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Analysis of citrates and benzoates used in poly(vinyl chloride) by supercritical fluid extraction and gas chromatography☆

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Abstract

Supercritical fluid extraction (SFE) has been demonstrated to be a useful tool in the determination of additives in polymeric materials. This paper describes the determination of some citrates and benzoates in poly(vinyl chloride) blended with 33–34% of plasticizer using off-line SFE followed by gas chromatography. Experimental factors affecting SFE have been studied by gravimetric analysis, followed by analysis of the extracts using a gas chromatograph equipped with a flame ionization detector. The extraction process is governed by the solubility of the plasticizers in the supercritical fluid or by their diffusion through the polymer matrix, which depend on the pressure and temperature used. Maximum extraction ($>$99%) is obtained at pressures and temperatures higher than 40 MPa and 80 °C, respectively. Due to purge losses, the collection efficiency of plasticizers into a liquid solvent ranges from 85 to 90%. The applicability of the SFE method is demonstrated using real samples and comparing the results with those obtained by conventional Soxhlet extraction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical fluid extraction; Citrates; Benzoates; Poly(vinyl chloride); Polymers

1. Introduction

The analytical determination of low-molecular-mass molecules used as additives in polymers is a increasingly studied subject. Conventional extraction techniques such as liquid solvent extraction, includ-ing Soxhlet, are normally used. Although this tech-nique has been shown to be effective for the extraction of analytes from many different samples, the method is time-consuming and often requires the use of large amounts of toxic solvents, which is environmentally unsound [1]. For this reason, in the last decade, novel analytical methods, such as super-critical fluid extraction (SFE) and microwave-as-sisted extraction (MAE), have been developed.

SFE has been used extensively as a quantitative procedure for a variety of analytes including poly-meric materials [2]. For instance, on-line SFE cou-pled to capillary supercritical fluid chromatography

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has been utilized for the analysis of additives in polypropylene [3,4], poly(vinyl chloride) (PVC) [5] and polyethylene matrices [6]. On the other hand, off-line SFE was used for the extraction of low-molecular-mass components from poly(ethylene terephthalate) films [7]. In addition, SFE has found important applications in the extraction of aromatic amines from rubber [8], stabilizers from polypropylene [9], organotin stabilizers [10] and light stabilizers and antioxidants from polymers used in packaging [11]. However, there are only few published works dealing with plasticizers used with PVC [2].

During the last years our research group has proposed methods for the determination of some of the additives used in polymeric materials, such as phthalates in plasticized PVC [12,13], phenol in various polymeric matrices [14], aromatic amines [15,16] and formaldehyde in paints [17,18].

Several experimental variables must be considered for SFE to be successful, including the choice of the supercritical fluid, the use of modifiers, pressure and temperature, extraction time, sample size and the method of analyte collection. Pressure (P) and temperature (T) influence analyte solubility in the supercritical fluid and diffusion rate of the analyte through the polymeric matrix. Theoretical models have been proposed to explain the influence of experimental conditions in the SFE of polymers [19–21].

In previous works, the SFE conditions for some of the phthalate plasticizers used in PVC were optimised to obtain high analyte recoveries at temperatures in the range of 90–100 °C and pressures above 34 MPa [22]. Compared with Soxhlet extraction, SFE of phthalates assured higher extraction efficiencies [23]. It was observed that PVC plastisols used in toy manufacturing normally contain high concentrations of phthalates, mainly bis(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP). These compounds are being questioned because of their potential toxicity and high migration rates in physiological fluids. Therefore, efforts have to be made to study the effects of the experimental conditions on SFE of other compounds, such as citrates and benzoates used as plasticizers in PVC matrices.

The aim of the present work is to select the adequate SFE experimental conditions for extraction of citrates and benzoates from plasticized PVC (a mixture of a PVC resin and a plasticizer, in this case benzoate or citrate) and compare the extraction efficiencies with those achieved using Soxhlet extraction.

2. Experimental

2.1. Materials and chemicals

Vestolit-B 7021 PVC homopolymer resin was supplied by Hüls (Marl, Germany). The plasticizers used were: *O*-acetyl tri-*n*-butyl citrate (ATBC) (Sigma–Aldrich, Milwaukee, WI, USA) and technical-grade Benzoflex-2860 (Velsicol, Basingstoke, UK), which is a mixture of benzoates composed by di(2-ethylhexyl) adipate (19%), diethyleneglycol dibenzoate (57%) and triethyleneglycol dibenzoate (24%), determined by GC. Organic solvents, 2-propanol (LiChrosol) and cyclohexane (Suprasolv) were supplied by Merck (Darmstadt, Germany). Abelló-Linde (Valencia, Spain) supplied supercritical-grade carbon dioxide.

Some toys made of plasticized PVC by Spanish manufacturers were used as real samples for analysis.

2.2. Instrumental

SFE was carried out by using an SFX-220 extraction system (ISCO, Lincoln, NE, USA) which consists of an SFX-220 extractor, an SFX-200 controller, a 100DX syringe pump and a temperature-controlled capillary restrictor. In this work, a linear fixed restrictor was used. Fluid flow and size of the bubbles increase with pressure, leading to higher purge losses. Samples were placed in stainless steel cartridges (2.5-ml internal volume). Analytes were collected into 15-ml graduated vials containing 8–10 ml of an organic solvent.

Extracts were analyzed off-line with a GC-17A system (Shimadzu, Kyoto, Japan) controlled by a data acquisition system CLASS-VP Version 4.2. The GC system was equipped with a Shimadzu AOC-20i auto-injector, a SPB-5 fused-silica capillary column (30 m×0.25 mm internal diameter and 0.25 μm film thickness) (Supelco, Bellefonte, PA, USA), a split-

splitless injector and a flame ionisation detection (FID) system. Helium was used as the carrier gas with a linear velocity of 50 cm/s. The injector and detector temperatures were 300 °C, the column temperature was programmed from 110 to 260 °C (10 °C/min heating rate). One μl of sample was injected in the split mode. The main parameters of the GC–FID method were similar to those optimised for the determination of phthalates in PVC plastisols [12,13]. The typical chromatograms of Benzoflex-2860 (Fig. 1A) and ATBC (Fig. 1B) under these experimental conditions show a clear peak distribution for both additives.

2.3. Procedure

Plastisols were prepared by mixing powdered PVC resin with plasticizers in concentrations of 50 parts of plasticizer per 100 parts of resin (phr). The mixture was cured at 150 °C for 15 min. Prepared plastisols and real samples were cut in 0.15-mm mean width sheets with a microtome.

All supercritical extractions were performed in the dynamic mode, with 2 min in the static regime at the beginning. Experiments were carried out by following a factorial experimental design looking for the optimum efficiencies. The limiting experimental conditions were as follows: temperature, 60, 80 and 100 °C, extraction time, 15 and 20 min, pressure, 26.3 and 39.5 MPa. Additional experiments were performed outside of the experimental range at higher pressure (52.6 MPa). The extraction chamber was filled with approximately 0.2 g of sample, accurately weighted. The restrictor was heated to 120 °C. The extracted analytes were solvent trapped by immersing the end of the restrictor in a vial with 8–10 ml of a liquid solvent. Cyclohexane for ATBC and 2-propanol for Benzoflex-2860, were used as collection solvents.

Soxhlet extractions were carried out in a typical Soxhlet apparatus. In this case, 2-g samples were extracted by refluxing 70 ml of organic solvent for 5 h. The solvent used in each case was the same utilised for the collection of analytes in the supercritical fluid extractions.

The extraction efficiencies were calculated as indicated in Eqs. (1) and (2).

$$\text{Efficiency (\%)} = \frac{\text{Relative mass loss (\%)}}{\text{Total plasticizer content (\%)}} \cdot 100$$

(1)

where

$$\text{Relative mass loss (\%)} = \frac{\text{Initial mass} - \text{Final mass}}{\text{Initial mass}} \cdot 100$$

(2)

Analyte recoveries in the extracts were determined in triplicate by GC using calibration curves. Standards were prepared in cyclohexane for ATBC and in 2-propanol for Benzoflex-2860 in concentrations ranging from 1 to 2 g/l. For each calibration curve, five spike levels were run in triplicate. Average raw peak areas versus concentrations were plotted, obtaining correlation coefficients higher than 0.99 in all cases.

3. Results and discussion

The SFE process can be divided into two stages: the extraction itself and the collection of analytes after extraction. The first stage includes the release of the analytes from the sample matrix into the supercritical fluid, the sweep of the analytes out from the extraction vessel and their transfer to the collection system. The first stage, i.e., extraction efficiency, can be studied by gravimetric measurements of selected samples. The whole process, including collection, is analysed in this work by chromatographic quantification of analyte recoveries.

The citrate and benzoate plasticizers are slightly polar species with solubility parameters (δ) ranging from 25 to 30 $(\text{J/ml})^{1/2}$ [23]. On the other hand, the mean solubility parameter of CO_2 reaches 20–25 $(\text{J/ml})^{1/2}$ for pressures and temperatures in the ranges of 26–52 MPa and 60–100 °C, respectively. Therefore, under these experimental conditions, it can be expected that the analytes studied would be sufficiently soluble in the supercritical fluid to permit efficient extraction from the polymeric matrix.

Samples were cut in sheets with mean sizes of 30 mm length, 6 mm width and 0.15 mm thickness, having a surface/volume (S/V) ratio higher than 10. This sample shape was selected because in previous
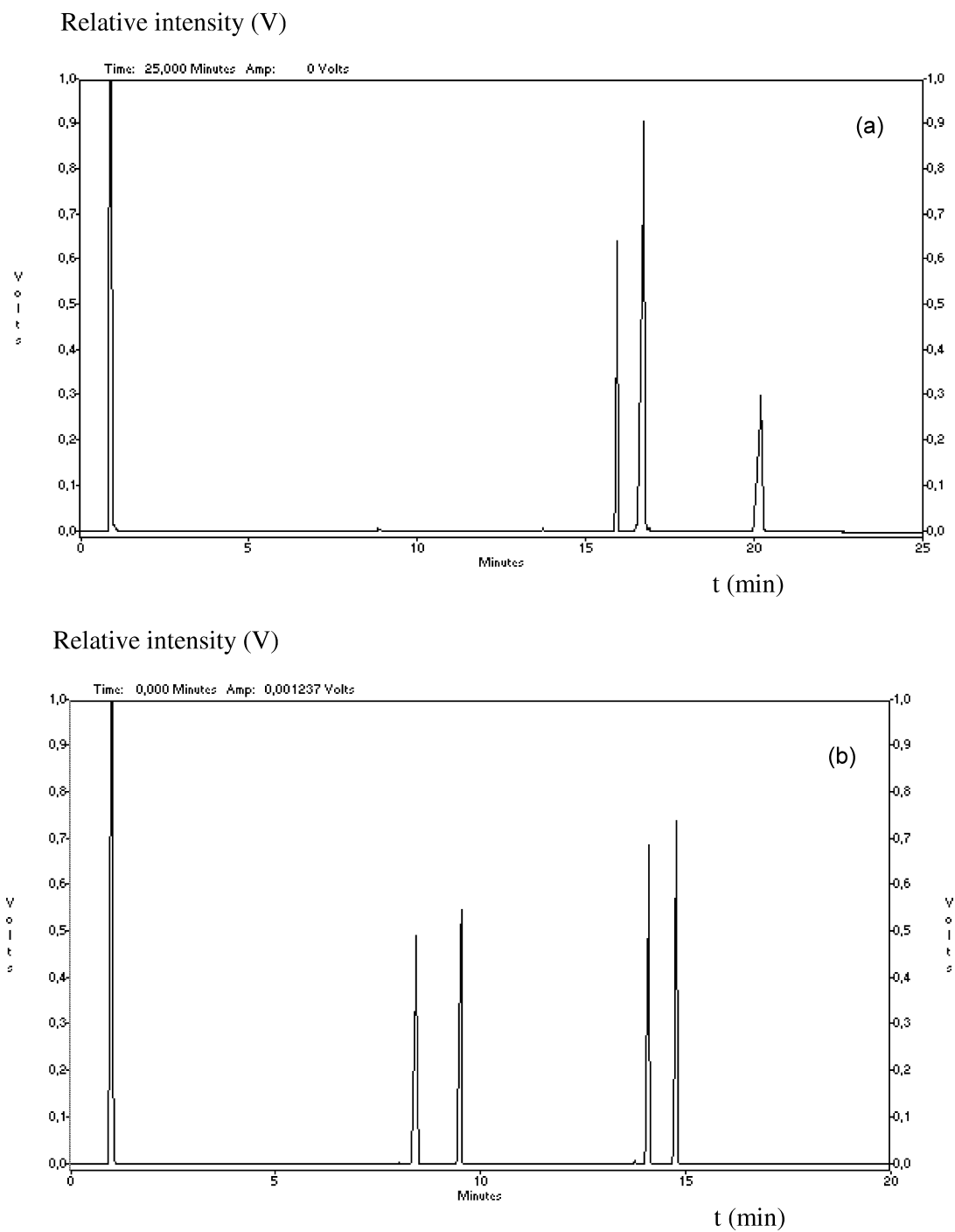
Relative intensity (V)

t (min)

Relative intensity (V)

t (min)

Fig. 1. Typical chromatograms of Benzoflex-2860 (A) and ATBC (B).

works it was stated that, the greater the *S*/*V* ratio, the more rapid and complete the extraction of plasticizers from PVC due to the shorter internal diffusion paths that the solutes must travel to reach the bulk fluid phase [11]. The sample size (0.2 g) was sufficiently large to obtain concentrated extracts ready for GC analysis in short extraction times.

In order to study the influence of experimental variables on extraction efficiencies, for both families of plasticizers, experiments were carried out as showed in Tables 1 and 2. A temperature increase at constant pressures decreases the solvent strength of a supercritical fluid. This fact can modify dramatically the extraction efficiency of ATBC when the temperature is raised from 40 to 80 °C at low pressures (~13 MPa), as can be observed in Fig. 2. At this pressure, the process is limited by the low solubility of the analyte in the supercritical fluid. However, at pressures above a certain threshold value, the increase in temperature has a beneficial effect on extraction efficiency because diffusion rate of the analyte in the polymer is enhanced, leading to much

Table 1
Experimental conditions and percentage extraction efficiencies for ATBC from plasticized PVC (50 parts per 100 parts of resin)

Temp. (°C)	Pressure (MPa)	Time (min)	Extraction efficiency (%)
95	46.1	30	100±1
100	39.5	20	100±1
80	39.5	20	100±1
60	39.5	20	98±1
100	26.3	20	98±1
80	26.3	20	97±2
60	26.3	20	95±2
80	52.6	15	99±1
40	52.6	15	94±1
100	39.5	15	99±1
80	39.5	15	98±1
60	39.5	15	97±1
40	39.5	15	94±1
100	26.3	15	96±1
80	26.3	15	95±2
60	26.3	15	94±2
40	26.3	15	92±2
80	13.2	15	55±1
60	13.2	15	77±1
40	13.2	15	82±1
100	39.5	10	97±1
100	39.5	2	95±1

Results are based on three replicate extractions.

Table 2
Experimental conditions and percentage extraction efficiencies for Benzoflex-2860 from plasticized PVC (50 parts per 100 parts of resin)

Temp. (°C)	Pressure (MPa)	Time (min)	Extraction efficiency (%)
95	46.1	30	99±1
100	52.6	20	99±1
80	52.6	20	89±2
100	39.5	20	99±1
80	39.5	20	92±2
60	39.5	20	74±2
100	26.3	20	92±2
80	26.3	20	88±2
60	26.3	20	70±2
100	39.5	15	98±1
80	39.5	15	89±1
60	39.5	15	69±2
100	26.3	15	88±1
80	26.3	15	83±1
60	26.3	15	69±1
40	26.3	15	51±1

Results are based on three replicate extractions.

faster extraction. For pressures above 26 MPa, SFE efficiency of citrate increased with the temperature (Fig. 2). The observed behaviour is due to the fact that the increase in temperature has a smaller effect on the solubility parameter of CO_2 at higher pressures.

Although all three variables influence the extraction efficiency of citrate and benzoates in some way, temperature produces a higher effect on the extraction of benzoates for pressures below 26 MPa. At
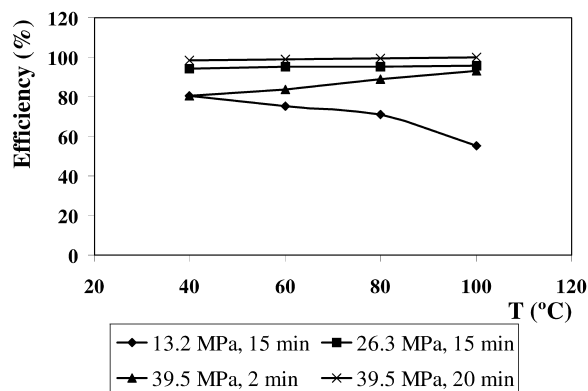

Fig. 2. Variation of extraction efficiency (%) with temperature for PVC with 50 phr of ATBC.

26.3 MPa, a very low extraction efficiency is ob-
served for benzoates at 40 °C, with a constant
improvement of extraction efficiency up to 100 °C
(Fig. 3). This indicates that the extraction process for
benzoates is more diffusion-controlled than solu-
bility-limited, although solubility limitations are also
important. Moreover, at high pressures, swelling of
the polymer by the supercritical fluid is significant
and results in much faster diffusion and hence,
extraction. It must be also indicated that the highest
temperatures used in the present work are approach-
ing the melting or softening point of the polymer,
which is near 100 °C [15]. This will also permit
faster diffusion of the analyte through the polymer
phase and will result in higher extraction efficiency.

Extraction efficiency increased with pressure for
both types of plasticizers. This increment is very fast
in the 13.2–26.3-MPa interval reaching a plateau at
pressures near 30 MPa. This can be due to the fact
that when pressure increases, the density of the
supercritical fluid and therefore its solvent strength is
higher.

Under the same experimental conditions, extrac-
tion efficiency for Benzoflex-2860 is lower than for
citrates (Fig. 4). At higher pressures, i.e., of 30 MPa
and 80 °C, high extraction efficiencies (100±1)%
were obtained in a 20 min extraction of ATBC.
Meanwhile, for efficient SFE of Benzoflex-2860,
temperatures of at least 95–100 °C must be used to
obtain good extraction efficiencies (99±1%). This
can be due to the higher compatibility of Benzoflex-
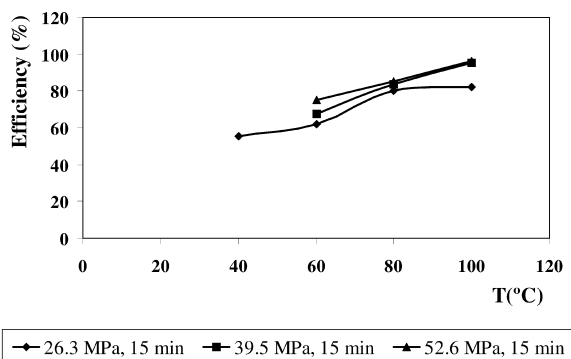2860 and the PVC matrix [13].

Fig. 3. Variation of extraction efficiency (%) with temperature for
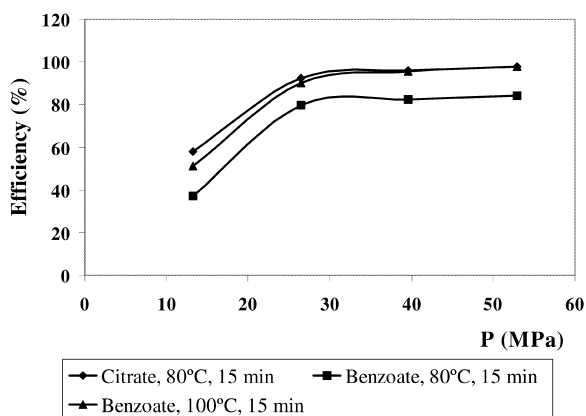PVC with 50 phr of Benzoflex-2860.

Fig. 4. Variation of extraction efficiency (%) with pressure.

The efficiency of the collection method is affected
by several factors: analyte solubility in the solvent,
amount of solvent, shape of the collection vial,
flow-rate of CO_2 and others. A small internal
diameter/length ratio of the trapping vial is preferred
in order to provide a longer path for the bubbles. The
amount of solvent is maintained by the continuous
addition of solvent during extraction.

Collection solvents were selected to guarantee
good solubility for the analytes. In previous work,
cyclohexane was used to trap phthalates [11,12].
This solvent also proved to be efficient for the
trapping of citrates. However, due to solubility
considerations, 2-propanol was selected for
Benzoflex-2860. This product is composed of a
mixture of three plasticizers, where di- and tri-
ethyleneglycol dibenzoates are the major components
(more than 70%). These compounds are soluble in
polar solvents such as alcohols.

Analyte recoveries for different temperatures and
pressures are shown in Figs. 5 and 6. The overall
behaviour is similar to that observed for the ex-
traction efficiencies. However, analyte recoveries are
lower than those obtained gravimetrically due to
purge losses from the trapping solvent. Temperatures
higher than 80 °C do not lead to more efficient
extraction of ATBC at 39.5 MPa, but are necessary
for the extraction of Benzoflex-2860 components
(Fig. 5). Di(ethylhexyl) adipate has the lowest
recovery values under all experimental conditions.
This may be due to the lower solubility of di(eth-
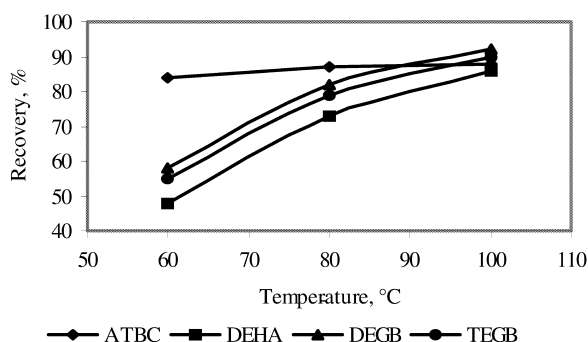ylhexyl) adipate in 2-propanol. Recoveries for

Fig. 5. Variation of analyte recovery (%) with temperature at 39.5 MPa and 15 min for *O*-acetyl tri-*n*-butyl citrate (ATBC), di(ethylhexyl) adipate (DEHA), di- and triethyleneglycol dibenzoates (DEGB and TEGB).
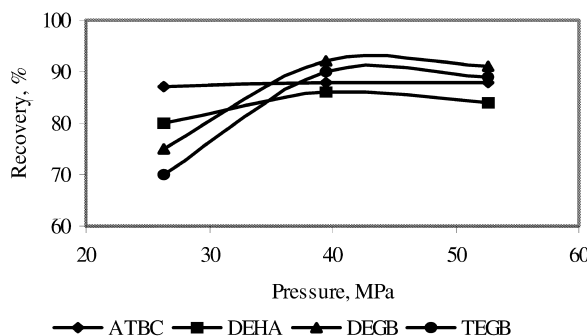

Fig. 6. Variation of analyte recovery (%) with pressure at 100 °C and 15 min for *O*-acetyl tri-*n*-butyl citrate (ATBC), di(ethylhexyl) adipate (DEHA), di- and triethyleneglycol dibenzoates (DEGB and TEGB).

Benzoflex-2860 decreased when pressure was raised from 39.5 to 52.6 MPa (Fig. 6).

Analyte recoveries for the plasticizers studied along the experimental conditions and the results of Soxhlet extractions are shown in Table 3. No significant differences were observed for the SFE recovery of citrates under any of the experimental conditions. Higher temperatures are suitable for the extraction of Benzoflex-2860 components. Recoveries of Benzoflex-2860 increased by 3–4% when the extraction time was increased from 15 to 20 min at 100 °C and 39.5 MPa. Results were also compared with those obtained for conditions optimised in previous works for SFE of phthalate plasticizers, i.e., 46.1 MPa, 95 °C, 30 min [11,12]. The differences in analyte recoveries are small and the experiments show similar gravimetric extraction efficiencies $(99 \pm 1)\%$.

When compared with Soxhlet extraction, SFE shows significantly lower recoveries for citrate and adipate plasticizers, but no significant differences were obtained for both benzoate type compounds, at 39.5 MPa, 100 °C and 20 min. Extraction efficiencies obtained for Soxhlet extraction were lower than those achieved for SFE demonstrating that losses occurred in the collection of analytes after extraction.

In order to evaluate the extraction efficiencies and recoveries of the plasticizers studied from real samples, SFE and Soxhlet extractions of different toys manufactured from plasticized PVC were performed (Table 4). SFE extraction conditions were: 46.1 MPa, 95 °C and 30 min. Relative mass losses

Table 3

Analyte recoveries of citrate and benzoate plasticizers under different SFE experimental conditions (five replicates) and Soxhlet extraction

Experimental conditions	*O*-Acetyl tri-*n*-butyl citrate[a]	Diethyl hexyl adipate[b]	Diethyleneglycol dibenzoate[b]	Triethyleneglycol dibenzoate[b]
39.5 MPa, 100 °C, 15 min	88 ± 2	86 ± 1	92 ± 1	90 ± 1
39.5 MPa, 100 °C, 20 min	88 ± 1	90 ± 2	95 ± 2	94 ± 2
52.6 MPa, 100 °C, 15 min	88 ± 1	84 ± 2	91 ± 3	89 ± 2
46.1 MPa, 95 °C, 30 min	89 ± 2	85 ± 2	91 ± 3	91 ± 3
5 h Soxhlet extraction	95 ± 6	97 ± 1	96 ± 1	95 ± 1

Results based on three replicate extractions.
[a] In cyclohexane.
[b] In 2-propanol.

Table 4
Results of SFE (46.1 MPa, 95 °C, 30 min) and Soxhlet extraction (5 h) of commercial PVC samples

Sample	Identified plasticizer	SFE		Soxhlet	
		2-Propanol	Cyclohexane	2-Propanol	Cyclohexane
Relative mass loss (%)					
1	Benzoflex 2860	43.9±0.1	44.0±0.1	35.1±0.8	–
2	Di(2-ethylhexyl adipate)	44.0±0.4	44.0±0.1	38.4±0.6	–
3	ATBC	–	60.9±0.3	–	52.3±0.5
Analyte recoveries (g of analyte/g of sample)					
1	Benzoflex 2860[a]	0.40±0.02	0.37±0.02	0.40±0.02	–
2	Di(2-ethylhexyl adipate)	0.19±0.02	0.35±0.02	0.40±0.2	–
3	ATBC	–	0.285±0.015	–	0.28±0.02

In each column, the solvent used either for SFE collection or Soxhlet extraction is indicated.
Results are based on three replicate extractions.
[a] Sum of concentrations determined by GC for the three Benzoflex-2860 components.

are higher for the SFE, probably because of the simultaneous extraction of other matrix components as well. In addition, some liquid solvent could remain in the Soxhlet-extracted samples, even after overnight drying. Recoveries for Benzoflex-2860 components and ATBC determined by GC are about the same for both extraction methods, when an adequate collection solvent is employed. Collection efficiency of di(2-ethylhexyl) adipate is low when 2-propanol is the collection solvent after SFE, but it increases when non-polar solvents, such as cyclohexane, are employed. However, optimum conditions for efficient SFE of adipates still have to be determined.

As observed for the system studied, liquid solvent extraction can be conveniently performed yielding quantitative results with no extra concentration step prior to the GC determination of the target analytes. In this case, the advantages of SFE are the following: SFE is faster than conventional Soxhlet extraction and reduces generation of liquid waste solvents and exposure of laboratory personnel to toxic solvents.

4. Conclusions

SFE of citrate and benzoate plasticizers from PVC derivatives is a fast and solvent-saving alternative to conventional liquid–solvent extraction. For quantitative extraction of citrate and benzoate plasticizers from PVC, the following conditions are adequate: 39–46 MPa, 95–100 °C, and 20–30 min. Citrates were collected in cyclohexane while benzoates have to be trapped in a more polar solvent, such as 2-propanol. For these experimental conditions, gravimetrically determined extraction efficiencies were higher than 99% for laboratory samples and higher than those obtained by Soxhlet extraction for real samples. Chromatographic recoveries for benzoates and citrates are similar for both extraction methods when analysing real samples.

Acknowledgements

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