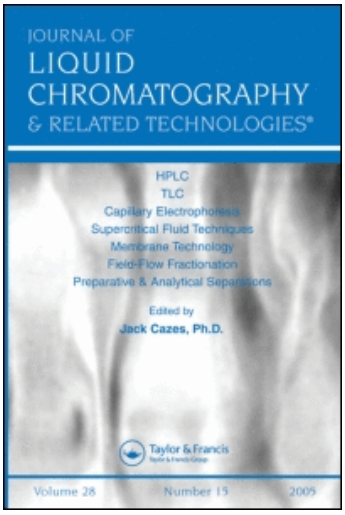

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Szap, Peter , Kesse, Ivar and Klapp, Jack(1978) 'The Analysis of Bisphenol a by High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 1: 1, 89 — 96
To link to this Article: DOI: 10.1080/01483917808068380
URL: http://dx.doi.org/10.1080/01483917808068380

JOURNAL OF LIQUID CHROMATOGRAPHY, 1(1), 89-96 (1978)

THE ANALYSIS OF BISPHENOL A BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

The quantitative analysis of bisphenol A (BPA) can be rapidly and accurately carried out by reverse phase liquid chromatography using a 1 foot micro Bondapak C-18/Porasil column and a gradient elution system consisting of water-acetonitrile where the latter increases from 45 to 75% over 20 minutes.

INTRODUCTION

Bisphenol A (4,4'-isopropylidenediphenol) is an important raw material used in the production of a variety of polymers such as epoxy resins, polycarbonates and polysulfones with epoxy resins consuming most of the production. Commercial bisphenol A varies from 92 to 99+% in purity and therefore it becomes increasingly important to monitor the quality quickly and accurately. Since 1956, the annual domestic production has risen from 37 MM pounds to 600 MM pounds at present and during this time many analytical techniques have been applied. The major high boiling impurities in bisphenol A were originally identified by Anderson, Carter and Landua [1] as 2,4'-bisphenol A (2,4'-isopropylidenediphenol); Dianin's compound (4,4'-hydroxylphenyl-2,2,4-trimethylchroman),

also called monophenol or codimer; and trisphenol [2,4-bis(α,α-dimethyl-4-hydroxybenzyl)phenol], also called BPX. Despite the widespread use of bisphenol A as a raw material for polymer production, no suitable quantitative and rapid analysis appears in the literature. Paper chromatography was employed by Anderson, Carter and Landua (1), Challa and Hermans (2), and Reinking and Barnabeo (3). Aurenge, Degeorges and Normand (4), and Zowall and Lewandowska (5) used thin-layer chromatography. Unfortunately, quantitative results are difficult to obtain with these techniques. Gas chromatography has also been tried for analysing bisphenol A. Direct injection by Tominaga (6) and Davis and Golden (7) led to problems of tailing and catalytic decomposition in the injection port which generated free phenol. Gill (8) acetylated bisphenol A and Brydia (9) employed trimethylsilylation prior to injection. These procedures, however, can be time consuming, cause detector fouling, or are susceptible to inaccurate results. Methylation is undesirable due to the toxicity of dimethylsulfate as the methylating reagent. This paper describes a liquid chromatographic procedure which is not only rapid, but provides accurate analyses for all the impurities of interest.

METHOD

Apparatus

A Waters Associates Model 204 Liquid Chromatograph equipped with a Model M660 solvent programmer, two Model 6000A pumps, a U6K closed loop injector, and a Model 440 dual channel UV detector at 280 nm was used. The column was 1 foot by 1/4 inch containing

micro-Bondapak C-18/Porasil (Waters Associates) and the gradient eluting system consisted of 45% acetonitrile and 55% water programmed to 75% acetonitrile at a 1.0 ml per minute flow rate over a 20 minute scan conforming to curve 7. Integration of the peaks was carried out with a Spectra Physics Minigrator operated under the following parameters: peak width 15; slope sensitivity 40; baseline parameter 3; tailing peak 50; minimum area 50; attenuation 1; spike and plateau reject 0. A Varian recorder Model A25 at a 10 mv attenuation was used.

Chemicals

The acetonitrile (non-spectro) was obtained from Burdick and Jackson and the water prepared by passing distilled water consecutively through a mixed bed ion-exchanger, carbon black, and a 0.45 Millipore filter, and then 3 drops of algae inhibitor (Ace Scientific, cat. JU-78-6440-01) plus 10 ml 3A ethanol added per liter. Reference samples of 2,4'-bisphenol A, Dianin's compound and BPX were supplied by C. D. Marshall of the Shell Development Co.

Procedure

A 1.0 g (to 0.1 mg) sample was dissolved in 50 ml acetonitrile containing 0.040 g m-trifluoromethylphenyl urea as an internal standard. A 10 microliter injection was made.

RESULTS

Table 1 summarizes the analyses of three different qualities of bisphenol A.

Typical retention times and response factors are shown by Table 2.

TABLE 1

Component, Weight %	Bisphenol A (Polycarbonate grade) A	B	C
H_2O (K. Fischer)	0.04	0.11	.13
Phenol	0.06	0.08	none found
2,4' isomer	0.04	3.35	4.19
BPX	none found	0.95	1.54
Dianin's	none found	0.05	0.08
Unknowns (a)	none found	0.29	0.81
Bisphenol A (b)	99.86	95.17	93.25
Setting point, corrected for H_2O content (c)	157.0°C	154.3°C	153.2°C

(a) The response factor used was the average of all the known components.

(b) Calculated by difference.

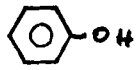
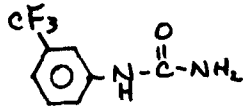
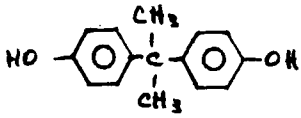
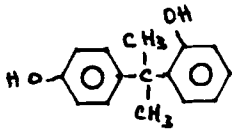
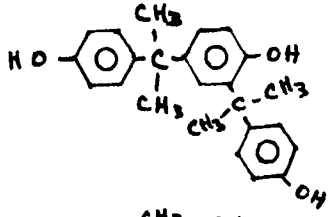
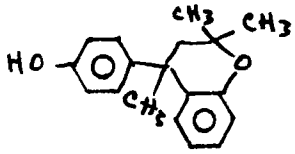
(c) Although the setting points generally conform to quality, correlation has not been found sufficiently adequate for the close quality control required.

Calculations were carried out as follows:

$$\% X = \frac{(Ax)(Fx)(Wis)(100)}{(Ws)(Ais)}$$

where Ax, Ais = peak areas of component X and the internal standard; Fx = response factor of component X; Ws, Wis = grams of sample and internal standard.

TABLE 2

Component	Structure	Absolute Retention (min.)	Relative Response, 280 nm
Phenol		5.5	0.85
Internal Standard		6.1	1.00
Bisphenol A		10.2	--
2,4' isomer		14.7	0.46
BPX		19.2	0.40
Dianin's Compound		21.8	0.51

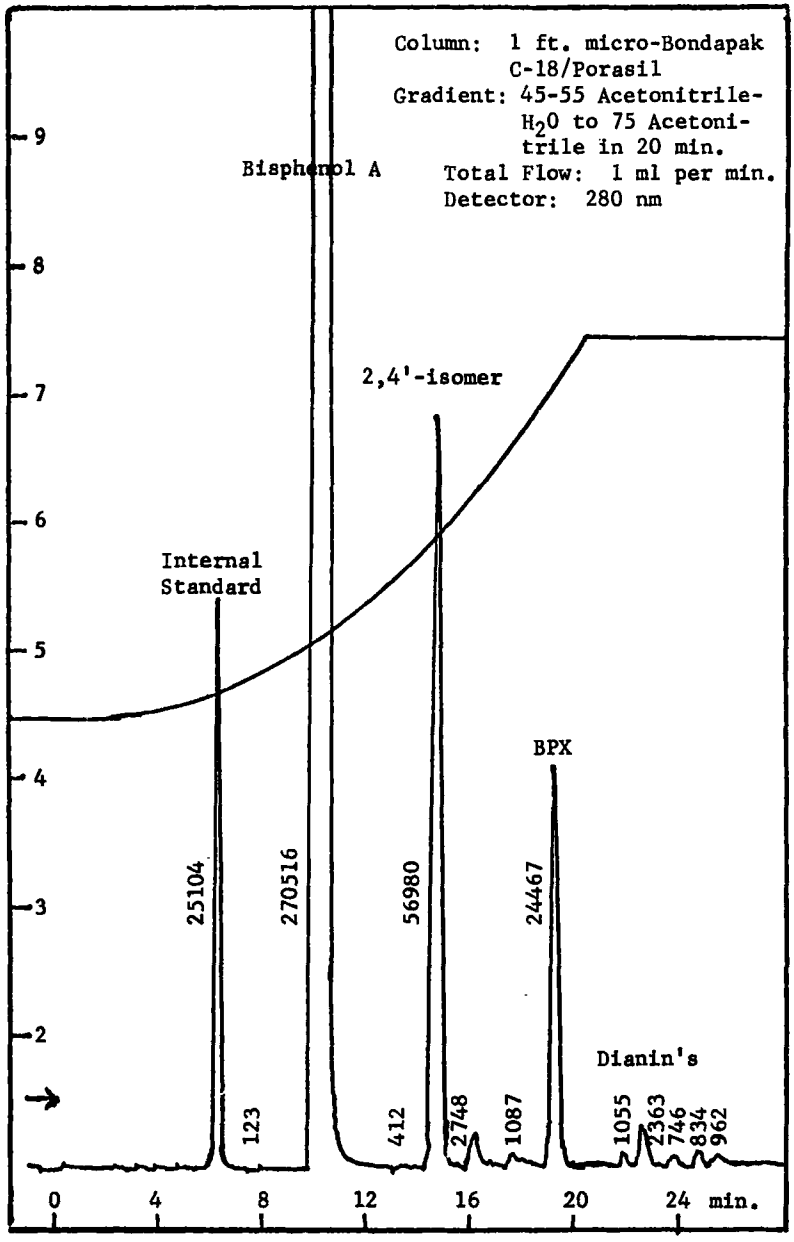


FIGURE 1

The chromatogram of sample C is shown by Figure 1. As the chromatogram indicates, baseline resolution is achieved for all components. The numbers at the side of each peak are integrator counts. The number of theoretical plates for BPX, e.g., is 23,600.

DISCUSSION

The most critical impurity with regard to epoxy resin production is considered to be BPX due to its phenolic trifunctionality which gives rise to greater cross-polymerization, thus leading to high viscosities. This can be shown by Table 3 which indicates a 0.96 coefficient of correlation between BPX content of bisphenol A and the viscosity of the subsequent bisphenol A - epichlorohydrin adduct.

The 2,4' isomer is considered of minor significance due to its functional similarity to bisphenol A. Dianin's compound, being monofunctional, acts as a chain terminator; its level, however, is usually too low to be effective.

TABLE 3

BPX Content	cps Viscosity of Liquid Resin at R.T.
<.02%	12,000
0.3%	14,400
0.8%	14,600
1.3%	18,200
1.5%	19,600

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