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## Note

# High-performance liquid chromatographic method for the simultaneous separation and determination of three additives in poly(vinyl chloride)

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The identification and determination of low-molecular-weight components such as plasticizers and stabilizers incorporated in polymers is of great importance, particularly when the polymers are intended for medical use. *In situ* identification is often feasible if the number of additives is restricted to one or two, but the analysis becomes extremely complex as the number of additives incorporated in the polymer matrix increases. In such instances, separation by selective solvent extraction or repeated fractional precipitation, which unfortunately are tedious and lengthy, is necessary[1,2]. The use of high-performance liquid chromatographic (HPLC) methods, however, has simplified the analysis of polymer additives considerably[3] and, in recent years, chromatographic methods including size exclusion procedures have been used extensively for the analysis of common polymer additives[4–7].

This paper reports an attempt to develop a simple, rapid, HPLC method for separating and determining simultaneously three additives commonly used in poly(vinyl chloride) (PVC).

## EXPERIMENTAL

The polymer additives, di-2-(ethylhexyl) phthalate (DEHP), epoxidized soyabean oil (Paraplex G62) and tris(nonylphenyl) phosphite (TNPP), were obtained from Indo-Nippon (Bombay, India) and used as received. Analytical-reagent grade carbon tetrachloride, dichloromethane and tetrahydrofuran (BDH, India) were distilled prior to use.

The chromatographic system consisted of a Waters Assoc. Model 6000A solvent delivery pump, a U6K injector, a Model 440 absorbance detector and an R-400 refractive index detector. A strip-chart recorder (Houston Instruments, U.S.A.) was used. A μPorasil column with carbon tetrachloride–dichloromethane (65:35, v/v) as the mobile phase was used for the separation. The flow-rate was 1 ml/min and the column effluents were monitored simultaneously with a UV detector (280 nm) and a refractive index detector.

Indigenously calendered PVC films containing the three additives (2% of each) were dissolved in tetrahydrofuran and the polymer was precipitated by adding meth-

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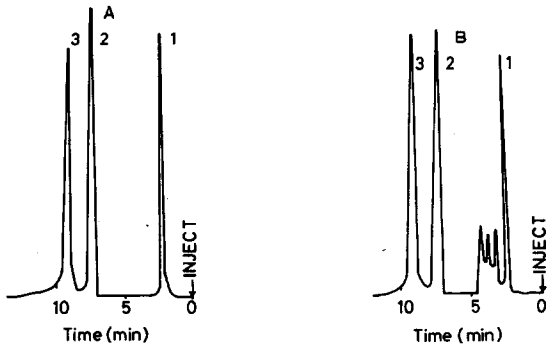


Fig. 1. (A) Chromatogram of a standard solution of three additives. Peaks: 1 = Paraplex G62; 2 = DEHP; 3 = TNPP. (B) Typical chromatogram of PVC extract. Peaks as in (A).

anol. The filtrate was evaporated to dryness in a vacuum oven. The residue was dissolved in carbon tetrachloride–dichloromethane (65:35, v/v) and used for the chromatographic analysis.

## RESULTS AND DISCUSSION

Fig. 1A is a chromatogram showing the peaks of Paraplex G62, DEHP and TNPP, and a typical chromatogram of the same components extracted from the PVC sample is illustrated in Fig. 1B. The extra peaks in Fig. 1B are unidentified impurities and probably arose from the PVC resin.

Paraplex G62 (peak 1) is epoxidized soyabean oil, consisting of a mixture of components of various chain lengths. Under the chromatographic conditions used the additive is unretained and elutes together as a single peak. However, the detector response was linear with the amount of the additive in the mobile phase.

Calibration graphs of the detector response (for DEHP and TNPP 280 nm was used for Paraplex G62 a refractive index detector was used) *versus* concentration in the injected volumes of each of the samples were constructed. Quantification of the additives extracted from the PVC films was subsequently achieved from these plots. The recoveries of the additives and the corresponding retention times are shown in Table I.

Typical additive levels in PVC, excluding plasticizer, are 0.1–1% (w/w)[7]. The

TABLE I

CHROMATOGRAPHIC DATA FOR THE THREE ADDITIVES

| *Sample* | *Retention time (min)* | *Recovery* (%)* |
|---|---|---|
| Paraplex G62 | 2.50 | 94.2 ± 3.1 |
| DEHP | 7.75 | 97.6 ± 3.8 |
| TNPP | 9.80 | 96.7 ± 2.9 |

* Average values from ten analyses with standard deviations.

involvement of many steps in the usual extraction procedures leads to further reductions in the amounts of the additives and, for reliable detection, a sensitive method is needed.

The limits of detection of the present method are 15 μg per 100 μl for DEHP, 10 μg per 100 μl for TNPP and 50 μg per 100 μl for Paraplex G62. These limits are sufficient for determination at the levels usually present.

Apart from having the required sensitivity, the present method substantially reduces the analysis time. Moreover, it offers a comparatively simple and rapid method, excluding the usual tedious extraction procedures, and could be extended to the routine analysis of commercially available polymers containing these additives.

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