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Short communication

High-performance liquid chromatography with multi-wavelength detection of the bisphenol A impurities

J. Poskrobko*, M. Dejnega, M. Kiedik

Institute of Heavy Organic Synthesis, 'Blachownia'ul, Energetyków 9, 47-225 Kędzierzyn-Koźle, Poland

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Abstract

A reversed-phase HPLC method was developed for the analysis of 15 impurities present in the process streams from the production of bisphenol A. UV spectra were taken for standard components. These were evaluated and the detection wavelengths of 254, 280 and 305 nm were selected for the chromatograms to be recorded. Concurrent detection at the wavelengths selected of the chromatograms taken makes it easier to identify the components and considerably improves the accuracy of the quantitative analysis. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Impurities; Bisphenol A

1. Introduction

Bisphenol A [2,2-(4-hydroxyphenyl)-propane], a condensation product of phenol and acetone, makes an important feedstock for the production of epoxy resins, polycarbonates, polysulfones, etc. In order to improve the process economics, the basic synthesis can be accompanied by additional operations: decomposition or isomerization of by-products. These have been intended to recover the useful components but they simultaneously are a source of further groups of compounds, in addition to the main reaction by-products. More than 30 various by-products can be formed and circulated in various sections of a continuously operated commercial plant. Among the impurities present in bisphenol A different types of compounds can be found [1–3]: monophenols and polyphenols including compounds with a double bond in an aliphatic chain (oligomers of *p*-isopropenylphenol), derivatives of chromen, flavan, indan, etc.

Various chromatographic methods have so far been employed to identify and analyze the impurities of bisphenol A: thin-layer chromatography, paper chromatography, gas chromatography [3–7] and high-performance liquid chromatography (HPLC) [8–10]. Most of them can be employed to determine a few main impurities only. Eight impurities determined by gas chromatography with the use of derivatization has been reported [7].

This paper intended to develop a HPLC method for the determination of reaction by-products present in the samples taken from various units of a commercial bisphenol A facility.

2. Experimental

The study employed a HP 1090 liquid chromato-

*Corresponding author.

E-mail address: poskr@icso.com.pl (J. Poskrobko)

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Table 1
List of compounds studied[a]

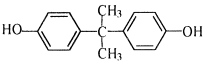
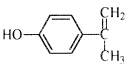
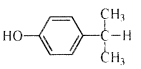
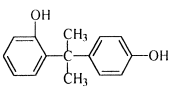
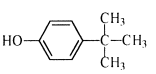
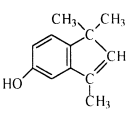
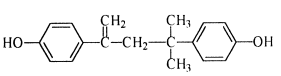
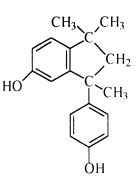
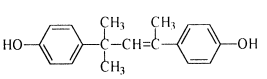
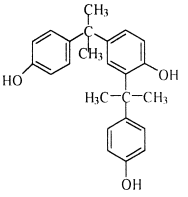
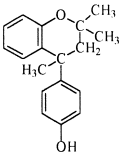
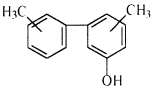
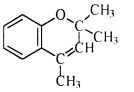
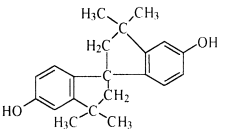
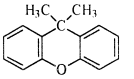
Peak No.	Retention time (min)	Compound	Structural formula
1	4.49	Phenol	
2	6.74	2,2-bis(4-Hydroxyphenyl)-propane (Bisphenol A)	
3		4-Isopropenylphenol	
4	7.78	4-Isopropylphenol	
5	8.93	2′,4″-Dihydroxy-2,2-diphenylpropane	
6	9.55	4-*tert.*-Butylphenol	
7	11.0	1,1,3-Trimethyl-5-indenol	
8	12.19	2,4-bis(4-Hydroxyphenyl)-4-methyl-1-penten	
9	12.59	1,1,3-Trimethyl-3-(4-hydroxyphenyl)-5-indanol	
10	12.90	2,4-bis(4-Hydroxyphenyl)-4-methyl-2-penten	

Table 1. Continued

Peak No.	Retention time (min)	Compound	Structural formula
11	14.25	2,4-bis(4-Hydroxycumyl)phenol, (trisphenol)	
12	16.11	2,2,4-Trimethyl-4-(4′-hydroxyphenyl)chroman, (codimer)	
13	16.38	Dimethylhydroxybiphenyl	
14	18.55	2,2,4-Trimethyl-2H-chromen	
15	19.78	1,1-Spiro-bis(3,3-dimethylindanol-5)	
16	21.96	10,10-Dimethylxantan	

[a] Peak numbers and retention times as per Fig. 1.

graph from Hewlett-Packard (Palo Alto, CA, USA), equipped with a diode array detection (DAD) system, which made it possible to collect data at a few wavelengths simultaneously and to take UV spectra. The determination was performed with a Hypersil ODS 120 Å, 5 μm column (200×4.6 mm) from Hewlett-Packard maintained at 40°C. The mobile phase was composed of methanol (HPLC grade) from Merck (Darmstadt, Germany) and water which was initially distilled and then additionally treated in a HP 661 water purifier from Hewlett-Packard.

The samples from different plant streams partially crystallized at room temperature and before weighing were melted at 60°C. About 0.5 g of the samples was dissolved in 10 ml of ethylene glycol and then introduced with the use of a 20 μl loop.

Standards of impurities were employed in the study which were obtained as described earlier [7].

3. Results and discussion

Table 1 presents the names and structural formulae for the standards employed, together with the num-

bers of their corresponding peaks and retention times for those peaks (please also refer to Figs. 1–3 for corresponding chromatograms).

DAD was employed to obtain the spectra for bisphenol A and standard impurities within 210–600 nm. Some compounds reveal their local absorption maxima at 254 nm, others at 280 nm, and the additional maximum at 305 nm can be observed for two compounds. Hence, these wavelengths were selected as working wavelengths for recording chromatograms.

3.1. Chromatographic resolution aspects

It was impossible to separate all the components as their properties were close to each other and any improvement in the separation of some compounds will result in decreased separation capacity for the remaining compounds. Determination of content of (5) and (12) is very important because concentration of the compounds attests to reaction of multi-stage isomerization of (5) to (2). The programme was thus optimized in order to separate (5) and (6), and to obtain the best possible separation for (12) and (13). The best results were obtained for the eluent flow-rate of 0.6 ml/min and when a gradient programme was employed: methanol–water (60:40) was used from the beginning of the analysis to minute 5. Then the methanol concentration was increased to reach 70% in minute 12.5 and a different concentration gradient was employed which brought the concentration to 100% in minute 17.5. The final concentration was maintained until minute 25. The retention times obtained at these conditions for the standard components are provided in Table 1.

Fig. 1 shows an example of analysis of a reaction mixture sample from a commercial plant; the sample contained an exceptional number of compounds. Individual peaks were identified on the basis of their retention times and agreement of the UV spectra for the impurities and standard compounds. Other peaks which can be seen in chromatograms represent unidentified components.

Fig. 2a presents the enlarged sections of chromatograms from Fig. 1, where dimers of (3) are eluted. The linear dimers (8, 10) and cyclic dimer (9) are partially coeluted. For linear dimers, unlike the cyclic dimer, the absorption is higher at 254 nm than at 280 nm. That difference makes it possible to clearly identify the corresponding peaks. Moreover, integration errors resulting from incomplete peak separation are reduced. At 254 nm absorption for the cyclic dimer (9) is nearly 20-times lower than at 280 nm. Thus, the share of this peak area in the total area integrated (for linear dimers) is almost negligible. This minimizes the error in quantitative determination of linear dimers. Similarly, the peak of the cyclic dimer (9) was integrated at 280 nm to reduce the effect from the neighboring linear dimers which have low bands in this range.

A similar situation was faced for a system of two peaks obtained at minutes 15.8 to 16.7 (Fig. 2b).

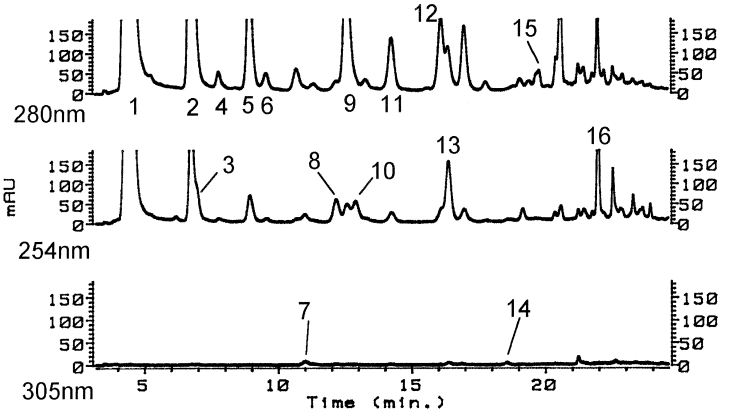


Fig. 1. Chromatograms for the reaction mixture, recorded at 254, 280 and 305 nm. Peak numbers as per Table 1. For analysis parameters refer to the text.

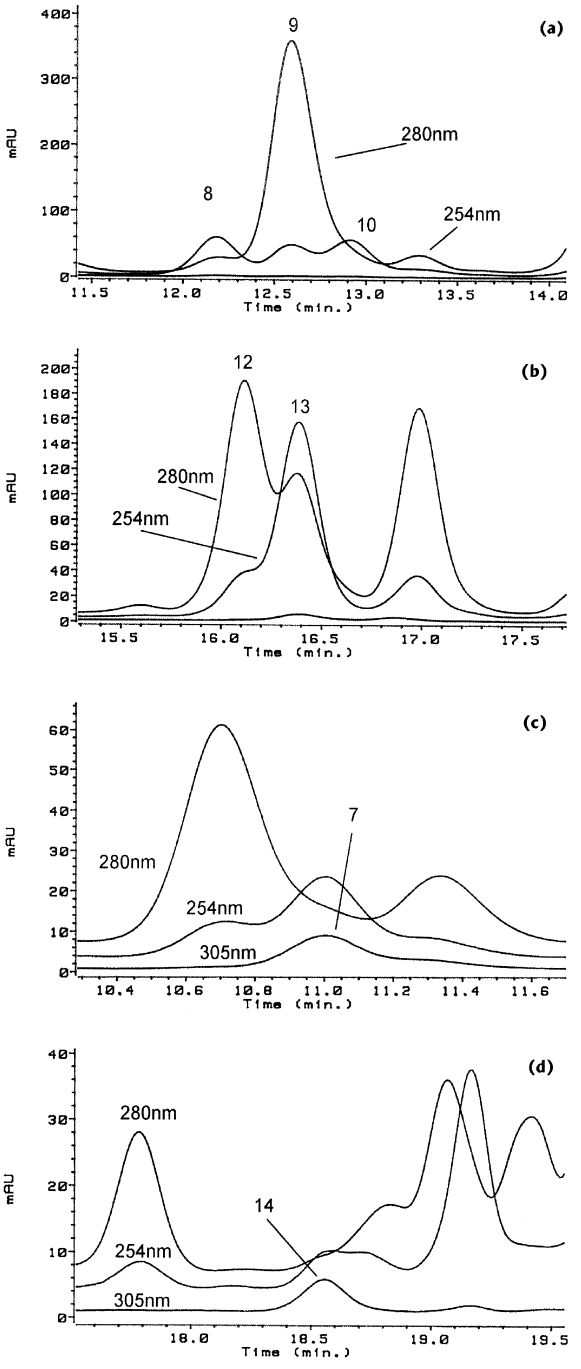


Fig. 2. Enlarged sections of overlapped chromatograms from Fig. 1.

(12) offers a much stronger absorption at 280 nm than at 254 nm while the peak of (13) is higher at 254 nm than at 280 nm. Hence, these compounds can be unequivocally identified and the error of their quantitative analysis can be minimized, despite the fact that their separation is not perfect.

(7) and (14) are present in the samples in small amounts and their separation is very poor (Fig. 2c and d, respectively). They are practically invisible at 280 nm. Their identification and quantitative determination became possible due to the fact that they were the only standards to have maximum absorbances at 305 nm.

Using the above gradient elution, (3) is eluted on the tail of the peak of bisphenol A. Since (3) is usually present in small concentrations it cannot be clearly distinguished from bisphenol A. This does not compromise monitoring of the process mixture since the concentration of (3) is proportional to that of (8). However, for the determination of bisphenol A purity the concentration of (3) needs to be known. In order to determine (3) analytically, the 40–100% gradient of methanol in water, over 30 min was employed, and with the flow-rate of 0.6 ml/min. Under these conditions (3) leaves the column just before the bisphenol A peak and it can be clearly seen at 254 nm and easily integrated. Fig. 3 shows a chromatogram for a product sample analyzed as above, where the (3) content is 30 ppm (w/w).

3.2. Quantitative aspects

The quantitative analysis was based on calibration by series of dilutions from the mixture of standards. The dependence between the area of the peak and the amount of each standard was determined. Table 2 presents the working wavelengths for individual components and the detector response factors f (expressed in conventional area units for the concentration of standard of 1 μg/ml).

The regression analysis of triplicate calibration data performed in the range 0.0005 to 0.025 g of the standards in 10 ml ethylene glycol has shown linear relationship with a correlation coefficient of about 0.94. The linearity range found corresponds to the by-products concentration range of 0.01 to 5% (w/w) in analyzed samples. (2) was calibrated in the range

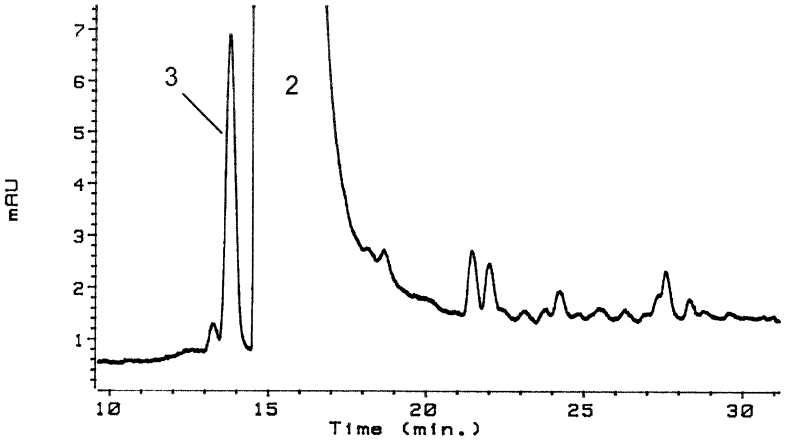


Fig. 3. Chromatogram for the determination of 4-isopropenylphenol (3) in the product. For explanation refer to text.

of amounts corresponding to concentrations of 5–30% in the sample.

(3) and (10) are difficult to prepare and store in pure form because they polymerize. Thus, in routine analyses to determine their concentration, we use detector response factor of (8).

In order to evaluate the content(s) of unknown components, the detector response equivalent to that for (2) was used. For the final section of the chromatogram in the case of unknown peaks with higher absorption at 254 nm, the detector response was used which was equivalent to that for (16).

Table 2 also provides results obtained from the calculation of concentrations for the compound determined in the sample from plant stream presented in Fig. 1.

The repeatability of the method was examined on one sample. Results are means of five replicates of the same sample which underwent the whole analytical procedure. Standard deviations (SDs) and relative standard deviations (RSDs) for the main compounds are reported in Table 2.

Table 2
Detector response factor (f) and component concentrations for exemplary sample

Peak No.	Wavelength (nm)	Detector response factor f	Concentration in sample (%, w/w)	SD	RSD (%)
1	280	7.81	70.0		
2	280	17.4	18.9	0.208	1.1
4	280	14.2	0.27		
5	280	18.1	1.12	0.047	4.2
6	280	1.11	2.58		
7	305	17.5	0.04		
8	254	42.9	0.10		
9	280	22.4	0.98	0.058	5.9
10	254		0.10		
11	280	20.4	0.53	0.027	5.1
12	280	13.4	0.78	0.098	12.6
13	254	119	0.11		
14	305	25.4	0.01		
15	280	26.0	0.09		
16	254	26.6	0.42		
Σ unknown			3.94		

4. Conclusion

The acquisition of the UV spectra allowed us to estimate the variety of the examined compounds. Hence the optimal detection wavelengths (254, 280, 305 nm) were selected for each group of the impurities. The chromatographic separation was optimized and simultaneously detection at three selected wavelengths was employed. This resulted in a method which is both handy in visualization of individual components and gives good quantitative findings. The method allows to determine 14 impurities of bisphenol A in one run as well as to estimate the contents of unidentified compounds.

The chromatographic separation was proved over a period of more than 2 years. Stability of calibration was also satisfactory and some minor corrections were introduced periodically, e.g., after the deuterium discharge lamp was replaced. The most serious practical problems result from chemical instability of some standards. But the eventual decomposition/polymerization of used standards becomes visible in the chromatograms of the calibration mixtures. Where it is necessary, the content of (3) is determined in an additional run.

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