DETERMINATION OF FREE PHENOL IN PHENOL RESOLE RESIN BY GEL PERMEATION CHROMATOGRAPHY

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The free phenol in phenol resole resin was determined by gel permeation chromatography with the high molecular polystyrene as the internal standard. The observed values were in close agreement with that obtained by gas chromatography. The reproducibility was about 4 per cent as the coefficient of variance.

Recently, gel permeation chromatography(GPC) is much used for analysis of phenol resole resins. However, the determinations of free phenol contents in phenol resole resins are not easy because of the dependence of peak areas of chromatogram on refractive indices, if a differential refractometer is used as a detector.

The application of the absolute analysis of free phenol by GPC is possible, but its reproducibility is not satisfactory. Therefore, the internal standard analysis was applied to GPC in this paper.

Experimental

The phenol resol resins made by the general method were used as the samples. The phenol and other alkyl phenols as authentic samples were reagent grade and the monodispersed polystyrene purchased from Pressure Chemical Co. of which M_{vis} was 16000($Mw/Mn \leqq 1.06$) was used as an internal standard.

Samples studied were analyzed in Waters Associates GPC, Model-200. The operating parameters were as follow: solvent, tetrahydrofuran(THF); temperature, $25°C \pm 2°C$; sensitivity, 2X; experimental theoretical plate number of polystyrene gel columns obtained with o-dichlorobenzene, 505 plates per foot; porosity ratings of five polystyrene gel columns, 15000-50000Å, 100-150Å, 50-80Å and 50-80Å.

Sample concentration, about 100mg of the resole resin and 25mg of the polystyrene per 25ml of THF in a mess flask. The adding of a column of high porosity, i.e. 15000-50000Å, gives efficiency to seperate polystyrenes from phenol resole resins.

<div align="center">Results</div>

In Fig.1 was shown the typical chromatogram of phenol resole resin with polystyrene as the internal standard. Peaks of free phenol, resole resin and polystyrene were separated enough for quantitative analysis respectively. Fig.2 shows the linearity of calibration curve of phenol. The correction coefficient of phenol was the reversal number of slope of calibration curve and was 1.19. The free phenol content in the phenol resole resin is calculated by the following equation.

$$\text{Free phenol } \% = \frac{(\text{A phenol}/ \text{A pst}) \ \times \ \text{Added pst weight} \ \times \ \text{K} \ \times \ 100}{\text{Sample weight}}$$

A: peak area

pst: polystyrene, used as the internal standard

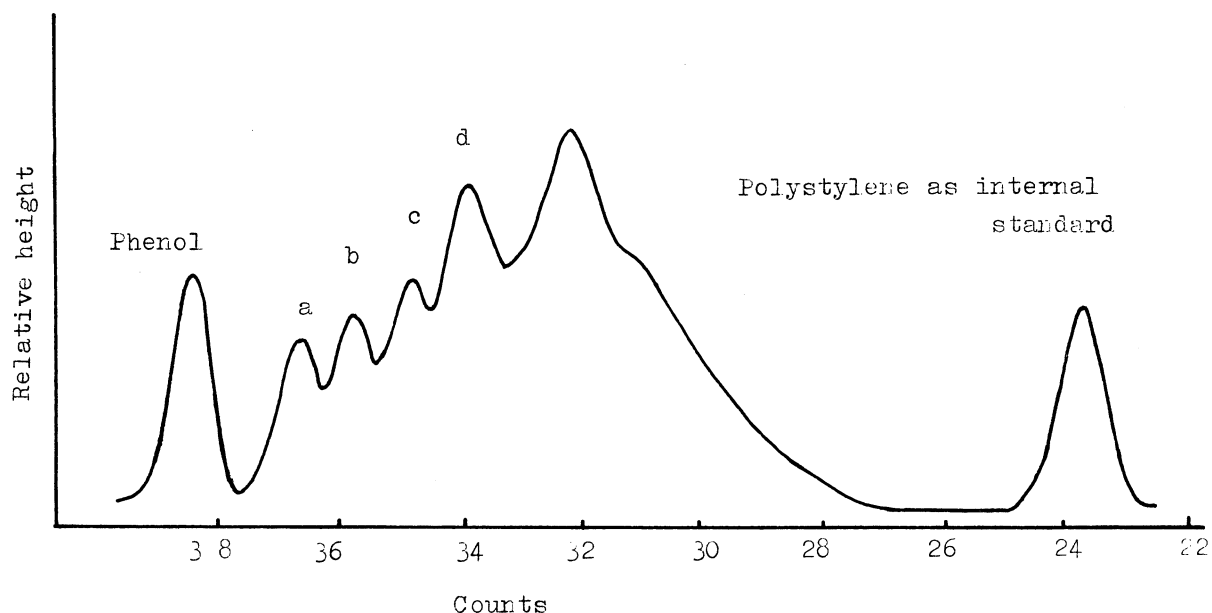K: correction coefficient: 1.19

Fig.1,   GPC curve of phenol resole resin

a: 2-Methylol phenol   b: 4-Methylol-, and 2-4 Dimethylol phenols   c: 2.4-Dimethylol phenol

d: 2.4.6-Trimethylol phenols

Table 2. Reproducibility of determination of phenol

No	obs.
1	9.5%
2	10.1
3	10.7
4	10.4
5	10.1
Average ($\bar{X}$)	10.2
Standard deviation (σ)	0.45
Coefficient of variation ($c = \sigma/\bar{X} \times 100$)	4.4

$$F = \frac{1}{0.840} = 1.19$$

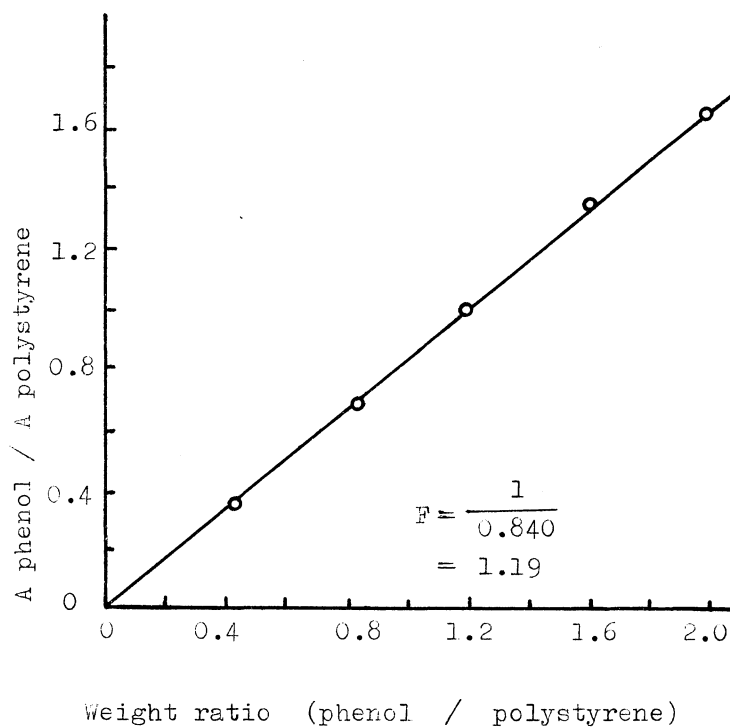Weight ratio   (phenol / polystyrene)

Fig.2. Calibration curve of phenol

A: peak area of chromatogram

The reproducibility of the determination of the free phenol was shown in Table 1 and the coefficient of variance was about 4 per cent. The observed values were in close agreement with added values and values obtained by gas chromatogramphy with p-cresyl acetate[1] or m-cresol[2] as internal standards, as shown in Table 2.

This procedure has the advantage that two informations about the free phenol content and the apparent molecular weight distribution[3] of phenol resole resins are obtained simultaneously. On the other hand, only one information about the free phenol is obtained by gas chromatography.

Furthermore, this procedure is applicable to the determination of free monomers in phenol novolac resins, p-ter bytylphenol resins, p-phenyl phenol resins, other alkyl phenol resins and other thermosetting uncured resin, i.e, epoxy resins and furan resins.

Table 3 shows K values of these alkyl phenol monomers.

A study of determination of isomers of mononuclear methylol phenols in phenol resole resin is in progress by means of this procedure.

Table 2.   Comparison of the predicted values and the observed
            value by GPC and GC

* obtained by GC

| Sample | Added | phenol % | | |
| | | Calcd | obs | |
			GPC	GC
Original resin	0	2.8*	-	2.8
1	4.3	7.1	6.7	6.9
2	5.4	8.2	8.7	8.9
3	7.3	10.1	9.5	9.7
4	9.9	12.7	13.2	13.1
5	19.3	22.1	22.8	21.2

Table 3.   K values of various compounds

Compound	K
Phenol	1.19
o-Cresol	1.16
m-Cresol	1.22
p-Cresol	1.21
o-Ethyl phenol	1.25
m-Ethyl phenol	1.31
p-Ethyl phenol	1.17
2.4-Xylenol	1.24
2.6-Xylenol	1.31
p-ter Butyl phenol	1.43
p-Phenyl phenol	0.822
Furfural	1.89
Furfuryl alcohol	2.21

K values in Table 3 were obtained by the same way on the free phenol in Fig.2.

This procedure is not applicable to the determination of free monomers in these resins modefied with other kind of phenol monomers, respectively.

1)   M.P. Stevens and D.F.Percival, Anal.Chem., 36, 1023(1964)

2)   F.Fujiwara, C.Sugimoto and H.Horiuchi, the 14th Annual Meeting of
      Thermosetting Resins of Japan (1964)

3)   M.Tsuge, T.Miyabayashi and S.Tanaka, ibid., The 21th Annual Meeting(1971)