Combined solvent extraction–mass spectrometry determination of free phenol traces in poly(vinyl chloride) products

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Abstract

A gas chromatography–mass spectrometry technique was used for the analysis of trace phenol in poly(vinyl chloride) products. A pre-concentration of samples was made by using a solid-phase extraction cartridge, previously developed for wastewater. The cartridge extraction of several samples yielded recoveries better than 90%. The relative standard deviation of overall recoveries for ten different samples was less than 7%. The detection limit achieved was less than 10 ppb (w/w) for free phenol measured in plastic materials.

1. Introduction

Increasing interest in the determination of free phenol in environmental samples has prompted the development of numerous methods for their quantitation. In terms of instrumentation, the proposed procedures are diverse. Colorimetry, gas–liquid and liquid–solid chromatography, and mass spectrometry have been most popular. The colorimetric standard procedure [1] is based on the reaction with 4-aminoantipyrine and oxidation under alkaline conditions to give a colored product. The main problem in using this method is the unspecificity among various phenols. For improved specificity, chromatographic methods have replaced colorimetry. Gas chromatography (GC) with flame ionization, electron-capture or mass spectrometric (MS) detection is commonly

used [2–9]. In other cases, phenols have been separated by liquid chromatography [10,11].

In polymer processing, a great number of additives can be used. Some of them, mainly antioxidants and ultraviolet absorbents, are typically phenol derivatives with sterically protected phenolic hydroxyl groups. Low-molecular-mass substituted phenols are too volatile for use in poly(vinyl chloride) (PVC). 2,2-Bis(p-hydroxyphenyl)propane, commonly known as bisphenol A, and 2,6-di-*tert*.-butyl-p-cresol, commonly known as BHT, are the most widely used materials. Products such as alcohols and phenols can be the result of stabilizer hydrolysis or oxidation.

Several chromatographic techniques can be applied to the analysis of polymer additives, including high-performance liquid chromatography [12–15], supercritical fluid chromatography [16–19] and capillary GC [20,21], which can be easily combined with MS. This technique offers better resolution and higher sensitivity.

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This is the reason why this technique has been chosen to identify and quantify free phenol in polymers.

Solid-phase extraction has been a very adequate method to isolate and purify many chemical compounds in a complex matrix, being a fast and reproducible method. It has been applied as a sample purification technique, trace enrichment and quick separation method. A great number of analytical techniques have used this extraction procedure as a complementary method, mainly GC [22].

Recently developed bonded-phase silica adsorbents have been used for the specific adsorption of organic compounds from water [23–25]. The wide variety of bonded phases available allowed the selection of the most effective sorbent for a particular application [26]. Several bonded phase materials have been evaluated for the sampling/concentration of phenols [27]. However, there are few examples of application to actual polymers.

The aim of this study is the extension of the GC–MS and solid-phase extraction technologies, used in other samples as wastewaters, to polymers and in particular to PVC products.

2. Experimental

2.1. Materials

All chemicals were analytical grade and were supplied by Panreac (Barcelona, Spain). Reagent-grade water was obtained from a Barnstead E-pure system (Barnstead, Dubuque, IA, USA). Bond Elut cartridges (Analytichem International, Harbor City, CA, USA) containing cyclohexyl (CH) as a bonded phase adsorbent were used for phenolic pollutants in wastewaters [22]; these were considered the best choice for a solid-phase adsorbent (containing 1000 mg per cartridge) in polymer studies.

As a first material Vestolit B 7021 (Huls) PVC resin has been used. This is a homopolymer, non-prestabilized, and capable of forming low-viscosity pastes easily. This suspension PVC resin, normally used for rotational moulding, has

been characterized by calculating the K value, using DIN 53726 standard, giving a final result of $K = 72.0$. By measuring mean molecular mass a value of 130 000 has been obtained. As phenol sources some industrial antioxidants as Irganox 1076 have been used.

2.2. Equipment

Analyses were carried out using a Shimadzu QP 1100 EX gas chromatograph–mass spectrometer (Shimadzu, Kyoto, Japan) equipped with a split/splitless injection system and a electron multiplier with ion converter as a detector. The limit of detection is 100 pg methyl stearate in the electronic ionization mode. Eluate samples were analyzed on a 30 m $\times$ 0.25 mm fused-silica SPB-5 capillary column (Supelco, Bellefonte, PA, USA) with a film thickness of 0.20 μm. The column temperature program was as follows: 55°C no hold, 10°C/min to 185°C with a 5-min hold, 10°C/min to 250°C with a final hold of 5 min. The linear rate of the helium carrier gas was 20 cm/s. A 2-μl volume of sample was introduced in the splitless mode with the injector at 250°C and the solvent vent was closed for 90 s after injection. The column was heat-traced (250°C) directly from the GC oven into the heated (250°C) mass spectrometer ion source. The MS was scanned from 10 to 1000 u twice every second, under standard electron impact conditions (70 eV). Data were collected and analyzed with an MS-PAC 1000 data system (Shimadzu) including the automatic quantitation software.

2.3. Operating procedure

Phenol pre-treatment in PVC derivatives is made by a Soxhlet extraction using sodium hydroxide aqueous solution (pH 10) over 1.000 $\pm$ 0.001 g of PVC product. This sample amount has been chosen because it has been previously considered as appropriate to obtain a representative quantity of phenol in final samples. The extracted phase is diluted to 70 ml with deionized water and stored in the dark until it would be pre-concentrated.

The phenol pre-concentration is made by using Bond Elut cartridges. First the cartridge was conditioned by addition of 1 ml of methanol, which was allowed to set for 5 min before being drawn off and 1 ml of 0.01 M HCl afterwards. The pH of samples was adjusted to 1–2 by addition of concentrated HCl to obtain the conversion of phenolate ion into phenol and 17.5 g of NaCl were added to the sample to decrease phenol solubility. It has been demonstrated that phenol recoveries in wastewaters are improved at NaCl concentrations between 20 and 25% [22].

Then the cartridge was adapted to a vacuum pump, Visiprep Vacuum Mainfold (Supelco) and the extract was aspirated through sorbent at 20 ml/min. Finally, the cartridge was washed with 0.01 M HCl and the vacuum left on for 10 min to dry the sorbent. The cartridge was eluted with 2 ml of methanol which was allowed to remain on the cartridge for a few minutes before being drawn off. After measuring the volume, the eluate was stored in glass-sealed vials in the dark until analysis.

GC–MS analysis was performed by injecting 2 μl of eluate in the splitless mode as described above. The use of methanol solutions for split-less injections is made because split injections resulted in poorly shaped chromatographic peaks. Quantitation of free phenol was done by comparing chromatographic peak areas for sample eluates with those of standards in the same concentration range.

3. Results and discussion

Because of its relatively high solubility in water and ionic characteristics, phenol has a short retention time. That is the reason why the GC–MS run must be started at low temperatures. A typical GC–MS run of a free phenol standard using selected ion monitoring (SIM) mode and centering on ion 94.0 is given in Fig. 1. It will be noted that a sharp peak is obtained at a relatively short retention time. The use of SIM mode in mass spectrometry results in a
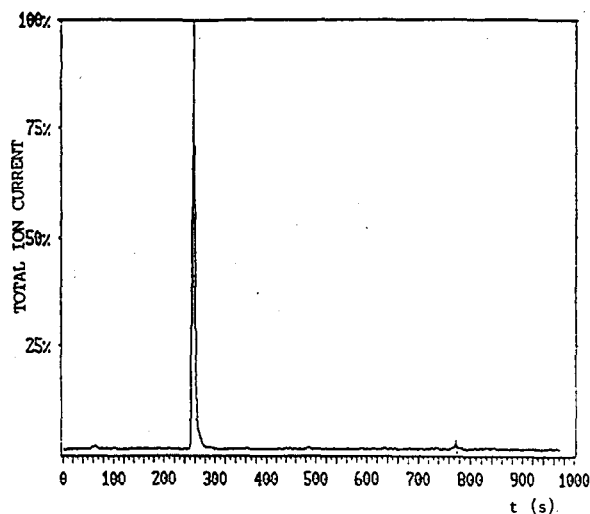

Fig. 1. Free phenol standard (5.0 ppm) chromatogram obtained by using the SIM mode.

better separation and peak quantitation and sensitivity improvement.

By operating with the method described above and preparing some adequate standards, a calibration line can be obtained as shown in Fig. 2. Samples can be quantitated by interpolation from a standard curve with linearity extending from 1.6 to 16.0 ng injected (slope = $1.22 \cdot 10^3$, y intercept = $-1.17 \cdot 10^3$, correlation coefficient = 0.9991).

Hydrophobic sample cleanup cartridges, as Bond Elut, offer a rapid alternative to other preconcentration techniques, which are necessary when the sample concentration is less than about 500 ppb. The common practice with these materials is to pass as much sample volume through as possible, without permitting breakthrough and a concomitant loss of recovery [28,29]. Unfortunately, for phenols, breakthrough occurs early so that the concentration advantage is reduced.

Moreover, in polymer samples it is important to assess the influence from other species in the matrix on free phenol recovery. A number of experiences have been made in order to quantify the breakthrough point of Bond Elut cartridges and to give a security interval of work. As shown by Fig. 3, a 70-ml sample can be considered as
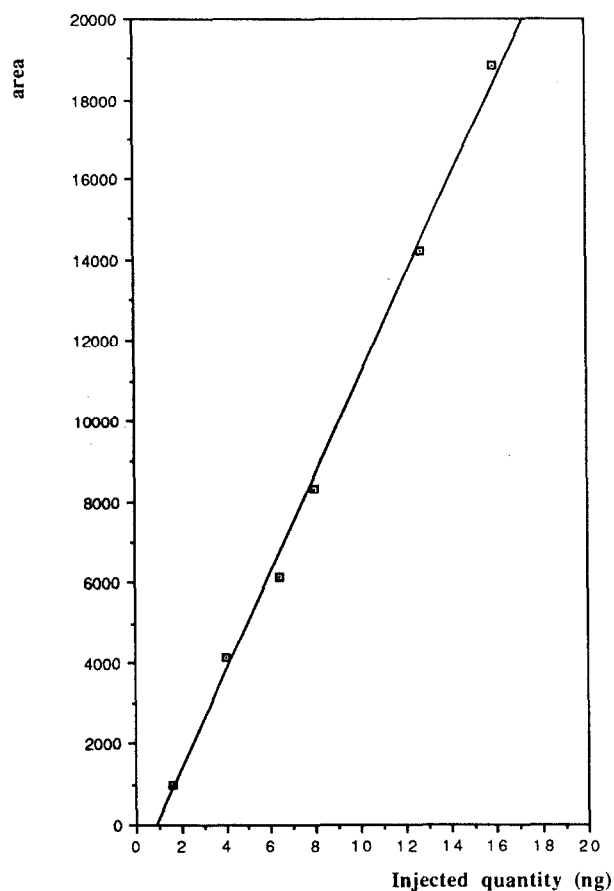
Fig. 2. Calibration curve for free phenol (SIM mode).

Fig. 3. Chromatograms of two 5-ng free phenol extracts: (a) 70 ml extract, (b) 90 ml extract.

the maximum quantity allowed to avoid break-through problems in a 5-ng free phenol extract.

By equilibrating the entire cartridge with solute, careful control of flow-rate is unnecessary. However, the absolute amount of solute trapped depends on the amount of adsorbent material in the cartridge. The standard deviation by mass of packaging material is approximately 2%, comparable to the precision in common solvent extractions.

A number of experiments have been carried out to obtain recoveries of phenol from some samples which were considered representative for the amount of free phenol in real samples. The results of analyses using the conditions described above are summarized in Table 1. As can be seen from Table 1, better recoveries are
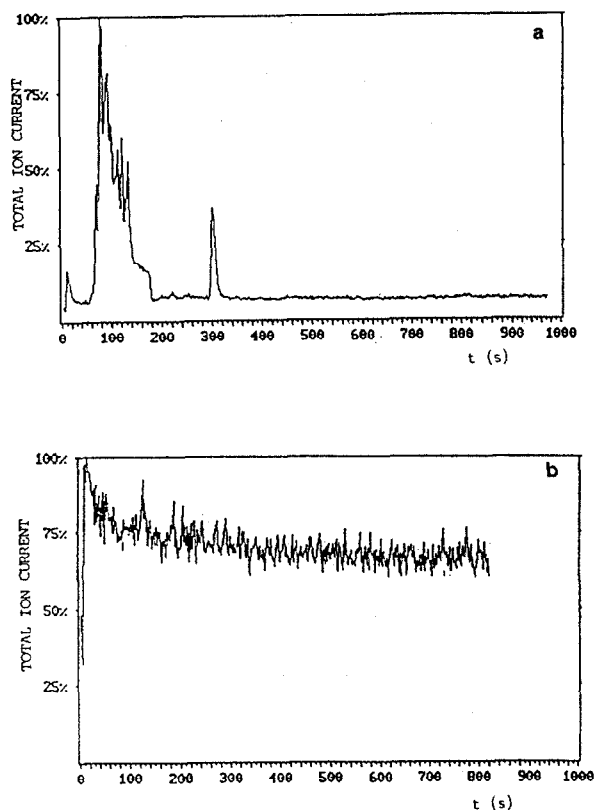
obtained in the interval 120–150 ppb. These results can be explained by some differences in apparatus sensitivity.

Some samples have been prepared in order to determine detection limits for free phenol in polymers. The restricted amount of sample that

Table 1
Free phenol recoveries from polymer samples

Phenol (ppb)	Recovery (%)	S.D. (%)
100	89	5
110	95	2
120	99	3
130	99	4
140	99	3
150	99	3

A 2-μl volume was injected; 55 to 185°C at 10°C/min. Three injections of every sample have been made.

Table 2
Sunlight and time of exposure effect in free phenol polymer sample

Time of exposure (min)	Apparent concentration (ppm)
0	4.9
30	4.6
60	3.7
90	3.2
120	2.9
150	2.5
180	2.0
210	1.8
240	1.6

can be passed through the cartridges is a real problem to obtain better detection limits. However, it was found that detection limits below 10 ppb for free phenol could still be achieved by GC–MS. This value could be improved by using larger injection volumes, but it has been proved that some problems could arise with capillary columns utilized during the present study using volumes larger than 2 μl. Thus, this method applied to polymers permits us to obtain detection limits very similar to wastewaters [4,5,22].

Finally, a study has been made to determine if sample degradation occurs if the sample is stored in any particular way. We have studied photochemical degradation for a 5-ppm phenol sample and some phenol loss due to sunlight has been observed. Results are summarized in Table 2.

As can be seen from Table 2 there is an important effect of sunlight in phenol apparent concentration. Hence, it would be better to store samples in the dark to avoid photochemical degradation.

4. Conclusions

From a practical standpoint, a new GC–MS method to determine free phenol in polymers has been proved to be as consistent as used in waters. Moreover, the cartridge adsorbent extraction method has several advantages: (a) very little solvent (2 ml) is needed for extraction so that the evaporative concentration step is eliminated; (b) the labor and equipment required for sample preparation are greatly reduced; (c) selective elution procedures yield a final eluate with fewer background interferences than obtained by common extraction procedures in complex samples as polymers. This factor could improve the accuracy and precision of the analysis.

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