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Note

Analysis of phenol–formaldehyde resins by high-performance liquid chromatography

A. ŠEBENIK and S. LAPANJE

Chemical Factory Donit, Medvode, and Department of Chemistry, University of Ljubljana, Ljubljana (Yugoslavia)

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In recent years, there has been a rapid development in high-performance liquid chromatography, due to the introduction of new adsorbents with large surface areas packed in long narrow-bore columns and new high-pressure pumps with operating pressures up to 8,000 p.s.i. (560 atm)[1,2]. Separations of organic substances that previously took several days can now be achieved in a few minutes.

Therefore, it appeared worthwhile to employ high-performance liquid chromatography for the separation and identification of the products of the reaction between phenol and formaldehyde. The reaction is complex and leads to insoluble and infusible resins, *i.e.*, cross-linked networks[3–6]. In the past, in addition to classical methods of analysis[3], paper[7], thin-layer[8–10] and liquid chromatography[11–16] have been applied.

MATERIALS AND METHODS

Phenol and formaldehyde were purified products obtained from OKI, Zagreb, Yugoslavia. All other reagents were of analytical grade and their quality was ascertained by gas chromatography.

A Perkin-Elmer (Norwalk, Conn., U.S.A.) Model 1220 analytical liquid chromatograph was used. The column was a 0.5 m × 0.2 mm I.D. stainless-steel tube filled with Merkosorb SI-60, 10 µ. The column was packed using a high-pressure slurry-packing apparatus[17]. For detection, a UV spectrophotometer monitoring at 254 nm and a reflection-type refractive index detector with a range from 1.31 to 1.55 were used. Pressures necessary for maintaining constant flow-rates ranged from 800 to 1500 p.s.i.

For the preparation of resins, phenol and a 37 % aqueous solution of formaldehyde were mixed in the molar ratio 1:1.5; the catalyst was either sodium hydroxide or hydrochloric acid. In some instances, phenol was replaced with *m*-cresol and 3,5-xylenol; the catalyst was then hexamethylenetetramine. Reaction times varied from 0.5 to 1.5 h, and the temperature from 70 to 100°. For injection of samples, the volumes of which ranged from 0.2 to 1 µl, an injector with a rubber septum was used.

RESULTS AND DISCUSSION

For achieving good resolution of the components of phenol–formaldehyde resins, mixtures consisting essentially of chloroform or dichloromethane proved to be the most convenient carriers. In the case of cresol– and xylenol–formaldehyde resins, this holds true only for dichloromethane. The addition of highly polar solvents, *e.g.*, methanol or ethanol, decreases the resolution. However, the addition of these solvents is necessary in order to achieve complete solubility. Acetone, which is an excellent solvent for all phenol–formaldehyde resins, is not suitable owing to high absorption in the ultraviolet region. Another good solvent which could be used is dioxane. Iso-octane and *n*-hexane[18,19], which are good solvents for cresol and xylenol, do not dissolve their formaldehyde resins; also, when added to solvents, they produce precipitation.

Fig. 1 shows the chromatogram of a test mixture. For the identification of individual components, the method of peak enhancement was employed. From the
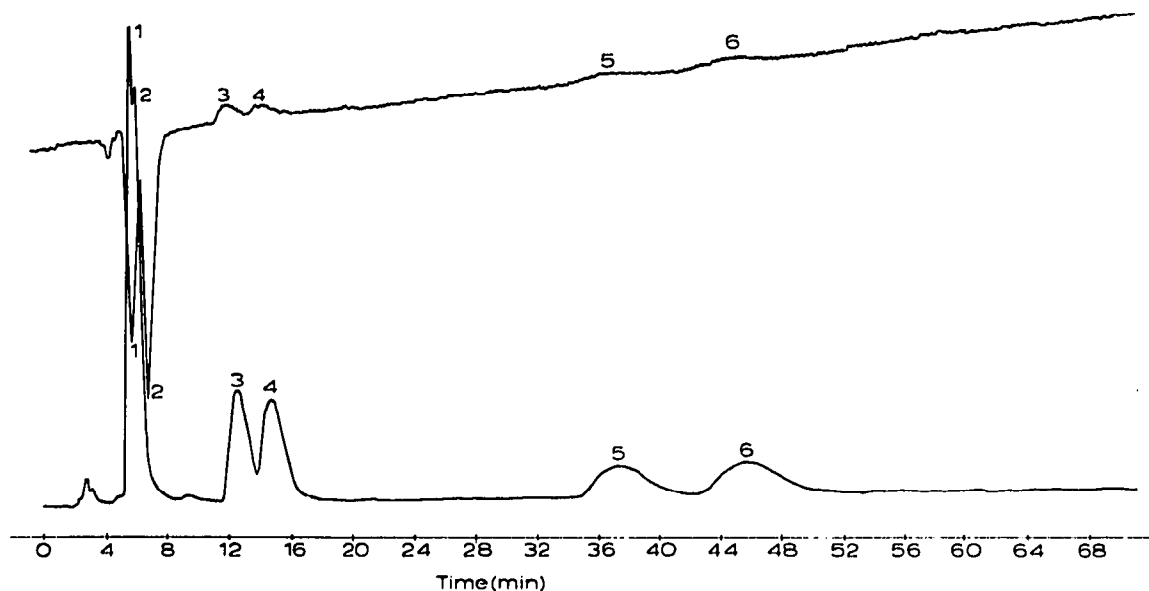

Fig. 1. Chromatogram of test mixture of pure phenolic compounds. Flow-rate, 0.75 ml/min; solvent, dichloromethane–dioxane–methanol (500:2:4). 1, Phenol; 2, bis-(2-hydroxyphenyl)methane; 3, 2-hydroxybenzyl alcohol; 4, bis-(4-hydroxyphenyl)methane; 5, 4-hydroxybenzyl alcohol; 6, 3-hydroxybenzyl alcohol. Lower curve, UV detector, 254 nm; upper curve, RI detector.

areas under the peaks and known compositions, the relative absorption factors with respect to phenol were determined, which were then used for the analysis of experimental mixtures. Relative retention times were also determined (Table I). The values refer to completely dried solvent and adsorbent. Drying, in general, increased the resolution[20].

Representative chromatograms of phenol–formaldehyde resins are given in Figs. 2–6. The chromatogram in Fig. 2 represents a low condensation resin in which there are essentially four components, three of which have been identified. Fig. 3 is

TABLE I

RELATIVE ABSORPTION FACTORS AT 254 nm AND RELATIVE RETENTIONS OF TEST COMPOUNDS

Compound	Relative absorption factor at 254 nm	Relative retention
Phenol	1.00	1.00
Bis-(2-hydroxyphenyl)methane	0.95	1.07
2-hydroxybenzyl alcohol	0.83	2.10
Bis-(4-hydroxyphenyl)methane	0.96	2.50
4-Hydroxybenzyl alcohol	0.83	6.30
3-Hydroxybenzyl alcohol	0.84	7.60

the chromatogram of an intermediate condensation product with ten components, of which six have been identified; the unidentified components are probably dimethylol compounds. The chromatogram in Fig. 4 was obtained from a high condensation product and contains sixteen components, of which five have been identified; the remainder are probably dimethylol and polynuclear compounds.

It has been suggested by Finn and James[21] that the number of possible components resulting from the reaction between phenol and formaldehyde might be as
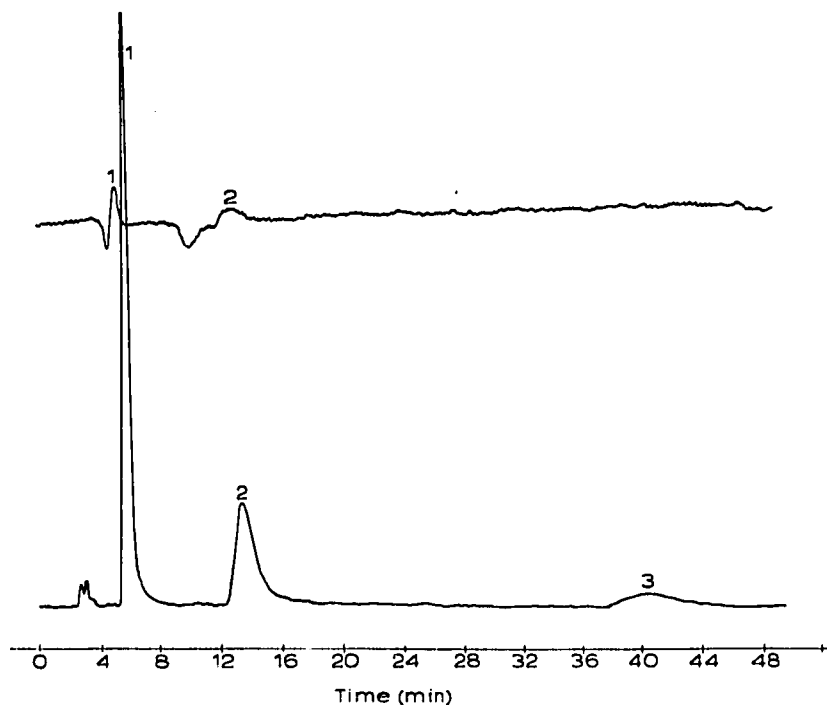

Fig. 2. Chromatogram of a low condensation phenol–formaldehyde resin catalyzed with NaOH. Flow-rate, 0.75 ml/min; solvent, dichloromethane–dioxane–methanol (500:2:4). 1, Phenol; 2, 2-hydroxybenzyl alcohol; 3, 4-hydroxybenzyl alcohol. Lower curve, UV detector, 254 nm; upper curve, RI detector.
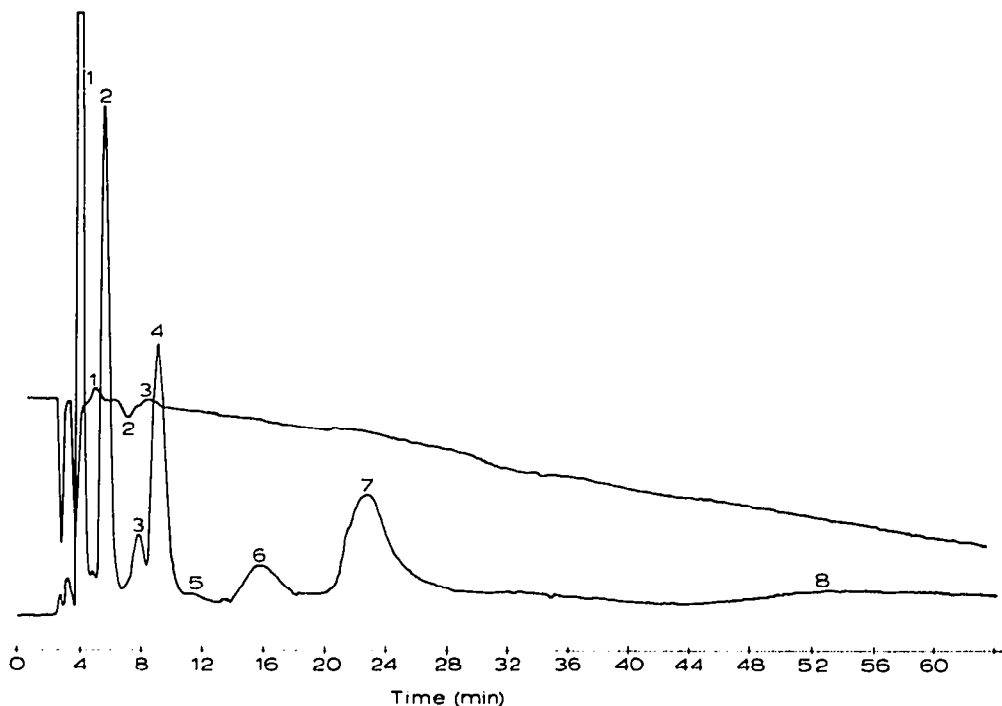
Fig. 3. Chromatogram of an intermediate condensation phenol–formaldehyde resin catalyzed with NaOH. Flow-rate, 0.75 ml/min; solvent, dichloromethane–dioxane (100:3). 1, Acetone; 2, phenol; 3, unidentified; 4, 2-hydroxybenzyl alcohol; 5, unidentified; 6, 4-hydroxybenzyl alcohol; 7, 8, unidentified. Lower curve, UV detector, 254 nm; upper curve, RI detector.

high as 25, depending on the experimental conditions of the synthesis, the type and amount of catalyst, and the molar ratio between phenol and formaldehyde. The highest number of components observed in our experiments is sixteen. Further experiments are necessary to find out if the disagreement is due to incomplete resolution or if some components are not formed.

In the case of the low condensation reaction (Fig. 2), the molar ratio between 2-hydroxybenzyl alcohol and 4-hydroxybenzyl alcohol is 3:1; moreover, the total amount of all other components is negligible. From this, it follows that at low temperature (70°) and with a short reaction time (30 min), two partial reactions predominate and that the reactivity of the *ortho*-position is about three times greater than that of the *para*-position. This finding is in agreement with those of Duval *et al.*[16] and Zavitsas *et al.*[22] obtained by other chromatographic techniques. The *meta*-position in the benzene ring appears to be unreactive.

Figs. 5 and 6 show the chromatograms of the products obtained in the reactions between *m*-cresol and formaldehyde and between 3,5-xylenol and formaldehyde, respectively. So far only the two reactants, *m*-cresol and 3,5-xylenol, could be identified. There is no doubt that the identification of the other components will be difficult.

In conclusion, it can be stated that regardless of the great similarly between individual resin components, liquid–solid chromatography appears to be a convenient
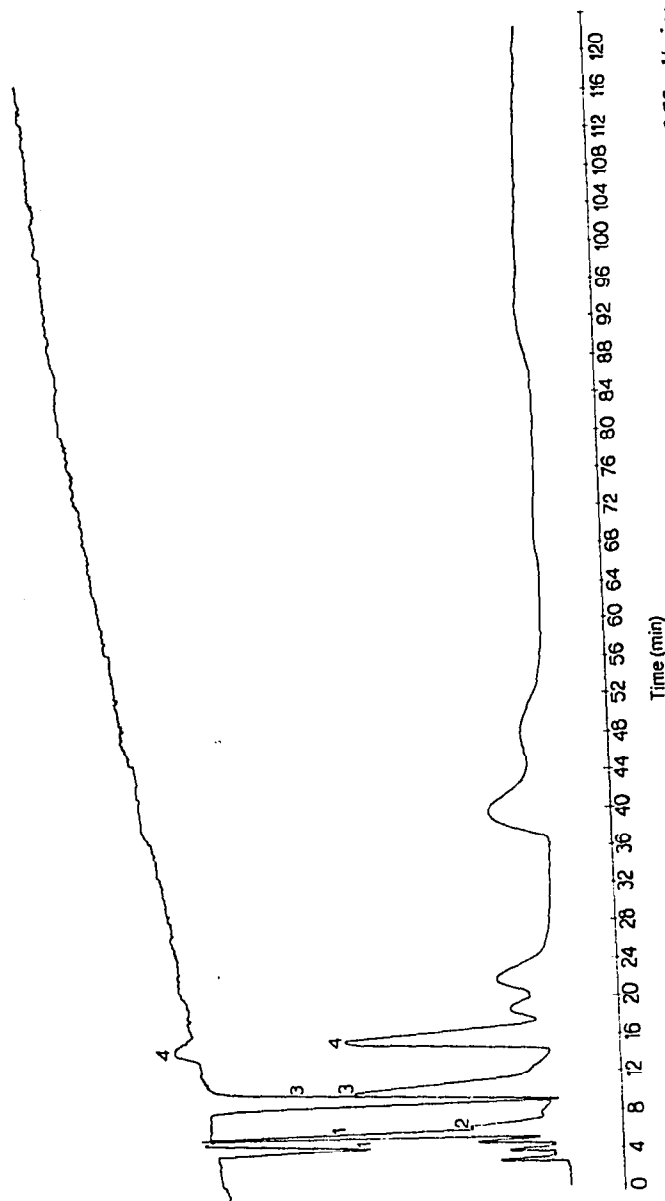
Fig. 4. Chromatogram of a high condensation phenol–formaldehyde resin catalyzed with HCl. Flow-rate, 0.75 ml/min; solvent, dichloromethane–dioxane–methanol (100:1:1). 1, Phenol; 2, bis-(2-hydroxyphenyl)methane; 3, 2-hydroxybenzyl alcohol; 4, 4-hydroxybenzyl alcohol; other peaks unidentified. Lower curve, UV detector, 254 nm; upper curve, RI detector.
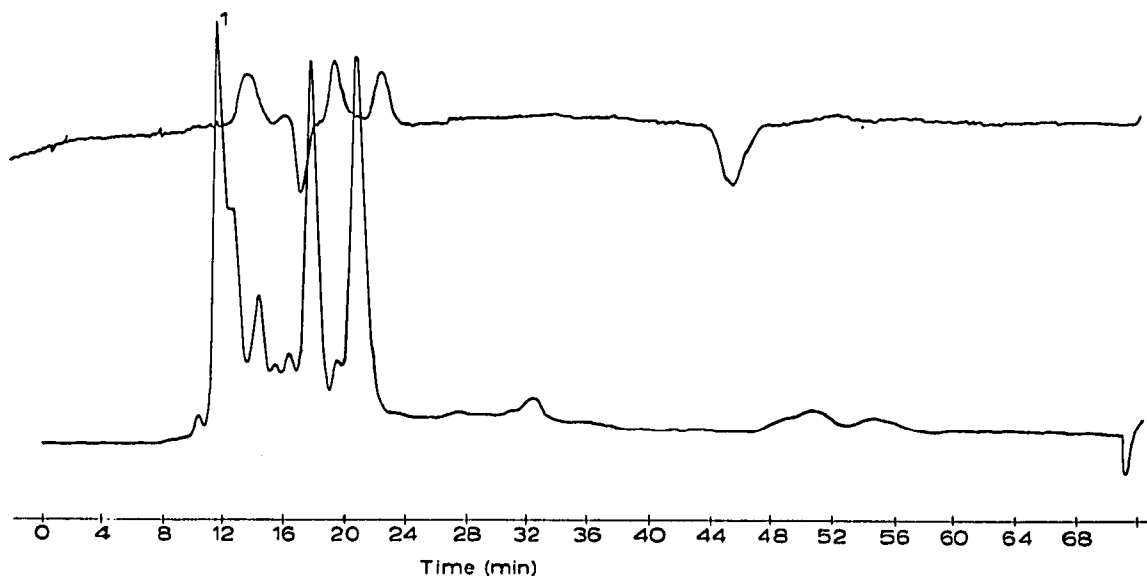
Fig. 5. Chromatogram of a low condensation *m*-cresol–formaldehyde resin. Flow-rate, 0.4 ml/min; solvent, dichloromethane–dioxane–methanol (500:2:4). 1, *m*-Cresol; other peaks, unidentified. Lower curve, UV detector, 254 nm; upper curve, RI detector.
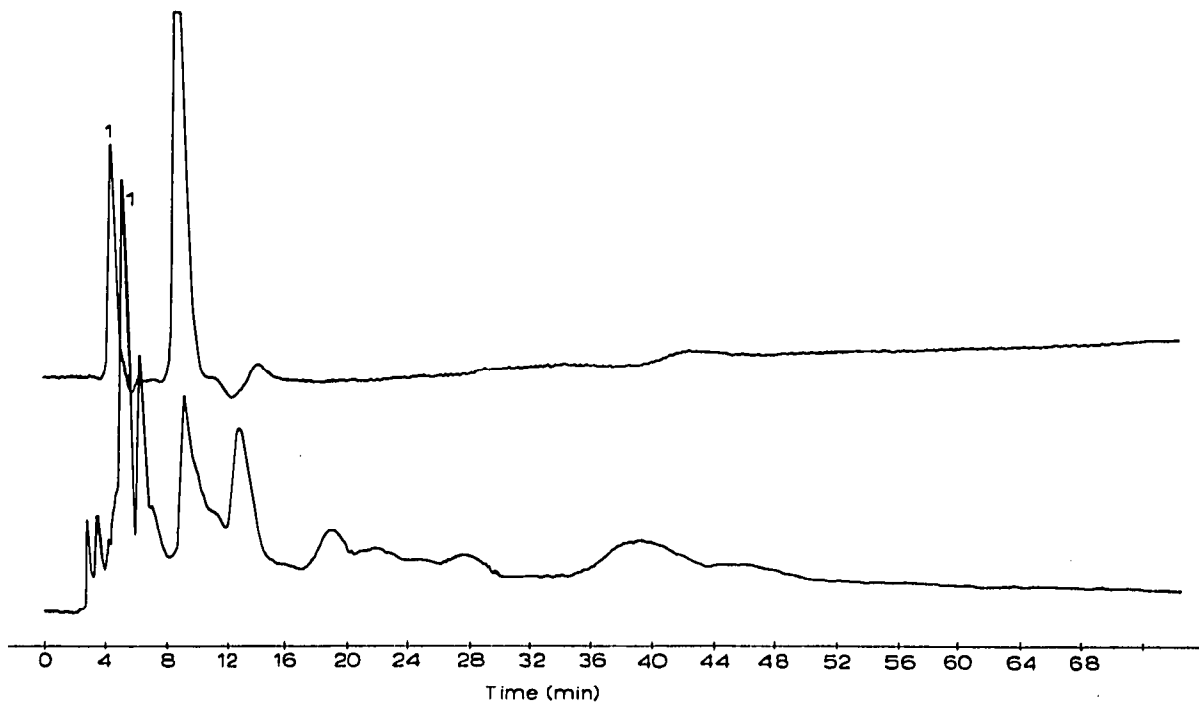

Fig. 6. Chromatogram of a low condensation 3,5-xylenol–formaldehyde resin. Flow-rate, 0.75 ml/min; solvent, dichloromethane–dioxane–methanol (500:2:4). 1, 3,5-Xylenol; other peaks, unidentified. Lower curve, UV detector, 254 nm; upper curve, RI detector.

method for their separation and identification. Compared with other chromato-graphic techniques, it is more rapid and gives better resolution and sharper peaks. Further improvement in the performance will be attempted by applying longer, narrower columns, lower flow-rates and a stronger adsorbent, *e.g.*, Merckosorb SI-60, 5 μ.

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