wavelength of 485 nm. It can be seen that this dependence is not linear but cubic, with the following parameters: $y = -4.11 \cdot 10^{-3} + 3.79 \cdot 10^{-3} x + 5.87 \cdot 10^{-5} x^2 - 3.53 \cdot 10^{-3} x^3$. However, at TBC concentrations above 18 ppm a linear relationship is obtained with a correlation coefficient $r = 0.9994$.

It was assumed that this non-linearity at low concentrations is due to the procedure of extracting TBC from styrene with 1 *M* sodium hydroxide.

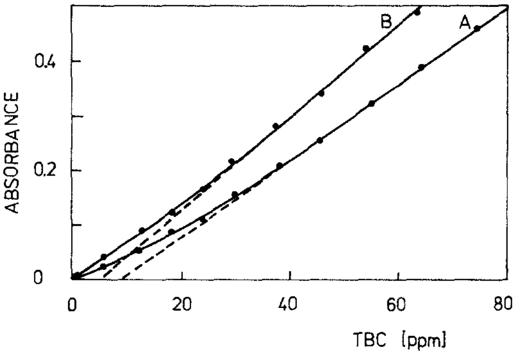

Fig. 1. (A) Calibration graph for UV–VIS spectrophotometric measurements. (B) Dependence of absorbance on TBC concentration after reaction with 1 *M* sodium hydroxide.

However, this assumption was not confirmed by the following experiments. Various amounts of TBC were weighed directly into 1 *M* sodium hydroxide, then shaken for the same time as in the above method in an arbitrary atmosphere. Finally the absorbance of the solution was measured at a wavelength of 485 nm at 1-min intervals for 18–20 min. These experimental values were expressed as the dependence of absorbance on TBC concentrations. It was found that the curve thus obtained, curve B in Fig. 1, also conforms to a cubic relationship at lower concentrations. This is most likely because of the oxidation processes of TBC followed by decomposition of products formed in alkaline medium; moreover, the relative portion of air present is higher at lower concentrations. The influence of the time on the reaction of TBC with sodium hydroxide is shown in Fig. 2. A continuous decrease of absorvance with time, which is linear after 12–15 min, can be seen.

This phenomenon can be explained with the help of Fig. 3, in which the absorbance of the TBC mixture with sodium hydroxide was continuously recorded at intervals of 4–60 min. Such UV–VIS spectra are characteristic of a system in which the compounds undergo mutual chemical changes.

From the results obtained it can be concluded that the reaction time of 15 min prescribed by the ASTM method [1] must be rigidly adhered to.

The calibration graph of the HPLC method for the determination of TBC [12], unlike that of the colorimetric analysis, shows a linear relationship with a correlation coefficient of 0.9998. The direct measurement of unchanged TBC by the former method is the reason for this behaviour.

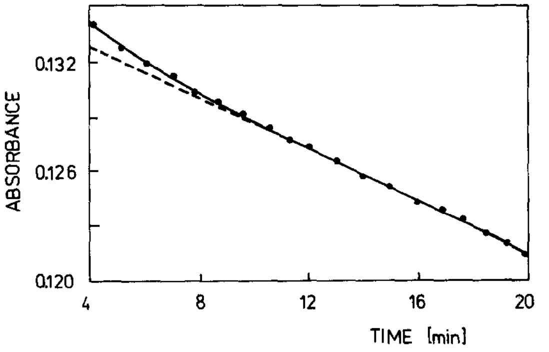

Fig. 2. Decrease in the absorbance of TBC solution with time (18.33 ppm TBC in 1 *M* sodium hydroxide).

For the comparison of both methods, standards, technical samples of styrene and samples containing oxidation products were analysed.

Standard samples

Table II summarizes the results of the analysis of various TBC concentrations performed in nine parallel determinations with HPLC and three parallel determinations with the UV–VIS spectrophotometric method. The accuracy of these results was confirmed by the Student and Lord test; evaluation of the comparison was confirmed by the Moor test at a significance level of 0.5. The results represented by confidence intervals agree well with the amounts added in both methods, when applied to standard (model) samples.

Technical samples

The results of the analysis of three technical styrenes are shown in Table III. Various differences between the HPLC and UV–VIS spectrophotometric measurements can be seen. HPLC separation of the above samples is illustrated in Fig. 4. Serious differences can be seen in these three chromatograms of technical styrenes. They can be explained by the presence of various amounts and types of TBC transformation products. The type and amount of these products are strongly dependent

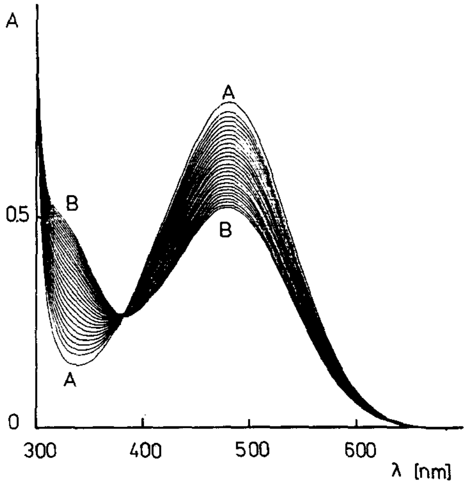

Fig. 3. UV–VIS spectra of 9.06 ppm TBC in 1 *M* sodium hydroxide scanned at 2-min time intervals: (A) reaction time 4 min; (B) reaction time 60 min.

TABLE II

RESULTS OF HPLC AND UV-VIS SPECTROPHOTOMETRY OF STANDARD SAMPLES

TBC added (ppm)	TBC found (ppm)	
	HPLC (mean ± S.D.)	UV-VIS (mean ± S.D.)
4.52	4.42±0.53	4.33±0.44
13.56	–	13.41±0.59
22.60	22.47±0.63	23.45±1.57
40.68	39.95±0.95	41.73±0.93
58.76	58.08±0.90	59.28±1.86

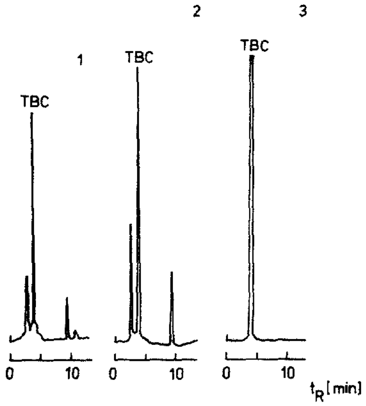

Fig. 4. Chromatograms of TBC in three technical styrenes (see Table III). Chromatographic conditions: reversed-phase glass column Separon SGX C_{18}, 5 μm particle size, 150 × 3.3 mm I.D., mobile phase, methanol-water-acetic acid (67:32:1, v/v/v); flow-rate, 0.5 ml/min; UV detector wavelength, 280 nm; injection, 20-μl sample with fixed loop.

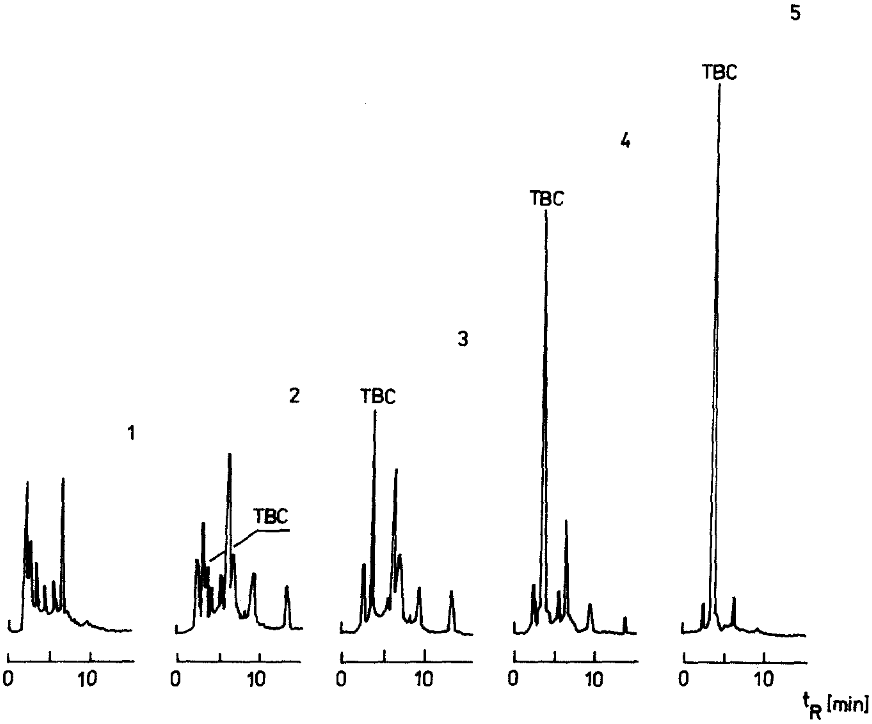

Fig. 5. Chromatograms of TBC oxidation products in styrenes (see Table IV). Chromatographic conditions as above. 1 = TBC_{OXI}; 2 = TBC_{OXII}; 3 = TBC_{OXIII}; 4 = TBC_{OXIV}; 5 = TBC_{OXV}.

TABLE III

THE RESULTS OF HPLC AND UV–VIS SPECTROPHOTOMETRY OF TECHNICAL SAMPLES

Sample No.	TBC found (ppm)	
	HPLC (mean ± S.D.)	UV–VIS (mean ± S.D.)
1	15.76 ± 1.90	17.52 ± 0.37
2	18.38 ± 1.84	26.70 ± 1.85
3	42.38 ± 0.27	44.96 ± 2.01

on storage time and temperature. It is evident that these conditions were different in individual styrene samples.

Styrene with TBC_{OX}

From the results of the HPLC method it can be seen that an increasing amount of original (unchanged) TBC remained as the saturation time with oxygen decreased. It is evident that the composition of the mixture strongly depends on the reaction conditions. HPLC separation of TBC-free styrene enriched with all prepared oxidation products as described in the Experimental section is shown in Fig. 5.

Finally, the results of styrene enriched with TBC_{OX} by both mentioned methods are shown in Table IV. Significant differences in the TBC content as determined by both methods can be observed. However, the TBC concentrations obtained by spectrophotometry are remarkably higher than the results obtained by HPLC, which may be because in the former method both the oxidation products of TBC and the products of interaction of TBC with styrene radicals are included.

TABLE IV

HPLC AND UV–VIS SPECTROPHOTOMETRIC RESULTS OF STYRENE ENRICHED WITH TBC_{OX}

Sample	TBC_{OX} added (ppm)	TBC found (ppm)	
		HPLC (mean ± S.D.)	UV–VIS (mean ± S.D.)
1. TBC_{OXI}	40.80	0	20.33 ± 0.18
2. TBC_{OXII}	41.36	2.77 ± 0.23	29.94 ± 0.65
3. TBC_{OXIII}	41.96	10.64 ± 0.39	31.55 ± 1.27
4. TBC_{OXIV}	40.16	20.58 ± 0.36	29.73 ± 0.49
5. TBC_{OXV}	40.48	35.59 ± 0.61	36.83 ± 0.76

CONCLUSIONS

From the results obtained it is evident that the main differences between the HPLC and UV–VIS spectrophotometric methods are as follows. With HPLC, TBC is separated from its oxidation products and thus is determined in unchanged form. With UV–VIS spectrophotometry the absorbance of the reaction products with alkaline hydroxide as a whole is measured. Therefore the results of both methods, in the absence of TBC oxidation products, as in the standard samples and in the technical styrenes, include only traces of TBC transformation products. But significant differences were observed in samples of technical styrenes which had been stored for a long time under poor conditions and in model styrenes enriched with TBC oxidation products.

It can be concluded that the UV–VIS spectrophotometry alone, although a simple and effective method, is not applicable for severely aged styrene samples. For this purpose, as well as for investigation of transformation processes of TBC during styrene storage and synthesis of polymeric materials on styrene basis, the HPLC method should be preferred.

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