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Analysis of Potentially Toxic Phthalate Plasticizers Used in Toy Manufacturing

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A plasticizer is a substance normally incorporated to a PVC resin or some other materials such as paints, to improve some of its properties as flexibility or processability. Phthalates, adipates, phosphates and some others are the main compounds used as plasticizers. Some of these compounds, as bis-(2-ethylhexyl) phthalate (DOP), are being questioned worldwide because of their potential toxicity to humans and the environment (Menzel et al, 1990). Thus, DOP has been included in the carcinogen list and a classification in the European substance list (Annex I of the Council Directive 67/548) has been demanded. On the other hand, public health authorities, supported by expert opinions, recommend a prudent use of plasticizers. According to Barber (1987), an increased liver tumor rate was found in rodents. The mechanism of tumor initiation by phthalic acid esters is thought to involve peroxisome proliferation, which is the large increase of sub-cellular microbodies which cause oxidative degradation of metabolites. Some other plasticizers, as di-isononyl-phthalate (DINP) and di-isodecyl-phthalate (DIDP) have shown a similar behavior, but straight-chain phthalates have only a minimal effect.

Plasticizers are the PVC additives most commonly used in the toy industry, especially in doll manufacturing. Thus, children may be exposed to those compounds, considering the high migration of plasticizers into the PVC derivatives. In order to protect children, the toys manufactured and distributed in the European Union must comply with the EEC Directive on safety of toys (Council Directive 88/378). Therefore, the European Standard Organization (CEN) was given mandates to produce standards on toy safety. Plasticizer requirements have been set in European Standard EN 71-5 (1993). But, at present there are no analytical methods included within the standard. Gas chromatography (GC) is the most common technique to be used with plasticizers, but the extraction of analytes from the polymeric matrix prior to identification and quantitation is necessary. Traditionally, the extraction has been performed with a Soxhlet system, but this method presents some drawbacks as the long time necessary to complete the process and the use of highly toxic organic solvents. Supercritical Fluid Extraction (SFE) is an important preparative technique which

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has been successfully applied to some phthalates in PVC plastisols by our research group (Marín et al, 1996). The aim of the present work is to compare the results obtained when both extraction methods are applied to real samples and, on the other hand, to study if some of the most common toys distributed in the Spanish market present phthalate concentrations which could be considered dangerous in the frame of the Toys Directive.

MATERIALS AND METHODS.

Samples for analysis were supplied by Spanish toys manufacturers. Some different samples were tested and 15 of them were selected taking into account the intended use of the toy and the differences in the structure of materials. Five of the samples were polyester-based paints of various colors, one of them a textile used in toys, an adhesive coating and the rest of samples were some PVC derivatives normally used in the toy industry, 5 plasticized PVC, 2 rigid PVC and the other one a PVC plastisol with a mixture of plasticizers (DINP, DOP and DIDP).

SFEs were carried out by using an ISCO SFX-220 extraction system which consists of an SFX 220 extractor, an SFX 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, the two - vial apparatus shown in Figure 1 was designed and previously tested.

All extractions with supercritical CO_2 were carried out in dynamic mode. Samples were cut with a cleaver to obtain sheets of 2.8 mm. thickness. The stainless steel extraction cell was filled with approximately 0.2 g. of material. Cyclohexane was used as collection fluid. The restrictor temperature was maintained at 120°C in order to avoid the freezing of it and the clogging of the restrictor tip. Paints were previously dried with pressurized air and the extraction cell was charged with glass wool to avoid loss of sample. SFE conditions were selected taking into account some previous studies about the optimization of the main variables involved in extraction to get the maximum efficiency and recovery of extracts. The selected conditions were temperature 95 °C, pressure 7000 psi and time of extraction 30 minutes. When paint samples were extracted, an additional 10 minutes run was performed in order to have a quantitative extraction. Efficiencies were calculated gravimetrically, while recoveries were determined by gas chromatography.

Analysis of extracts was performed with a GC-9A (Shimadzu) coupled with an C-R4A Chromatopac and equipped with a split / splitless injection system and a flame injection detector. A Supelco capillary column 15 m x 0.53 mm. and I.D. 0.50 µm. with SPB-5 as stationary phase was used. Chromatographic conditions were as follows: column temperature 260 °C, linear rate of the helium carrier gas 20 cm/s. A 0.5 µL. volume of sample was injected in the split mode with the injector at 300 °C.

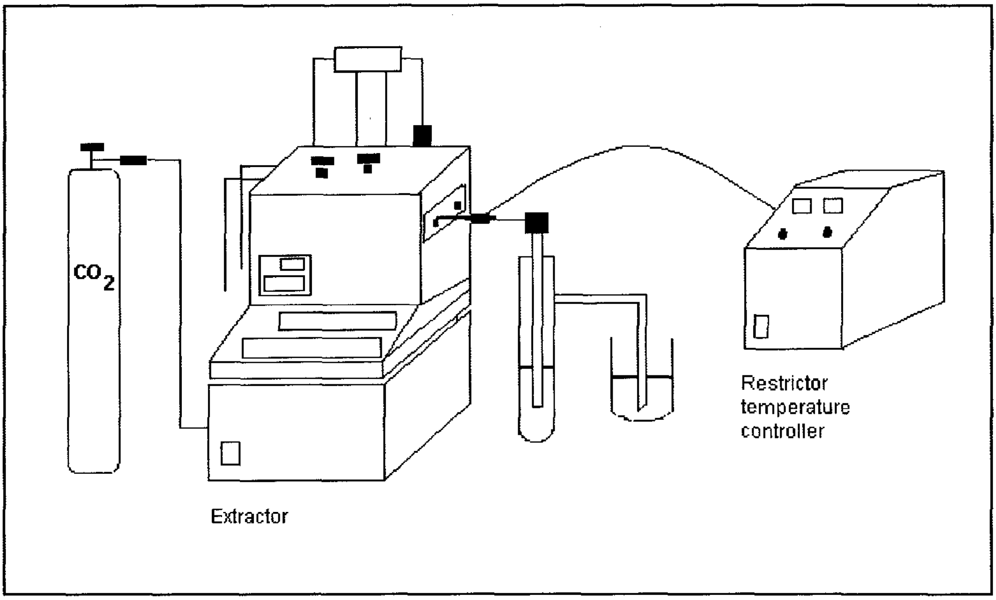

Figure 1. Scheme of the 2-vial apparatus used.

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.

RESULTS AND DISCUSSION.

In order to evaluate the efficiencies for extraction and recoveries of phthalate plasticizers, mainly DOP, Soxhlet extractions and SFEs were carried out with the above indicated conditions. Chromatographic analysis was used and the calibration curves for the standards were linear ($r^2 > 0.998$) in the range 10-1000 ppm.

DOP was extracted in each case with both methods and the obtained results are presented in Table 1. As it can be observed, higher efficiencies of extraction are obtained with SFE, presenting better results from 8.5% in PVC samples to 48% in rigid PVC formulations.

In order to know DOP recoveries, a chromatographic study has been carried out and results for different samples are presented in Figures 2-4. Figure 2 shows results for paints, Figure 3 for samples with DOP concentration lower than 2% and Figure 4 for samples with DOP concentration higher than 10%.

Table 1. Extraction efficiencies for DOP. Comparison of Soxhlet and SFE.

SAMPLE	SOXHLET (%)	SFE (%)
Orange paint	44.87	45.51
Yellow paint	45.79	46.16
Dark blue paint	1.34	2.01
Light blue paint	7.44	8.90
Dark red paint	5.15	6.30
Textile	17.91	19.56
Adhesive coating	23.31	24.45
Rigid PVC-1	15.32	27.53
Rigid PVC-2	11.97	23.33
Plasticized PVC-1	29.49	37.75
Plasticized PVC-2	19.98	23.95
Plasticized PVC-3	30.30	39.69
Plasticized PVC-4	24.77	33.79
Plasticized PVC-5	27.57	32.40
Plasticized PVC-7	36.92	48.97

Note that the two-vial system (scheme in Figure 1) was used. With a single vial, analyte is lost due to CO_2 dragging analyte along, so that it is necessary to trap DOP with two vials. As it can be observed in figures, DOP recoveries obtained with SFE are considerably better than those obtained with Soxhlet. Two different set of results can be discussed. When DOP concentration is lower than 2% (w/w), a clear increase in recoveries is observed. This is even more important with paint samples (recoveries are at least 3 times higher when SFE is used, Figure 2). On the other hand, when DOP concentrations are higher than 10%, recoveries are higher for SFE extracts with an increase in recoveries between 8% in PVC samples to 52% in textiles.

Some points must be considered when studying extraction of different samples. Thus, paints show important quantities of DOP recovered when an additional extraction is carried out. Therefore, it is necessary to perform some repeated SFEs if we want to be sure that a quantitative extraction has been obtained. For example, when an additional 5-minutes extraction is applied to the yellow paint, 12.53% of the total amount of DOP is obtained. This concentration is even higher for the orange paint, i.e. 39.69%. When an additional 5-minutes extraction is carried out with PVC plastisol samples, different results are obtained but as a

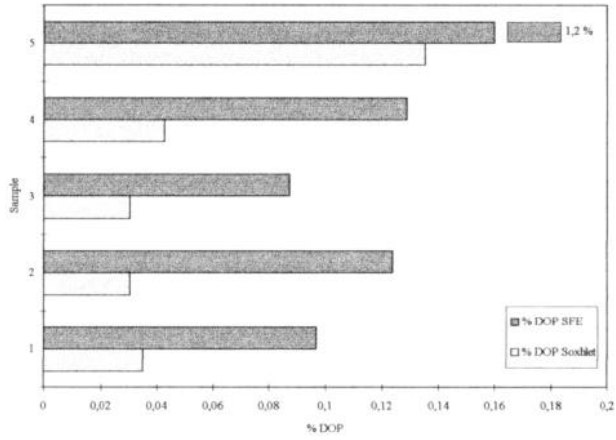

Figure 2: DOP recoveries from paint samples (< 1% DOP).

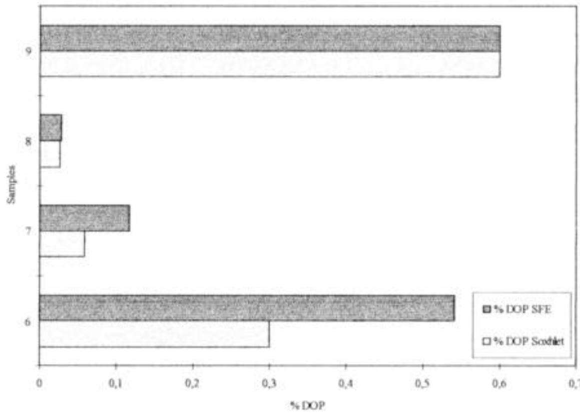

Figure 3: DOP recoveries from toy material (< 2%).

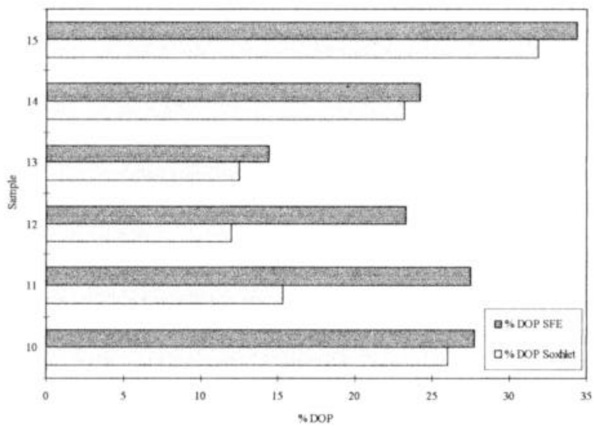

Figure 4: DOP recoveries from toy materials (> 10% DOP).

general rule, no DOP is recovered (only 3.11% in PVC-5 sample). This result leads us to conclude that a 30-minutes SFE is enough to get a quantitative extraction in PVC samples.

In order to compare the obtained recoveries, interactions between different matrices and analyte must be considered with an evaluation of the ability of pure CO_2 to extract phthalates. One point to be taken into account is the matrix morphology, because the lower the particle size, the higher recoveries are obtained. The reason for that behavior comes from the fact that molecular diffusion is favored when the particles are small. Paint particles show an important adsorption with DOP with a decrease in extraction efficiency, requiring the use of longer times to get a quantitative extraction.

The results of this study show that an increase in extraction efficiency for phthalate plasticizers is obtained when SFE is used instead of a traditional Soxhlet method. In addition, DOP recoveries are clearly higher in SFE extracts.

Some additional conclusions can be obtained. Potentially toxic DOP can be found in paints and coatings normally used in toys, but with low concentrations. Therefore, these materials can be considered reasonably safe for children. Unfortunately, the situation is completely different when PVC derivatives are analyzed. PVC products used as basic materials in toys, normally contain high DOP concentrations and therefore a effort should be made to replace this toxic plasticizer with some less dangerous to children.

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