OFF-LINE SFE OF BIS(2-ETHYLHEXYL) PHTHALATE FROM PVC MATERIALS

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Received February 23, 1995
Accepted May 21, 1995

Off-line supercritical fluid extraction with pure CO_2 was used to isolate and quantify bis(2-ethylhexyl) phthalate (DIOP) from PVC samples. Two modes of analyte trapping, onto an inner solid surface of a fused silica capillary (i.d. 0.5 mm) and direct bubbling through a bulk liquid (2-propanol), have been compared. Collected samples were analyzed by high performance liquid chromatography with UV detection. Quantitative recovery of over 95% was obtained in spite of limited operating parameters of home-made SFE device (maximum of pressure 30 MPa and of temperature 70 °C) for samples containing 10 or less wt.% of DIOP.

Chemical additives in technical polymers form a wide range of compounds differing in volatility, molecular weight and thermal stability. The content of additives varies greatly between manufacturers and is not usually specified by standard polymer measurement.

The analysis of polymer additives generally involves several steps as extraction, extract enrichment and cleanup, analyte separation and detection. More recently, starting with works by Krukonis et al.[1–3] and Okamoto[4], supercritical fluid extraction (SFE) in off-line mode or in connection with GC or HPLC proved to be very efficient method for isolation and quantification of lower oligomers and chemical additives from polymer matrices[5–15]. In comparison with conventional extraction methods as Soxhlet or sonication, which use classical liquids, SFE provides shorter extraction times, mild extraction temperatures, decreasing risk of analyte degradation and usually removes enrichment steps.

Simultaneously, supercritical fluid chromatography has been applied successfully to the analysis of polymer additives[16–19] using flame ionization detection (FID) and Fourier-transform infrared (FTIR) detection. Direct coupling of SFE with SFC (refs[20–26]) increases sensitivity of analysis in comparison with use of either technique separately.

The extractability of the most additives ranging from BHT (butylhydroxytoluene, $M_r = 218$) to Irganox 1010 ($M_r = 1\ 178$) is very good with pure CO_2, only exceptionally methanol is used as an entrainer[27].

The extraction efficiency almost in all cases increases with higher values of particle surface/weight ratio and with increasing temperature and pressure. Higher temperature increases analytes volatility and supports polymer swelling, which improves conditions for analyte migration inside polymer matrix.

From the viewpoint of PVC additives Hunt et al.[27] optimized extraction conditions (temperature, pressure, time and particle size) to develop reproducible method for extraction of diisooctyl phthalate (DIOP) used as a plasticizer. They found extraction efficiency of over 95% in comparison with liquid extraction at pressures 30–40 MPa and temperatures above 80–90 °C with pure CO_2.

Chlorinated polyethylene wax, Topanol CA, is under these conditions not fully extracted and methanol-modified CO_2 must be used to enhance extraction yield.

Kane et al.[10] found the same levels of DIOP as obtained by Soxhlet extraction. The extraction time was one order of magnitude less for SFE.

Levy et al.[11] performed SFE/gravimetry of PVC with pure CO_2. In comparison with expected extractables concentration, the quantitative recovery was achieved and a strong dependence of extraction time on flow-rate of CO_2 was found.

In this study, SFE with pure CO_2 was used and optimized for isolation of bis(2-ethylhexyl) phthalate (DIOP) from PVC folies (flow covering).

EXPERIMENTAL

All supercritical extractions were performed on a home-made system, equipped with a capillary sample trap, as previously described[28]. The drawbacks of the device were relatively low values of attainable extraction pressure (30.0 MPa) and temperature (70 °C).

Commercial PVC folies were supplied by manufacturer (Fatra Napajedla, Czech Republic) with defined content of DIOP: NOVOFLOR STANDARD (NS, 9.7 wt.%), FATRAFLOR STANDARD (FS, 8.9 wt.%) and ANTISTATIK (AS, 17.7 wt.%).

Two forms of PVC were used for extraction: granules of volume 3–6 mm^3 and ground sample obtained by milling with solid CO_2 in a ball mill. In all experiments ≈0.1 g of PVC sample was loaded into a changeable cartridge of volume 1 ml.

Samples were analyzed by HPLC and evaluated by the method of absolute calibration. Standard solutions of DIOP and dibutyl phthalate (DBP), which is sometimes used as a plasticizer in mixture with DIOP, were prepared into 2-propanol.

Liquid chromatography unit consisted of a high pressure pump VCM 300 (Laboratorni pristroje Prague, Czech Republic), a six-port valve (VICI VALCO, Switzerland) with a 20 µl sample loop, a UV detector LCD 2040 (Laboratorni pristroje Prague, Czech Republic) used at 227 nm, and a packed column (150 mm × 3.2 mm) with Separon SGX C18, particle size 7 µm (Tessek, Prague, Czech Republic). As a mobile phase, 2-propanol–water (7 : 3) was used.

Samples from extraction experiments were transferred into a calibrated flask and made up to volume of 25 ml with 2-propanol. The analyte content was calculated from a peak area vs concentration calibration graph, constructed from five standard solutions of increasing concentration for both investigated plasticizers.

RESULTS AND DISCUSSION

Testing of Analyte Collection Methods

Two collection methods, trapping onto an inner solid surface of a fused silica capillary of i.d. 0.5 mm (ref.[28]) and bubbling through 5 ml of 2-propanol (column height 5 cm), were used in this work. To ascertain their collection efficiences, five replicate spike experiments were performed. The choice of 2-propanol as a trapping solvent was made with respect to its relatively low volatility and consistency with the mobile phase used in LC.

An amount of 10 μl of standard solutions of DIOP and DBP were sampled into a changeable cartridge of internal volume 0.6 ml, filled with silanized glass wool. The extractions were performed for 50 min at pressure of 27.0 MPa and temperature of 70 °C. A fused silica capillary (15 cm × 20 μm i.d.) was used as a restrictor. Volume flow-rate of CO_2 measured at ambient conditions was 80 ml min^{-1}. Percentage recoveries of DIOP and DBP with relative standard deviations (RSDs) given in parentheses for spike experiments in two different trapping modes were determined:

Trapping mode	Solid surface	Bubbling into 2-propanol
DBP	88.5(5.1)	96.9(3.2)
DIOP	86.8(6.2)	95.1(4.1)

Relatively good results with corresponding values of RSDs were obtained by the collection method proposed by Vejrosta et al.[28]. The method is based on the idea to use small inner diameters capillaries (0.3–0.5 mm) for trapping of precipitated analytes on the inner solid capillary surface. The method was found efficient at the trapping of higher polycyclic aromatic hydrocarbons (PAHs) starting with fluoranthene[29] and can be used with a cryofocusing device.

In this work, the trapping capillary (fused silica, i.d. 0.5 mm) was kept at normal temperature. In the case of phthalates, direct bubbling into 2-propanol proved to be more efficient with lower RSD values and was further used in all quantitative experiments.

SFE of Real PVC Samples

Because of limitations imposed on operating parameters of the home-made SFE device (max. pressure 30.0 MPa, max. temperature 70 °C), it was expected[27] that the optimum values of extraction pressure and temperature will be their limiting values. This assumption was verified on extractions of freeze-ground NS at different pressures, carried out at 70 °C for 80 min. The resulting recoveries were calculated from the total content of DIOP, given by the manufacturer's formulation (the RSD values are given in parentheses).

Pressure, MPa	15	20	25	30
Recovery, %	43.1(4.5)	67.5(3.9)	86.1(4.2)	96.4(4.6)

From the pressure dependence of percentage DIOP recovery follows the quantitative DIOP recovery at pressure 30.0 MPa and temperature 70 °C.

In the moment, when extraction pressure and temperature cannot be further increased, the extraction time is the only parameter which can be minimized.

Under pressure of 30 MPa, extraction temperature of 70 °C and CO_2 volume flow-rate of 80 ml min^{-1} (measured at ambient conditions), a series of extractions of freeze-ground NS were performed at different extraction times:

Time, min	40	50	60	70	80
DIOP rec., %	81.1	87.2	95.6	96.2	96.4
RSD	3.6	4.2	4.7	4.1	4.3

The gain in recoveries obtained after 60 min of extraction is negligible mainly with respect to RSD values. This extraction time was considered to be sufficient for quantitative extraction in further experiments.

TABLE I
Percentage recoveries of DIOP from PVC folies for different particle size

Sample	SFE[c]		Sonication[d]
	solid surface	2-propanol	
NS[a]	73.1(8.6)	96.8(4.3)	84.4
NS[b]		77.8(5.8)	60.5
FS[a]	75.4(7.8)	95.3(4.8)	80.7
FS[b]		57.6(6.3)	49.4
AS[a]	57.8(6.1)	75.7(6.4)	63.9
AS[b]		23.0(8.6)	11.4

[a] Freeze-ground. [b] Granules. [c] SFE conditions: p = 30 MPa, t = 70 °C, time 60 min at CO_2 volume flow-rate 80 ml min^{-1}. [d] Sonication conditions: 30 ml of 2-propanol, t = 30 °C, time 80 min.

In Table I the average results of five replicate supercritical extractions of PVC samples are presented. Together with the results obtained from the SFE with both trapping modes and for different particle size, the DIOP recoveries of liquid extractions by 2-propanol in an ultrasonic bath are presented. The DIOP recoveries were calculated from the determined extracted amounts and the content of DIOP given by the manufacturer's formulation.

As follows from the results, under pressure 30.0 MPa and temperature 70 °C, DIOP is quantitatively extracted during 60 min only from samples with maximum content of DIOP around 10%.

One of the reasons for nonquantitative extraction of AS can be larger particle size. The milling of AS with solid CO_2 was not able to produce such fine particles as in the case of NS and FS. In comparison with the almost dust produced by milling of NS and FS folies, visibly larger particles of irregular shape were obtained by milling of AS folie with solid CO_2.

To compare the kinetics of SFE with that of extraction of liquid, the PVC samples were extracted by 2-propanol in 50 ml flasks, located in an ultrasonic bath. Sample amounts were the same as in the SFE experiments, extraction temperature was 30 °C, volume of 2-propanol 30 ml and extraction time 80 min. The samples were extracted as in the freeze-ground state, as in the form of granules (1–4 mm^3). In spite of longer extraction time the DIOP yields from the liquid extraction are significantly lower in comparison with the SFE.

CONCLUSION

The SFE with pure CO_2 was used for the determination of bis(2-ethylhexyl) phthalate (DIOP) content in commercial PVC flow covering samples. Quantitative results have been obtained for freeze-ground samples at pressure 30 MPa and temperature 70 °C during 60 min for total content of DIOP around 10%. The SFE efficiency is strongly dependent on sample particle size. Remarkably shorter extraction times in comparison with liquid extraction (2-propanol) have been found.

This work has been supported by the Grant Agency of the Czech Republic, Grant No. 203/93/2157, which is gratefully acknowledged.

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