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## Note

### Gas chromatographic determination of the oligomer of molecular weight 340 in epoxy resins

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About 90% of epoxy resins in industrial use are reaction products of epichlorohydrin and bisphenol A [2,2-bis(4-hydroxyphenyl)propane]. They consist of a mixture of oligomers with molecular weights (MW) of 340, 624, 908, 1192, etc. Epoxy resins are known to be potent sensitizers<sup>1</sup>. It is mainly the MW 340 oligomer (diglycidyl ether of bisphenol A) that may cause allergic contact dermatitis<sup>1</sup>. Therefore, it is important to know the amount of MW 340 oligomer in epoxy resins and products in order to be able to evaluate health risks for the user.

Chromatographic methods, mainly reversed-phase high-performance liquid chromatography (RP-HPLC), but also gel permeation chromatography (GPC), have been developed for the quality control of epoxy resin formulations<sup>2-6</sup>. RP-HPLC methods usually give more detailed information than GPC methods<sup>4,5,7</sup>. Reliable quantification of oligomers is possible by HPLC<sup>7</sup>, and quantification of the MW 340 oligomer by the external standard method has been reported<sup>8</sup>. Thin-layer chromatography (TLC) can also be used to indicate the presence of epoxy oligomers<sup>9</sup>. This method is cheap and simple, but it is not always as specific as other chromatographic methods.

In this work, a simple and sensitive gas chromatographic (GC) method to determine the amount of MW 340 oligomer in epoxy resins is described. The resin is extracted with ethanol containing an internal standard.

#### EXPERIMENTAL

About 50–200 mg of epoxy resin (accuracy 0.1 mg) were dissolved in a test-tube in 5.0 ml of ethanol (99.5%) containing a known amount of bis(2-ethylhexyl) isophthalate (Analabs, purity 98+%) as internal standard. Liquid epoxy resins were transferred to the test-tubes with a Finnpiptette. The test-tubes were shaken for 30 min in an SM-apparatus (Edmund Bühler).

A Hewlett-Packard 5750 G gas chromatograph, equipped with a flame-ionization detector (FID) and a glass column (1.8 m × 4 mm I.D.) packed with 3% SE-30 on Chromosorb W HP (80–100 mesh), was used. The column temperature was 240°C and the carrier gas (nitrogen) flow-rate was 30 ml/min. The injector and detector temperatures were 270 and 290°C, respectively. The identification was confirmed<sup>†</sup> by GC combined with mass spectrometry (GC-MS) using a similar column and an LKB-9000 instrument (electron energy 70 eV).

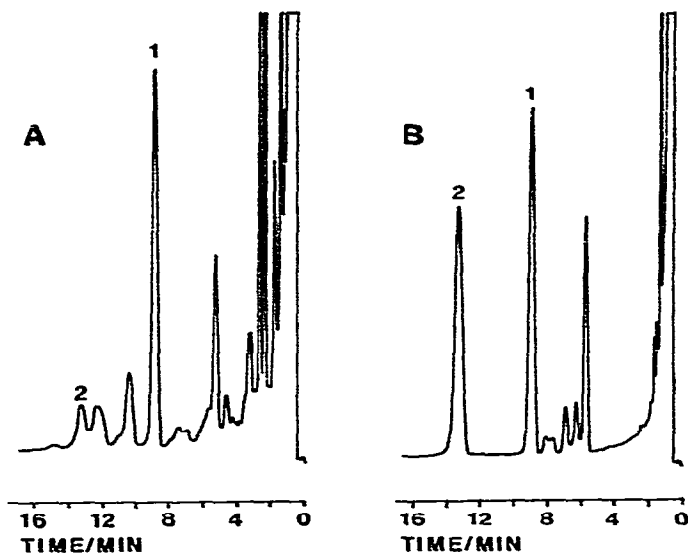


Fig. 1. Gas chromatograms of two epoxy resins at 240°C. Column: 3% SE-30 on Chromosorb W HP (80–100 mesh). Peaks: 1 = internal standard, bis(2-ethylhexyl) isophthalate; 2 = MW 340 oligomer (amount: A, 0.3%; B, 1.7%). Attenuation:  $64 \times 10$ .

TLC plates coated with 2 mm thick silica gel layers and the solvent system chloroform–acetonitrile (85:15) were used for the preparative isolation of MW 340 oligomer. The pure oligomer was isolated with acetone from the fraction at  $R_f$  0.75–0.85 and used to determine the relative response factor ( $n = 3$ ).

The method was tested using different commercial liquid epoxy resins.

## RESULTS AND DISCUSSION

The recovery was determined by repeated extraction with ethanol. The amount of MW 340 oligomer extracted in the first extraction step was 92–98% of the total amount extracted. The recovery varied with viscosity and amount of epoxy resin extracted. Thus, the internal standard method is to be preferred, as losses in the recovery of MW 340 oligomer can be compensated for. Chromatograms of two epoxy resins are shown in Fig. 1.

Under the analytical conditions applied, the response factor for the MW 340 oligomer was determined to be 0.52 (coefficient of variation = 0.07) relative to the internal standard bis(2-ethylhexyl) isophthalate.

The detection limit was estimated to be about 10 ng, which is lower than that in the TLC method<sup>9</sup> (detection limit about 500 ng) and the same as that in the HPLC method<sup>8</sup>. Ethanol rather than acetone was chosen as the solvent to decrease the amount of other soluble ingredients, such as hydrocarbons, which may interfere in the GC separation as indicated in Fig. 1 (sample A). When interfering substances are present, other internal standards may be used, such as D-sucrose octaacetate, which elutes after the MW 340 oligomer. The response factor relative to that standard was not determined in this work.

TABLE I  
AMOUNT OF MW 340 OLIGOMER IN SOME EPOXY RESINS

<i>Epoxy resin No.</i>	<i>Sample weight (mg)</i>	<i>Amount found (%)</i>	<i>Coefficient of variation*</i>
1	50	26	0.02
	200	29	0.06
2	50	4.4	0.08
	200	5.3	0.06
3	50	1.9	0.04
	200	2.3	0.05

\*  $n = 4$ .

The amount of MW 340 oligomer varied slightly with the amount of epoxy resin sample (Table I), probably owing to difficulties in obtaining representative samples, as epoxy resins 1–3 were viscous mixtures of solid resin and xylene–butanol solvent. The liquid resin portion, including the MW 340 oligomer, was instead readily dissolved in the xylene–butanol phase. However, efficient mixing, small amounts of sample and properly chosen equipment should minimize these problems.

The results showed that the amount of MW 340 oligomer in different liquid epoxy resins can easily and reliably be determined by the GC method described. For other types of epoxy resins, such as water-based resins, and cured epoxy products some modification of the method would be required.

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