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Analysis of poly(vinyl chloride) additives by supercritical fluid extraction and gas chromatography

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Abstract

The use of supercritical fluid extraction (SFE) is growing, with an expanding range of applications in many different fields as a consequence of its advantages compared with traditional extraction methods. In order to develop an analytical method to determine dibutyl phthalate (DBP) and dioctyl phthalate (DOP) traces (<20 ppm) in flexible poly(vinyl chloride) (PVC) formulations, a maximum efficiency in the extractive process and an adequate separative system are needed to avoid interferences between these two plasticizers and other additives that could be present at high concentrations in flexible PVC formulations. In order to determine the optimum SFE conditions, the extraction time, temperature and pressure were controlled. The separation and quantitation of individual components in the PVC extracts were carried out off-line by using a semicapillary column in gas chromatography (GC). Samples with different DOP content (41.18%, 33.33% and 23.08%) and DBP content (41.18%), as well as samples with both plasticizers (20.59% DOP and 20.59% DBP) were prepared. Some other samples were also prepared to study detection limits for these two PVC additives. Recoveries and reproducibilities were studied in every sample. Finally, this method was compared with Soxhlet liquid extraction. Determination by gravimetric analysis of the total extracted material was found to be particularly suitable for PVC. This study demonstrates the potential of SFE to shorten extraction times with similar or even better extraction efficiencies compared with traditional liquid methods.

Keywords: Extraction methods; Dibutyl phthalate; Dioctyl phthalate; Phthalates; Poly(vinyl chloride)

1. Introduction

Plastic products have found widespread use in modern society and poly(vinyl chloride) (PVC) is one of the most widely used. The versatility of PVC can be attributed to the range of properties which can be reached through the use of additives. Plasticizers are the additives most commonly used. Nowadays, more plasticizer is consumed in processing PVC than any other thermoplastic resin. A plasticizer is a substance which is added to a material (usually a plastic, resin or elastomer) to improve its pro-

cessability, flexibility and stretchability [1]. There is no stoichiometric upper limit to plasticizer uptake. This enables a processor to adjust the flexibility of the basic polymers (such as PVC) over a wide range. Phthalates are the plasticizers most commonly used, specially di(2-ethylhexyl), DOP, because of its cost (86% share of the world plasticizer market). The properties of a plasticized polymer depend strongly on the concentration and chemical structure of the plasticizer [2].

Analysis of polymer additives can be complicated owing to their physical properties and their inclusion in a matrix that is insoluble in most solvents, so that the range of analytical techniques that could be

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performed without prior separation from the polymer matrix is limited. Consequently, the analysis can be considered as a two-stage procedure: the extraction of the additives from the polymer followed by identification and quantitation. Polymer additives from real samples have usually been extracted by liquid extraction, for example using a conventional Soxhlet system. However, liquid extractions have a number of drawbacks. Extraction times are long, taking several hours or even days. Liquid extraction procedures often involve precipitation and reconcentration steps, which can cause some loss of the analytes and some contamination through the concentration of solvent impurities. Furthermore, liquid solvents are often toxic. Therefore, the use of large solvent volumes not only means high costs but also environmental disposal problems and, on the other hand, Soxhlet extraction requires large sample size.

SFE is a relatively new sample preparation method. The compressibility of a supercritical fluid is large at temperatures just above critical and this means that small changes in pressure can produce big changes in the density of the fluid. An additional advantage of SFE is its potential for selective extraction [3,4] which can be performed by changing conditions, particularly the temperature and density of the fluid.

The range of samples SFE has been applied to, continues to broaden: environmental [5,6], amines extraction [7,8], food [9,10], textile [11], phenols [12] and polymer analysis, mostly antioxidants and UV stabilizers [13–17].

In the case of PVC, only a few papers analyzing plasticizers have been published. Hunt and Dowle [18] extracted DIOP (diisooctyl phthalate) from PVC.

On the other hand, dynamic off-line supercritical fluid extraction is a commonly used SFE mode. In this extraction mode there is an aspect of special interest: the analyte trapping system. This system

must be efficiently performed. One type of trapping system that may be used is a liquid trap. The restrictor is simply placed in a vial which contains the liquid solvent. The analyte is trapped into the solvent, while the decompressed fluid vents to the atmosphere. The liquid solvent must be compatible with the analyte and the extraction fluid when modifiers are used. When CO₂ is used as extraction fluid, there can be a great deal of cooling associated with the decompression of the fluid. Because of this cooling, it is possible for the collection fluid to freeze and for small pieces of ice to clog the restrictor tip. This is the reason why the restrictor is often heated. The flow of compressed fluid for liquid trapping is usually maintained below 1 ml/min because upon decompression of the fluid, approximately 500 ml/min of gas is produced. This large volume of gas can cause violent bubbling of the liquid and could lead to some analyte loss.

In the present study we analyzed different PVC formulations with DOP as plasticizer. The use of SFE as an alternative to liquid extraction was investigated and the extraction time, temperature and pressure were varied in order to determine the optimum SFE conditions. We also investigated two ways to collect DOP in SFE and extracts were compared with Soxhlet extraction. Extracts were analyzed via off-line with GC.

2. Experimental

2.1. Materials and chemicals

A Vestolit B 7021 (HÜLS) PVC resin has been used. This is a non prestabilized homopolymer, capable of forming low viscosity pastes easily. This suspension PVC resin, normally used for rotational moulding, has been characterized by calculating the

Table 1
Characteristics of plasticizers

Property	DOP	DBP
Viscosity dyn., 20°C	77–82 mPa s	20–22 mPa s
Density rel., 20°C	0.983–0.984 g/ml	1.046–1.047 g/ml
Refraction index, 20°C	1.486–1.487	1.492–1.493
Volatility (2h/130°C)	Max. 0.2% by weight	Max. 2.0% by weight

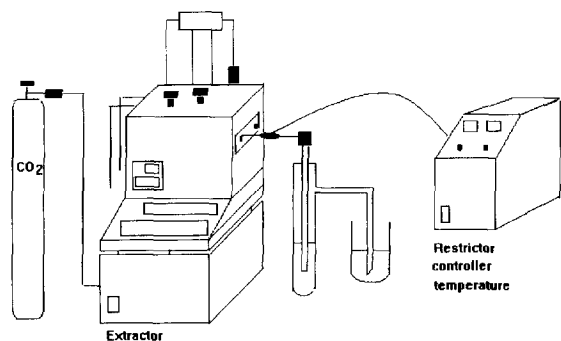


Fig. 1. Scheme of the 2-vial apparatus used.

K value, using DIN 53726 standard, giving a final result of $K=72.0$. This parameter is related to the molecular weight distribution in the resin. By measuring mean molecular mass, a result of 130.000 has been obtained. Another parameter to characterize the resin is the particulate size distribution. Obtained

values are: volume mean diameter: $[D(4,3)]=23.4 \mu\text{m}$; surface mean diameter: $[D(3,2)]=5.7 \mu\text{m}$.

DOP (chemically pure grade) was supplied by Probus (Barcelona, Spain) (characteristics in Table 1), cyclohexane was supplied by Scharlau (Barcelona, Spain) and CO₂ supercritical grade was supplied by Liquid Carbonic (Spain). DBP was supplied by Hüls Española (Barcelona, Spain).

2.2. Instrumental

SFEs were carried out by using an SFX 220 extraction system (ISCO, Lincoln, NE, USA) which consists of an SFX 220 extractor, an SFX 200 controller and a D-syringe pump with a capillary restrictor and a temperature controller. Flow-rate in restrictor was 1.5 ml/min. In order to trap DOP and DBP, the apparatus shown in Fig. 1 was necessary and its efficiency was evaluated.

Analysis of extracts was performed with a GC

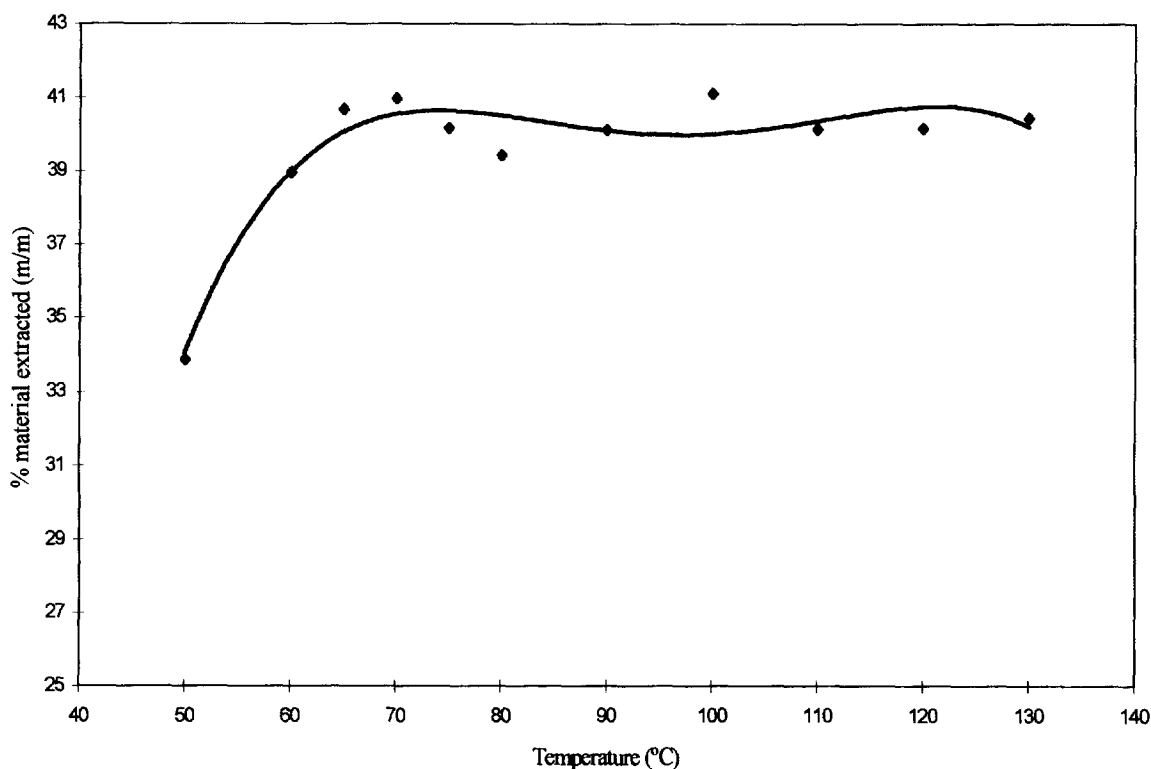


Fig. 2. Variation of the concentration of extracted material (% m/m) with extraction temperature for a plastisol 100:35:35 (PVC-DOP-DBP). Extraction pressure, 51.711 MPa; extraction time, 25 min.

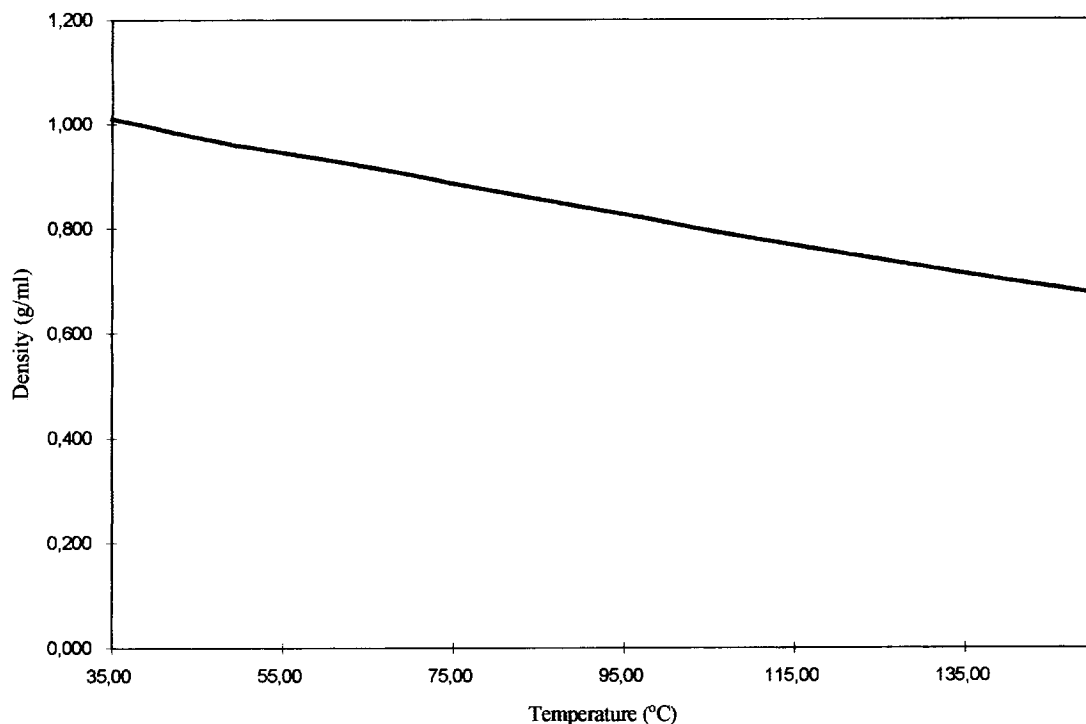


Fig. 3. Variation of CO₂ density with temperature.

Shimadzu model GC-9A (Shimadzu, Kyoto, Japan) coupled with a C-R4A Chromatopac system equipped with a split/splitless injection system and a flame injection detector. A capillary column 15 m × 0.53 mm and I.D. 0.50 μm with SPB-5 as stationary phase from Supelco (Supelco, Bellefonte, PA, USA) was used.

2.3. Procedure

All extractions with supercritical CO₂ were performed in dynamic mode. The extraction cell was filled with approximately 0.2 g of material. Samples were cut with a cleaver to obtain sheets of 2.8 mm of thickness. The restrictor was maintained at 120°C and was placed into a few millilitres of cyclohexane.

Soxhlet extractions were carried out with a typical Soxhlet apparatus with 70 ml of cyclohexane in a reflux for 5 h and 2 g of sample were necessary in every extraction. Soxhlet extractions and SFEs were

performed in triplicate as well as chromatographic analysis of each extract in order to study the reproducibility.

Plastisols were prepared by mixing powdered PVC with plasticizer. Air was eliminated in a vacuum chamber and then they were cured at 150°C for 15 min. In cases where DOP was not enough to mix, DINP (diisononyl phthalate) was used. DOP concentrations were 70, 50, 30, and 10 parts per hundred resin.

Quantitation of the plasticizer extract was carried out by a calibration plot and standards were prepared by weighing DOP and dissolving it in cyclohexane. Optimization of conditions was carried out with a 100:35:35 PVC–DOP–DBP paste and gravimetrically analyzed. Chromatographic conditions were as follows: the column temperature program was held at 260°C. The linear rate of the helium carrier gas was 20 cm/s. A 0.5 μl volume of sample was injected in the split mode with the injector at 300°C.

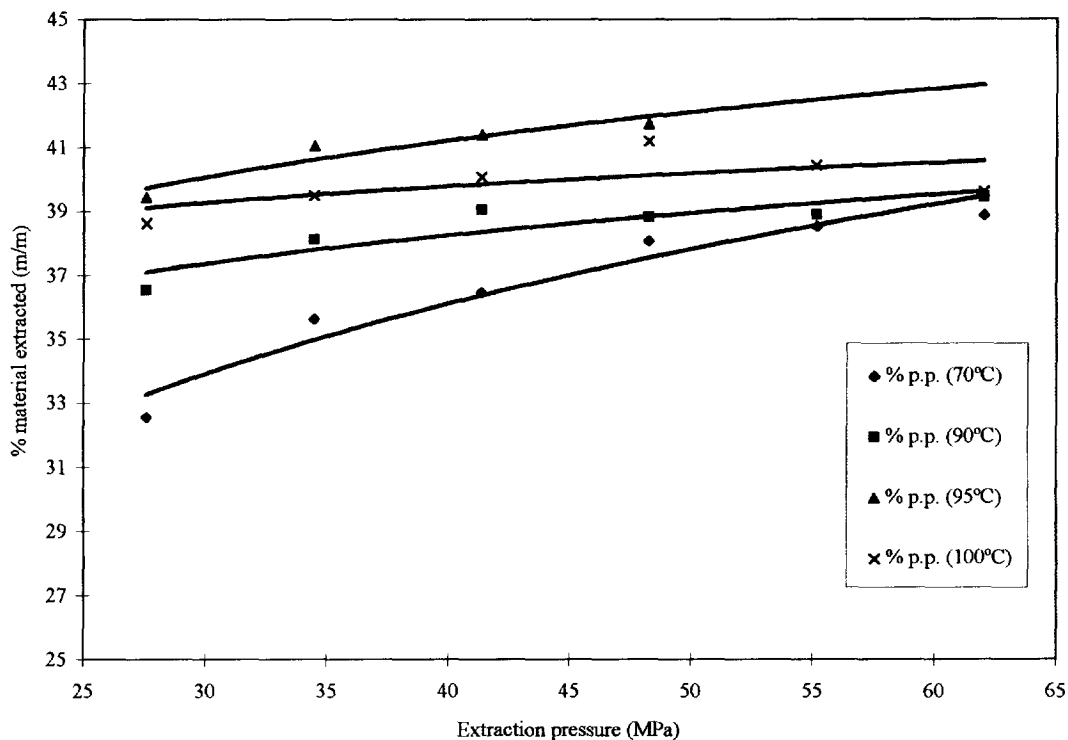


Fig. 4. Variation of the concentration of extracted material (% m/m) with extraction pressure at different extraction temperatures. Extraction time, 25 min.

3. Results and discussion

3.1. Effect of temperature

Fig. 2 shows the variation suffered by the plastisol with a 41% (w/w) of plasticizers DOP and DBP, when extraction conditions were 25 min and 51.711 MPa as extraction pressure. The plot shows a typical shape: when temperature is low, extraction efficiency is low, rising gradually and reaching a plateau when temperature is increased being not possible to improve extraction efficiency.

Temperature may cause some effects on phenomena taking part during the extraction process. These effects will be the following:

1. A decrease in CO_2 density dropping off its solvation power (Fig. 3).
2. An increase in the diffusion coefficient of additives in the polymer, increasing mass transfer

into the extracting solvent. Variation of diffusion coefficient with temperature is given by the Arrhenius type equation:

$$D = D_0 \exp(-E/RT) \quad (1)$$

where: E is the activation energy, D_0 is the pre-exponential factor, R is the gas constant.

3. An increase in temperature will also affect the physical structure of the polymer and can cause the polymer to melt or soften. There should be an increase in the rate of extraction when a semicrystalline polymer is in rubbery rather than glassy (g) structure. In PVC, T_g is below 0°C , so molecules are easier to extract when extraction temperature was raised above T_g .

It is possible to attribute the fast increment in mass loss during the extraction between 50 and 90°C (Fig. 2) to the increase in the diffusion coefficient with

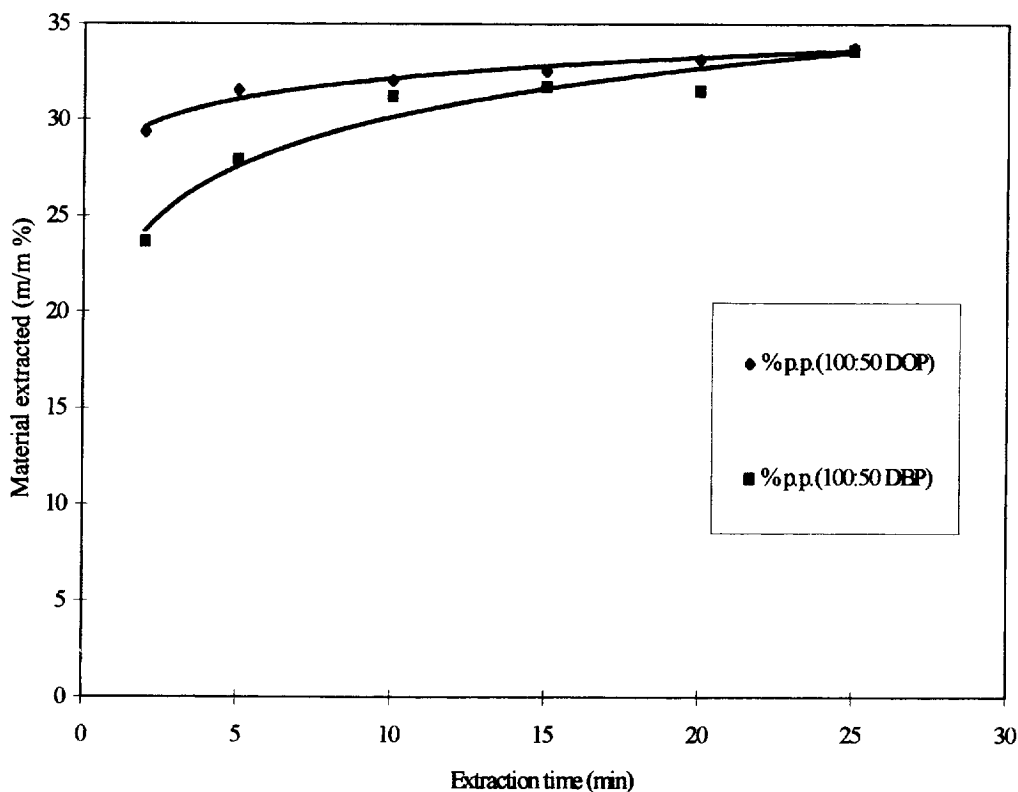


Fig. 5. Variation of the concentration of extracted material (%m/m) with extraction time for plastisols 100:50 DOP and 100:50 DBP. Extraction pressure, 48.263 MPa; extraction temperature, 95°C.

temperature. In addition, at high temperatures, softening suffered by the polymeric matrix allows that the CO_2 could penetrate the sample to drag analytes out of it. Both, diffusion coefficient and matrix softening increase extraction efficiency overcoming, the drop of supercritical CO_2 power solvent as a consequence of its density decrease. Therefore, higher temperatures make extraction easier but it is necessary to find a compromise due to the thermal stability of the analytes. A thermogravimetric analysis shows that plasticized PVC starts degradation at approximately 200°C. Plasticizers do not suffer degradation but evaporation. At 110°C, DBP loses 0.65% (w/w) and DOP loses 0.56% after 25 min. A temperature between 80 and 100°C is adequate for extraction.

It is also important to measure the extent of swelling in polymers caused by sorption of gases because CO_2 sorption will cause the plasticization

(formation of a solution) of the polymer. As Chiou et al [19] observed, plasticization can reduce the T_g and the polymer will become a rubber instead of a glassy system whose T_g is not much higher than the sorption temperature. As is shown in Fig. 2, the amount of additive obtained increases with temperature. The thermal stability of the additives must also be considered when an extraction temperature has to be selected.

3.2. Effect of pressure

The variation of the extracted plasticizer amount with pressure at different temperatures is shown in Fig. 4. At low temperatures (70°C), when pressure is increased, the amount of extracted material is also increased. If the temperature is 90°C, extraction efficiencies are higher than 70°C (isotherm). At temperatures higher than 90°C, extraction increases

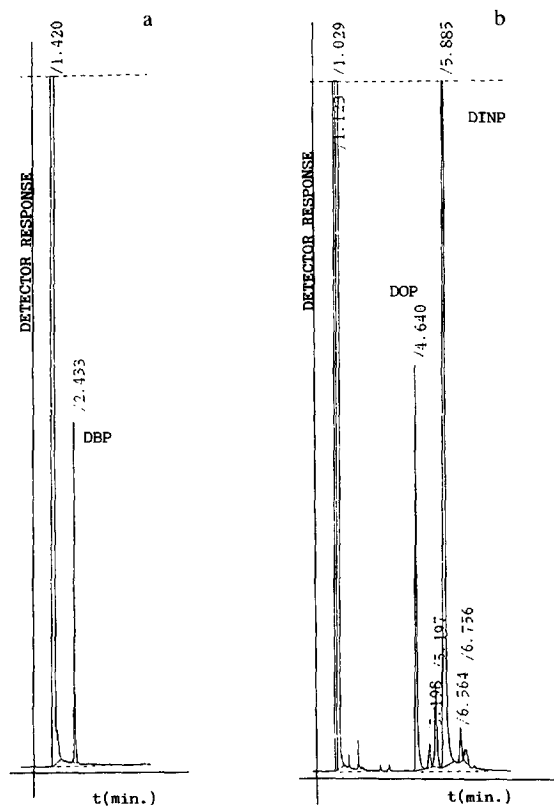


Fig. 6. Chromatogram of plasticizers. a: DBP; b: DOP+DINP.

even if pressure is low. Although for dense gases pressure is inversely proportional to diffusivity, CO_2 sorption by the polymer has been found to be enhanced at higher pressure. Hence an increase in pressure might cause an increase in the rate of diffusion of the solutes through the polymer matrix. In addition, solute solubility is enhanced at higher

Table 2
SFE extracts for DOP

Sample	% extracted (DOP+DINP)	1 vial	2 vials	Soxhlet
100:70	41.8±0.3	33.7±0.4	40.0±0.8	41.1±2.0
100:50	33.4±0.5	26.0±1.0	32.0±3.0	33.0±2.0
100:30	33.4±0.2	17.8±0.6	19.3±0.2	20.2±0.4
100:10	33.5±0.1	5.8±0.1	6.5±0.5	6.3±0.3

Total DOP in PVC is 41.30%, 33.31%, 20.02%, 6.68%, respectively. Extraction conditions: pressure, 48.263 MPa; temperature, 95°C and time, 25 min.

Results based on three replicate extractions.

Table 3
SFE extracts for DBP

Sample DBP	% material extracted SFE
100:70	40.1±0.7
100:50	33.5±0.3

Total DBP in PVC is 41.30% and 33.31% respectively. Extraction conditions: pressure, 48.263 MPa; temperature, 95°C and time, 25 min.

Results based on three replicate extractions.

pressures and constant temperature causing an improvement in extraction efficiency.

3.3. Extraction time

When extraction conditions are 95°C and 48.263 MPa, the variation of the percentage extracted material with time is shown in Fig. 5. At the same extraction time, the amount of obtained plasticizer is higher for DOP than for DBP. This may be caused by the fact that DBP is strongly bound than DOP in matrix sorption sites. The amount of extracted material increases with time. The process may be limited by diffusion.

3.4. Composition of extracts

Two chromatograms of DOP, DBP and DINP (in pastes where it was necessary) are shown in Fig. 6a and b.

Peak area vs. concentration graphs were plotted for standard DOP solutions in cyclohexane considering concentrations between 200.8 and 1972 ppm (m/v). Straight lines were obtained ($ax+b$, $a=0.68$, $b=-61.50$, $r^2=0.998$).

Table 2 shows % DOP determined by SFE-GC compared with Soxhlet extraction when a single vial or a two vial system (scheme in Fig. 1) were used. With a single vial, analyte is lost due to CO_2 dragging analyte along so it is necessary to trap DOP with two vials. Results obtained with SFE are comparable to those obtained with the Soxhlet extraction method. Finally, a sample with 0.03% in DOP was prepared with DBP and DINP (total plasticizers amount in plastisol was 36.85%). Recovery of DOP was 0.033%. It was necessary to make a new calibration with standards in the range

between 2 and 22 ppm ($a=0.007$, $b=-2.08$). A calibration plot gives a linear correlation ($r^2=0.997$).

In order to confirm that SFE methods are adequate to other phthalates as DBP, a similar study has been developed. Results are presented in Table 3. As it can be observed, the obtained results are very similar to those presented in Table 2, i.e. recoveries near 100%.

4. Conclusions

Extraction of DOP in PVC with a moving stream of supercritical CO₂ is a fast and reproducible alternative to liquid extraction. Total solute extraction efficiencies over 98% compared with liquid extraction are obtained for 20–25 min, temperatures over 95°C and pressures above 41.368–48.263 MPa. Results are reproducible and there is no significant gain in extraction when longer extraction times with supercritical CO₂ are used. Extractions are faster than Soxhlet, the amount of sample to extract is 10 times lower and organic solvent volume is minor, generating little waste. Off-line SFE–GC has been demonstrated as a valid technique to analyze the plasticizers most commonly used in PVC technology.

References

- [1] L. Meler, *Plastics Additives*, Gächter and Müller Eds., Cincinnati, 4th ed., 1993.
- [2] F. Stühlen and L. Meier, *Kunstst. Rdsch.*, 19 (1972) 118.
- [3] S.B. Hawthorne and D.J. Miller, *J. Chromatogr. Sci.*, 24 (1986) 258.
- [4] J.M. Levy, R.A. Cavalier, T.N. Bosch, A.M. Rynaski and W.E. Huhak, *J. Chromatogr. Sci.*, 27 (1989) 344.
- [5] S.B. Hawthorne and D.J. Miller, *Anal. Chem.*, 66 (1994) 4005.
- [6] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller and J. Pawliszyn, *Anal. Chem.*, 66 (1994) 909.
- [7] T.S. Oostdyk, R.L. Grob, J.L. Snyder and M.E. McNally, *Anal. Chem.*, 65 (1993) 596.
- [8] V. Janda, J. Kríz, J. Vejrosta and K.D. Bartle, *J. Chromatogr. A*, 669 (1994) 241.
- [9] K.G. Miller, C.F. Poole and T.M.P. Chichila, *J. High Resolut. Chromatogr.*, 18 (1995) 461.
- [10] H. Engelhardt, J. Zapp and P. Kolla, *Chromatographia*, 32 (1991) 527.
- [11] C. Hume Kirschner, S.L. Jordan, L.T. Taylor and P.D. Seemuth, *Anal. Chem.*, 66 (1994) 882.
- [12] H.B. Lee, T.E. Pearl and R.L. Hung-You, *J. Chromatogr.*, 639 (1993) 263.
- [13] H. Daimon and Y. Hirata, *Chromatographia*, 32 (1991) 549.
- [14] M. Ashraf-Khorassani and J.M. Levy, *J. High Resolut. Chromatogr.*, 13 (1990) 742.
- [15] M. Ashraf-Khorassani D.S. Boyer and J.M. Levy, *J. Chromatogr. Sci.*, 29 (1991) 517.
- [16] N.J. Cotton, K.D. Bartle, A.A. Clifford, S. Ashraf, R. Moulder and C.J. Dowle, *J. Appl. Polym. Sci.*, 14 (1991) 164.
- [17] J.W. Oudsema and C.F. Poole, *J. High Resolut. Chromatogr.*, 16 (1993) 198.
- [18] T.P. Hunt and C.J. Dowle, *Analyst*, 116 (1991) 1299.
- [19] J.S. Chiou, Y. Maeda and D.R. Paul, *J. Appl. Polym. Sci.*, 30 (1985) 4019.