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Determination of phenol in poly(vinyl chloride)

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SUMMARY

There are strong indications that some poly(vinyl chloride) (PVC) plastics may contain phenol. This would be particularly harmful in the case of PVC used as a raw material for toys. An analytical method for determining phenol in PVC was therefore designed. The method is based on dissolving the whole sample in tetrahydrofuran and precipitating PVC by addition of water. After filtration the solution is ready for injection into an HPLC instrument. For quantitative analysis *p*-cresol is used as internal standard and it is added to the THF solution before precipitation. The method is applicable in the concentration range 50–3000 mg phenol/kg PVC. The detection limit is about 10 mg phenol/kg PVC but may be easily increased ten-fold by gentle removal of tetrahydrofuran from the sample solution and cleaning of the sample with C_{18} cartridge, which allows the injection of larger volumes and thus improves sensitivity.

The method has been submitted for collaborative study in municipal laboratories in Finland.

INTRODUCTION

There are several possible sources of the contamination of poly(vinyl chloride) (PVC) with phenol, *e.g.*, from the residual stabilizer in raw material or from various additives[1]. PVC used for toys is an especially undersirable case of such contamination.

Although there are several high-performance liquid chromatographic (HPLC) methods for the determination of phenol, they are mostly designed for the analysis of environmental samples[2–5] and no method for these kinds of samples has been published. The detection of phenol is normally carried out using UV detection, although fluorescence and electrochemical detection, which offer better selectivity or higher sensitivity, are also applied.

EXPERIMENTAL

The HPLC instrument consisted of an N-6000A pump, an M-710 WISP automatic injector, a Novapak C_{18} column (100 × 8 mm I.D.) in an RCM-100 column chamber and a Maxima 820 data station. The detectors employed were an M-490 UV detector (280 nm), an M-420 fluorescence detector (excitation wavelength 280 nm,

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emission wavelength 305 nm) (all from Millipore and Waters Assoc.) and an ESA 5100A electrochemical detector (0.8 V potential). The mobile phase was methanol–water–acetic acid (40:60:1) at a flow-rate of 1 ml/min.

Sample preparation

A 0.5-g sample of PVC, which had been cut into small pieces, was dissolved in 10 ml of tetrahydrofuran (THF) and 1 ml of *p*-cresol (Aldrich-Chemie) (1000 mg/l in THF) was added as an internal standard. The dissolution normally required overnight shaking. Then 15 ml of water were added to the sample to precipitate PVC. After standing for 15 min, the turbid sample was injected into the HPLC instrument. Standards were prepared by adding 1 ml of internal standard solution to 25 ml of 160, 30 and 5 mg/l phenol standards in THF–water (40:60).

Sample clean-up by solid-phase extraction

THF was released under vacuum from 10 ml of sample solution made as described above. Acetic acid (100 μl) was added to the sample and the mixture was quantitatively transferred into a Sep-Pak C_{18} column (Millipore–Waters) (conditioned with 5 ml of methanol and 10 ml of water). After trapping the fraction, the Sep-Pak column was washed with 5 ml of water and the phenol and *p*-cresol were eluted with 2 ml of methanol–water (60:40). The eluate was transferred into 10-ml measuring flasks, which were filled to the mark. Injections of 50–400 μl of this solution into the HPLC instrument were made.

Preparation of contaminated PVC sample

A 300-mg amount of phenol was accurately weighed and dissolved in 500 ml methanol which was blended with 100 g of PVC powder. The PVC powder was raw material (Neste) intended for the manufacture of toys and, according to the manufacturer and our analysis, was free from phenol and *p*-cresol (<1 mg/kg), although it did contain ordinary additives. Methanol was released from the slurry under vacuum and the dry cake was thoroughly ground and screened to give a homogeneous sample to be blended with pure PVC to obtain samples with known phenol content for recovery studies and for the laboratory testing of the method.

RESULTS AND DISCUSSION

As THF dissolves PVC samples, it was natural to avoid elaborate and less reproducible extraction of the sample with other solvents. The calibration graphs for both phenol and *p*-cresol were linear ($r^2 = 0.999$) from 150 to 2 mg/l and 25–100 μl. Injection of both compounds dissolved in either the eluent or 40% THF gave peaks of equal height for the same injection volume, so the injection of samples into solvents stronger than the eluent had no reducing effect on the plate count. The peak height for 25–100-μl injections increased linearly, but larger injection volumes made the peak heights less linear, although the peak area naturally still increased linearly. The peak height for the 200-μl injection was only 1.9 times higher than that for the 100-μl injection.

The standards were stable for several weeks when stored in the dark at 4°C, although storage for 2 weeks at room temperature destroyed 15% of both phenol and *p*-cresol.

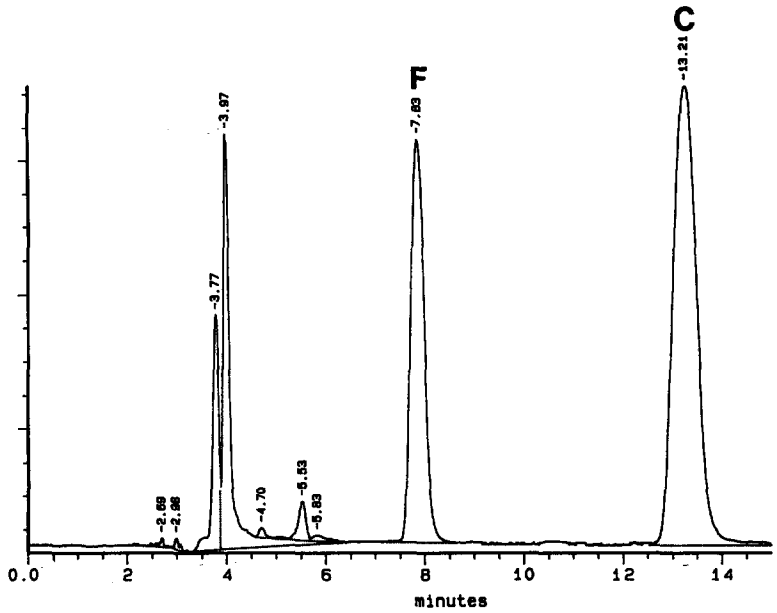

Fig. 1. Chromatogram obtained from a 50-μl injection of sample prepared according to the described procedure. F = phenol; C = *p*-cresol. The starting material was PVC spiked with 600 mg/kg of phenol. For other details see text. Sensitivity, 0.02 a.u.f.s.

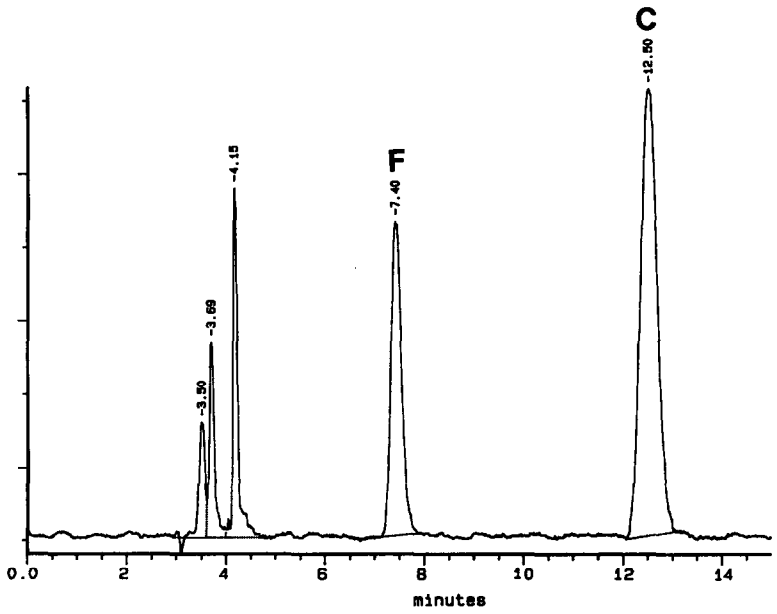

Fig. 2. Chromatogram obtained from a 400-μl injection of sample prepared according to the described procedure with Sep-Pak C_{18} clean-up. F = Phenol; C = *p*-cresol. The starting material was PVC spiked with 60 mg/kg of phenol. The concentration of internal standard (*p*-cresol) was reduced to one tenth. For other details see text.

TABLE I

RESULTS FROM COLLABORATIVE TESTING OF THE METHOD

Nominal	*Observed*	*n*	*R.S.D. (%)*
3000	3060	7	6.1
2700	2717	7	7.0
3000	3050	7	5.8
0	0	7	
600	637	6	7.1
600	625	6	5.4
480	483	6	7.3

No peak at the retention time of *p*-cresol was found in 2000 mg/l phenol standard, nor did the injection of *p*-cresol of equal strength give any peak at the retention time of phenol. None of the PVC samples studied showed any peak at the retention time of *p*-cresol. The recovery for a spiked sample (Fig. 1) containing 600 mg/kg of phenol was 104% for phenol and 101% for *p*-cresol, a relative standard deviation 0.9% ($n=4$) being found for the ratio of phenol to *p*-cresol. For the actual samples in which phenol was found, its identity was confirmed by the use of fluorescence detection in addition to the normally used UV detection, and also by semi-preparative chromatography followed by mass spectrometric identification of the isolated compound[6].

The method was submitted to seven municipal and industrial laboratories for collaborative testing. The results from this study are presented in Table I. As can be seen, the results are very satisfactory and only a few results from one laboratory had to be eliminated on the basis of Grubb's test.

The utilization of trace enrichment to increase sensitivity is not hindered by disturbing peaks, but the injection of samples from which THF was released under vacuum resulted in a rapid increase in back-pressure. Therefore, Sep-Pak C_{18} treatment of samples was applied. The recovery for phenol in this treatment was 97.8% and for *p*-cresol 98.3%. For samples spiked at the 60 mg/kg level, the recovery was 99.6% for phenol and 103.0% for *p*-cresol and the relative standard deviations for four parallel determinations were 4.4 and 2.7%, respectively (Fig. 2). The use of volumetric flasks in sample preparation was needed only for recovery studies, otherwise quantification was based on the internal standard method.

In a limited experiment, electrochemical detection was applied. The concentration of internal standard solution was reduced to one tenth and the recovery for samples spiked at the 30 mg/level was 92.5% for phenol and the standard deviation was 4.2% for four parallel samples made with the sample preparation procedure without Sep-Pak C_{18} clean-up.

The method described provides a simple and reproducible analysis of phenol in PVC with simple sample preparation and with detection at the ppm level.

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