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Determination of phenol in polymeric materials by supercritical fluid extraction combined with gas chromatography–mass spectrometry

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Abstract

A two-level factor design has been used to optimise the supercritical fluid extraction (SFE) of phenol in polymeric materials with four main factors (temperature, pressure, static time and amount of modifier). The minimum conditions required were 40°C, 13.9 MPa, 5 min as static time and no methanol, while optimal conditions were 110°C, 48.3 MPa, 15 min as static time and 80 µl of methanol. After the static time, all experiments took 15 min to be run in dynamic mode. Extractions were performed using an off-line mode with a single vial filled with a few millilitres of methanol. Determination was carried out by capillary gas chromatography with mass spectrometric detection. Samples were prepared using a known amount of phenol mixed with a poly(vinyl chloride) resin that was plasticized with dioctyl phthalate. Maximum recoveries were obtained at 110°C, 48.3 MPa and a static time of 5 min in the absence of methanol. Therefore, the use of modifier does not seem to be important for the analysis of phenol in polymers. Under the optimum conditions found, the SFE method was compared favourably with Soxhlet liquid extraction for different real samples. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Plastics used in normal life contain many additives, for the purpose of changing their polymer properties in some way, such as plasticisers, antioxidants or stabilizers. Analysis of polymer additives can be difficult and tedious due to their inclusion in a matrix that is insoluble in most solvents. Therefore, the quantitative extraction of the analyte from the plastic before determination is necessary. Polymer additives have normally been extracted by a liquid–solid extraction system, such as Soxhlet. This method eventually gives good efficiencies but it presents a

number of drawbacks, such as the long extraction time and the large amount of solvents required.

Supercritical fluid extraction (SFE) is an analytical technique, the applications of which have been growing continuously over the last few years. This fast and clean technique is replacing traditional extraction methods for organic compounds in many different samples. Carbon dioxide is the extraction solvent that has been selected for most of the recent SFE studies because of its favorable characteristics, such as its relatively low critical temperature and pressure, low cost, high purity and low toxicity and reactivity. Many different samples have been extracted with supercritical CO₂, e.g. cholesterol in noodles [1], polychlorinated biphenyls (PCBs) from

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river sediments and polyaromatic hydrocarbons (PAHs) from urban air particulate matter [2], *N*-nitrosamines from fried bacon [3], semivolatile compounds from lemon peel [4], etc. However, CO₂ polarity is low and it may be necessary to develop an appropriate strategy for the improvement of supercritical extraction efficiencies for polar and ionic compounds [5].

Analysis of polymers is one of the most recent uses of SFE, giving faster extraction times and higher efficiencies. Thus, it is possible to obtain residual oligomers from polyethylene terephthalate (PET) [6], Irgafos 168 and Irganox 1010 from commercial polypropylene [7], aromatic amines from rubber [8], flame retardants from polyurethane foams [9] and others.

In some previous work by our group, efforts were focused on the extraction of some of the most common additives used in poly(vinyl chloride) (PVC) samples, i.e. phthalate plasticisers [10,11]. Variation in extraction efficiencies with the temperature and pressure of pure CO₂ was studied, and the optimum conditions were determined. Extractions were carried out for PVC samples spiked with dibutyl phthalate (DBP) and bis(2-ethylhexyl)phthalate (DOP). In addition, in the field of phenol determinations, we developed a solid-phase extraction (SPE) coupled to mass spectrometry (MS) method for PVC derivatives [12]. The results obtained were good, but the extraction procedure was too long and complicated for real samples. For this reason, we sought to develop a SFE–GC–MS method that may be used more conveniently in routine practice.

In polymer processing, the use of a great number of additives as antioxidants and ultraviolet absorbents is common [13]. Some of them are phenol derivatives with sterically protected phenolic hydroxyl groups. 2,2-Bis(*p*-hydroxyphenyl)propane, commonly known as bisphenol A, and 2,6-di-*tert*-butyl-*p*-cresol, commonly known as BHT, are two of the most widely used. When these compounds are added to polymers, it is possible to find some degradation products, such as light alcohols and phenols. GC with flame ionization detection (FID), electron-capture detection or MS detection is commonly used as the technique for the identification and determination of phenol in polymers [14,15].

Phenol extraction from a soil matrix using supercritical CO₂ was previously considered by some authors, such as Llompert et al. [16]. In contrast, Hedrick and Taylor [17] and Lee et al. [18] extracted phenol from aqueous matrices by means of derivatizing agents. However, the use of SFE for the extraction of phenol from polymers has not been considered as an alternative. In the present work, the SFE of phenol from polymeric matrices is studied. The extraction conditions have been optimised and results were compared with those obtained using Soxhlet extraction for spiked and real samples.

2. Experimental

2.1. Materials and chemicals

The PVC resin used was Vestolit B 7021 (Hüls, Germany), which was characterised in a previous work [10]. In order to prepare samples spiked with phenol, the use of a plasticizer was necessary and DOP (industrial grade) was selected. Phenol (analytical grade) was supplied by Panreac (Barcelona, Spain), analytical-grade methanol by Rectapur (Prolabo, Barcelona, Spain) and supercritical grade CO₂ was supplied by Abelló Linde (Valencia, Spain).

2.2. Instrumentation

SFEs were carried out by using an SFX 220 extraction system (ISCO, Lincoln, NE, USA), which consists of an SFX 220 extractor, a SFX 200 controller and a D-syringe pump, as indicated in a previous work [10]. Collection of extracts was performed using a capillary restrictor, the end of which was introduced into a graduated dark vial containing 8 ml of methanol (off-line mode). The restrictor was equipped with a temperature controller, which made possible the control of the temperature throughout its total length. Samples were placed in stainless steel cartridges (internal volume, 2.5 ml).

Extracts were analysed using two different instruments: A Shimadzu QP-1100-EX gas chromatograph–mass spectrometer (Shimadzu, Kyoto, Japan) equipped with a split/splitless injection system was used first. A 30 m×0.25 mm fused-silica capillary

Table 1
Experimental design for the optimisation of SFE conditions for phenol in PVC derivatives

Experiment	Pressure (<i>P</i>)	Temperature (<i>T</i>)	Static time (<i>t</i>)	Methanol (<i>V</i>)	Phenol recovery (%) (corrected)
1	–	–	–	–	64±7
2	–	–	+	–	84±8
3	–	–	–	+	91±7
4	+	–	–	–	82±6
5	–	+	–	–	79±3
6	–	–	+	+	84±4
7	+	–	+	–	84±5
8	–	+	+	–	71±5
9	+	+	–	–	100±2
10	+	–	–	+	89.4±0.9
11	+	–	+	+	88±1
12	–	+	+	+	80±4
13	+	+	+	–	95±2
14	+	+	–	+	73±2
15	+	+	+	+	80.1±0.2
16	–	+	–	+	68.5±0.9
17	0	0	0	0	89.1±0.8

A 5.4-mg amount of phenol was used per gram of sample.

(+)=high level.

(–)=low level.

(0)=middle level.

column with SPB-5 as the stationary phase and a film thickness of 0.20 μm was used (Supelco, Bellefonte, PA, USA). The MS was scanned in position ion from 10 to 1000 m/z twice every second, under standard electron impact conditions (70 eV), and data were collected and analysed with an MS-PAC 1000 data system (Shimadzu).

In addition, a Shimadzu GC-9A gas chromatograph controlled by CLASS-VP 4.2 (Shimadzu) software was used. The system was equipped with a flame ionization detector and a split/splitless injector with a capillary column (15 m×0.53 mm I.D., 0.50 μm , with SPB-5 as the stationary phase) from Supelco.

2.3. Sample preparation and operating procedure

Plastisols were prepared by mixing powdered PVC with DOP and an adequate amount of solid phenol. Air was eliminated in a vacuum chamber and then the mixture was cured at 150°C for 15 min. These plastisols contained 36% (w/w) DOP and 0.54% (w/w) phenol.

All extractions with supercritical CO_2 were per-

formed in dynamic mode (time, 15 min). The extraction chamber was filled with approximately 0.2 g of material. Samples were cut with a cleaver to obtain sheets of approximately 2.8 mm thickness, which is the most adequate size as has been previously observed [11].

Soxhlet extractions were carried out with a typical Soxhlet apparatus (70 ml of methanol in a reflux for 4 h). A 2-g amount of sample was necessary in every extraction. Quantitation of the phenol extract was carried out by a calibration plot and standards were prepared by weighing an appropriate amount of phenol and dissolving it in methanol. GC-MS analysis was performed by injecting 1 μl of extract in the splitless mode. The column temperature program was as follows: 55°C for 1.5 min; then to 260°C at 10°C/min and 260°C for 15 min (injection temperature, 250°C). Analyses were carried out in the selected ion monitoring (SIM) mode centred on ion 94.0. When GC-FID was used, the temperature program was as follows: 55°C for 1.5 min; 5°C/min to 90°C, held for 1 min and 10°C/min to 260°C, held finally for 15 min (injection temperature, 300°C). The solvent vent was closed for 90 s after injection

in both instruments. Quantitation of phenol was performed by comparing chromatographic peak areas for sample extracts with those of standards in the same concentration range. Extracts were analysed in triplicate.

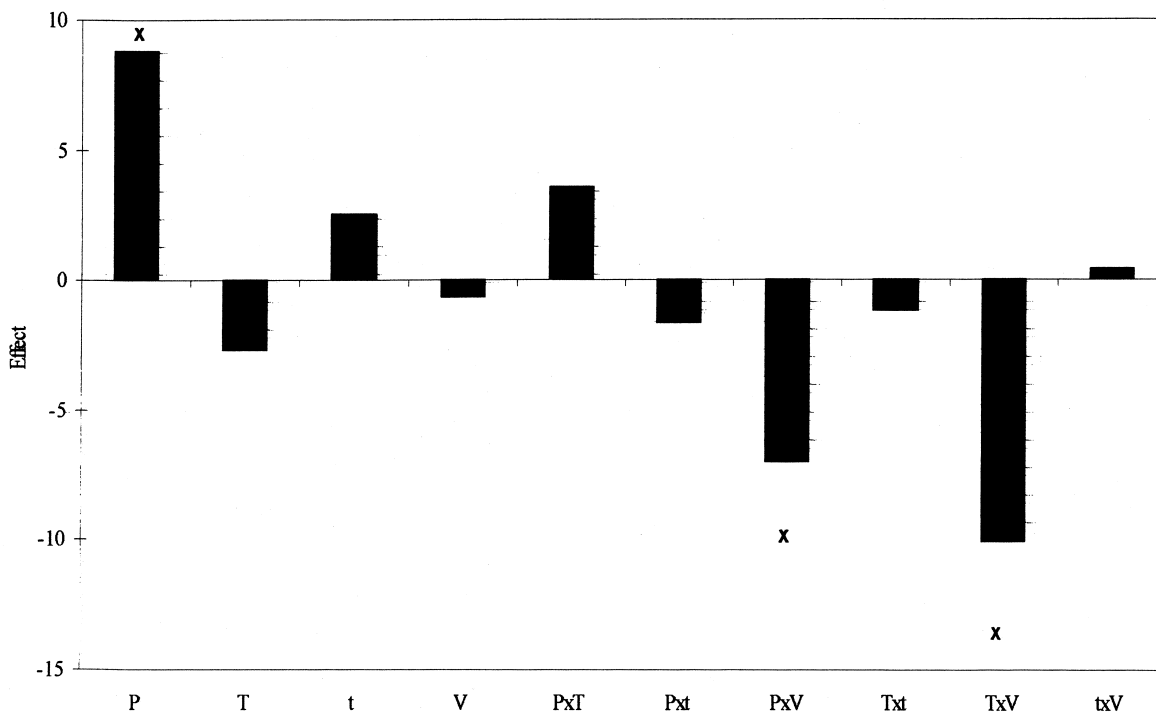
The effect of different parameters on the supercritical extraction of phenol in polymeric matrices was studied using a four-factor design, with two levels for each factor. The selected factors were supercritical CO₂ pressure (*P*) and temperature (*T*), static time (*t*) and amount of methanol added to the extraction chamber (*V*). Maximum and minimum levels of each factor were selected according to the instrumental limitations and to the results of previous work [10]. The selected levels were as follows: Pressure 13.9 and 48.3 MPa; temperature, 40 and 110°C; static time, 5 and 15 min and amount of modifier, 0 and 80 µl of methanol. This experimental design required sixteen experiments, which were performed in duplicate. In order to complete the design, an additional set of conditions was selected

(31 MPa, 80°C, 10 min of static time and 40 µl of methanol). The experiments were run in a randomised order.

3. Results and discussion

Experiments and the results obtained are shown in Table 1. A factorial design has some advantages over parameter-to-parameter optimisation, as a lower number of experiments are required, along with an easy estimation of any interaction between parameters.

The highest absolute recovery obtained under the indicated conditions for the extraction of phenol from a PVC plastisol was 95.0%. Additional experiments with conditions near the point of maximum recovery were carried out, but no improvement in recovery was observed. This may be due to the loss of phenol during the process of sample preparation



x = Significant variables and interactions. The horizontal line indicates the statistical significance bound for the effects.

Fig. 1. Main effects and interactions diagram in the experimental design of SFE for phenol in PVC derivatives.

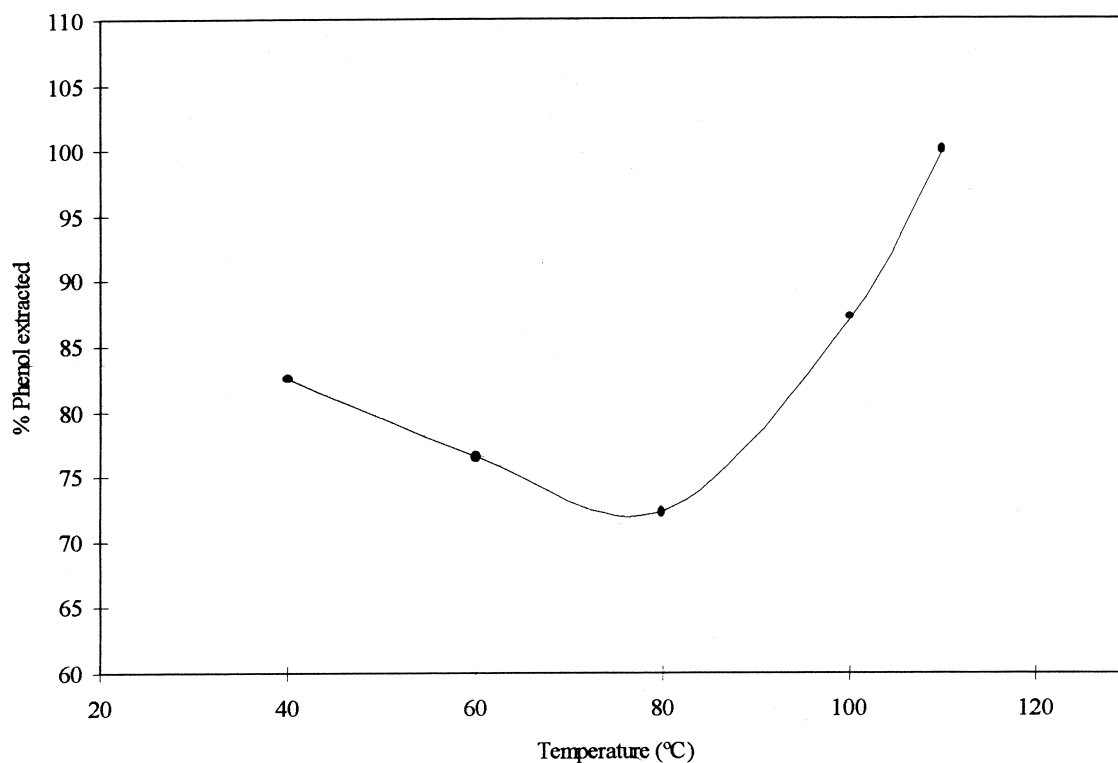
(mainly curing in an oven). Therefore, some new experiments were required. A solution of phenol in DOP with a similar quantity as in plastisol was prepared and this sample was treated in the same way as the PVC plastisol. Then, an aliquot of this solution was dissolved in methanol and analysed by GC. It could be concluded that some phenol was lost during the preparation of the plastisol. This is the reason why the obtained results were corrected, and 95% corresponds to a recovery of 100%.

Statistical analysis of the variables was performed and the results are presented in Fig. 1. It may be noted that the pressure is the only statistically significant variable (for a Student's *t*-test significance of 95%). Temperature and static time have some minor bearing. In contrast, the influence of the amount of modifier added was practically negligible. When interactions between variables were analysed, it could be seen that only CO₂ pressure and tempera-

ture with amount of methanol have statistical significance.

The effect of CO₂ pressure may be due to the fact that it could be high enough to improve the fluid density. Therefore, under certain conditions, the CO₂ polarity was very similar to phenol polarity and the analyte was extracted in a more efficient way. The recovery of phenol increases with CO₂ pressure at a constant temperature. This effect has been observed in most samples, especially polymers.

Surprisingly, the amount of modifier does not seem to influence the recovery of phenol. Methanol was selected as the modifier because of its ability to improve CO₂ polarity, as has been indicated for many kinds of samples. The modifier was spiked onto the polymer sample prior to the start of extraction with the selected conditions. The most important effect of the addition of modifier was obtained at low temperatures (40°C, 13.9 MPa, 5 min



48,3 MPa, 5 min as static time and 0ul of MeOH.

Fig. 2. Recovery of phenol. Variation with temperature.

static time and 80 μl of methanol), giving a 91% corrected recovery, in contrast with 67% at 110°C. This fact is also observed at high pressure (48.3 MPa): 89% at 40°C and 73% at 110°C. The influence of the addition of modifiers to polymeric matrices was previously studied by Lou et al. [19] and similar effects were found. The small improvement in the extraction yield observed on addition of modifier at low temperatures may be due to the fact that the diffusion rate of phenol increases when the PVC particles are swollen by the modifier molecules. The smaller effect of the addition of modifier at higher temperatures is most likely due to the fact that the diffusion of phenol into PVC is relatively fast. Therefore, the action of the modifier in the extraction of phenol from PVC derivatives is more effective at lower extraction temperatures.

There is also an important interaction between modifier and pressure. When the pressure is high, the ability of CO_2 to extract polar compounds is higher and it may be possible that CO_2 could extract or sweep away the methanol added to the sample. The

result is a lower amount of methanol available to the sample and, hence, the effect of the modifier is practically negligible. Another possible explanation suggested by Lou et al. [20] might be that the extracted modifier causes a closed structure in the polymer and prevents extraction of the analyte.

The effect of the temperature of supercritical CO_2 on the sample can be explained. At high temperatures, CO_2 density and its solvent strength are low and a decrease in extraction yield should be observed consistently. However, the diffusion coefficient of phenol in the PVC matrix increases with temperature, like the extraction rate. If the pressure is high enough, the solubility of phenol is not the limiting parameter for extraction and a high temperature will improve the yield. However, when the pressure is low, the supercritical CO_2 solvent strength is low and the solubility of phenol is the rate-limiting step, so that an increase in temperature will cause a decrease in recovery. The variation in the recovery of phenol with temperature is shown in Fig. 2. A minimum was observed at 80°C and it was caused by

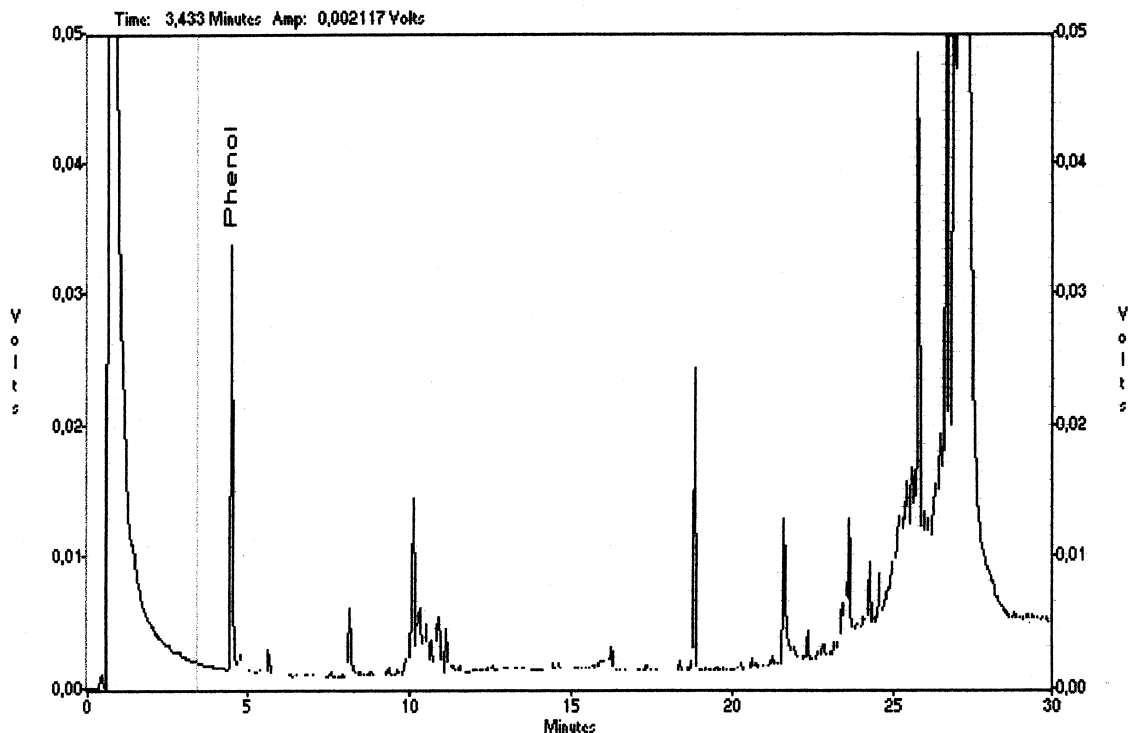


Fig. 3. Chromatogram of a SFE extract for sample 1 (split mode).

minimal phenol solubility at 48.3 MPa. The optimum conditions were 48.3 MPa, 110°C, 5 min as the static time and no methanol.

As an additional point, a Soxhlet extraction was carried out using the conditions referred to above for the same spiked sample. The total recovery obtained was 63%. Therefore, SFE is a better extraction method for the determination of phenol in PVC samples because higher recoveries are obtained, while the time needed and the amount of solvent required are clearly lower.

3.1. Phenol determination in real samples

In order to validate the proposed method of extraction for phenol from PVC derivatives, some real samples were selected. The total phenol content of them was extracted by SFE under the optimum conditions and determined by GC–MS. A typical chromatogram of phenol extracted from a polymeric

sample is shown in Fig. 3. The phenol peak is clearly observed and can be quantified without any problem in every case. The rest of the peaks observed at higher retention times are representative of other additives, such as plasticizers (DOP) or stabilisers.

The results obtained are shown in Fig. 4. As can be seen, recoveries for Soxhlet extraction are higher in samples with a high phenol content. However, when the phenol concentration is low, extraction with supercritical CO₂ resulted in higher recoveries than those obtained when Soxhlet extraction was used. Therefore, extraction of phenol with supercritical CO₂ is more effective when the total concentration in the polymer is low, which is the usual case in PVC derivatives.

This result may indicate that the pure carbon dioxide may become saturated with phenol. It has been shown that the solubility of phenol is only 3% (w/w) in liquid carbon dioxide at 25°C [21]. Therefore, some caution should be taken for the analysis

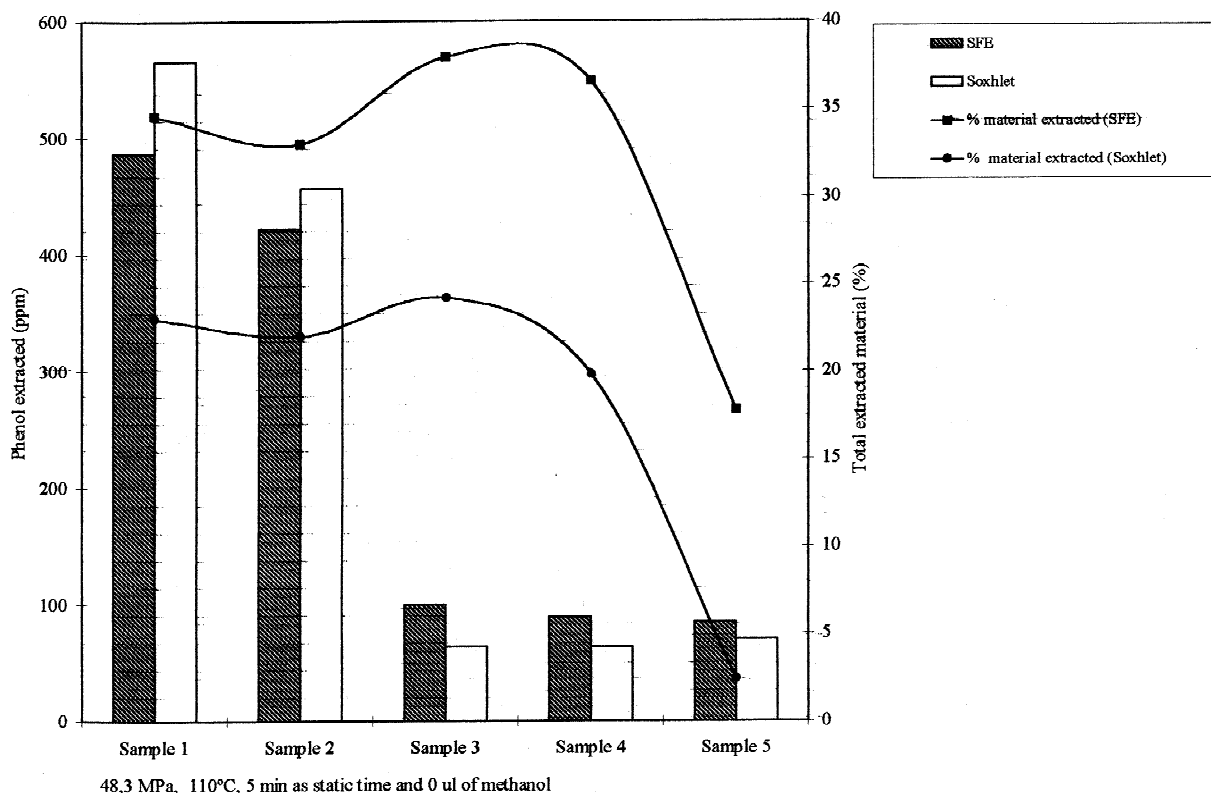


Fig. 4. Phenol recovery (mg phenol/kg material) and % material extracted from polymeric samples.

of phenol in polymers when an unusually high concentration is expected. As pointed out above, the addition of a polar modifier does not enable higher recoveries in the extraction.

4. Conclusions

A new SFE–GC method to determine phenol in some PVC derivatives has been developed and it has proved to be consistent. The optimum conditions for the supercritical extraction of phenol have been obtained and recoveries near 100% are obtained for 5 min static time, 110°C, high pressure (above 48 MPa) and using pure CO₂ as the supercritical fluid. The use of a polar modifier did not give rise to any additional improvement in recoveries, except at low temperatures, i.e. 40°C. Supercritical extractions in spiked and real samples give yields that were higher than those obtained by Soxhlet extraction, and had the additional advantages of a shorter analysis time and a reduction in the amount of organic solvent used.

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