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Prof. Dr Snežana Šerbula

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DETERMINATION OF PHTHALATES IN PVC BY FTIR AND A PRECIPITATION METHOD

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Abstract

Phthalates are widely used as plasticizers in plastic materials and given their physicochemical properties, they can easily migrate from plastics and thus pollute the environment. In this investigation medical equipment made from PVC was used. In order to isolate phthalates from PVC and determine then precipitation method and Fourier Transform Infrared Spectroscopy (FTIR) was used. The obtained FTIR spectra show the presence of phthalates in the investigated plastic samples. The characteristic FTIR spectra absorbance band at 743 cm⁻¹ and doublet bands at 1579 cm⁻¹ and 1599 cm⁻¹ prove the presence of phthalates in PVC samples. Based on the absorption intensity, it can be determined which plastic sample contains the most phthalates. The absence of given absorbance bands in FTIR spectra of plastic samples that was released from phthalates by the precipitation method shows the efficiency of the precipitation method. The FTIR method ensures rapid, reliable and not expensive qualitative determination of phthalates.

Keywords: phthalates, PVC, FTIR, precipitation

INTRODUCTION

Phthalates are a class of organic compounds produced by esterification of phthalic acid with different aliphatic alcohols. The chemical structures of phthalates are similar, the difference is in the ester groups attached to the benzene ring in an ortho position. The basic chemical structure of phthalates is given on Figure 1.

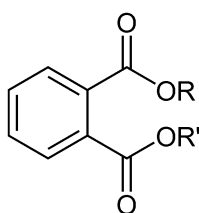


Figure 1 The basic chemical structure of phthalate ($R, R' = C_nH_{2n+1}, n = 1-15$)

The physicochemical properties of phthalates depend on molecular mass of phthalates. The common feature of all phthalates is colourless, odourless, volatility, high density, solubility in non-polar solvents [1]. With an increase of length of hydrocarbon chain and thus, increase in molecular mass, their insolubility in polar solvents increases.

Phthalates are commonly used as plasticizers in the production of plastics. The most commonly used phthalate is di-*n*-ethyl hexyl phthalate (DEHP). 15-30% phthalates are added to polymers, such as PVC, in order to transform the glassy unmodified PVC into a soft and flexible rubbery material, and in this way make it easier to process these plastic materials [2]. Since phthalates are physically bonded to the plastic, they can easily leach out to their environment, including beverages, food products, air and water [3]. In this way, humans are exposed to phthalates in several ways: through ingestion, inhalation and dermal contact throughout their lifetimes. Literature data indicate the effect of phthalates on human health and phthalates are classified as endocrine disruptors and affect reproduction [4–6].

Instrumental techniques for the separation and detection of phthalates are different and depend on the physicochemical properties of phthalates and the matrices being examined. The most commonly used techniques are liquid (LC) and gas (GC) techniques coupled to mass spectrometry (MS detection systems). The Fourier Transform Infrared Spectroscopy (FTIR) has the significance in the pre-screening for phthalates in plastic materials, because this technique is reliable, non-destructive, does not require special preparation of the samples, thus it is more rapid and far less costly than the GC-MS method.

The aim of this paper is the analysis of presence of phthalates in medical equipment, which is a reliable source of phthalates, because it is made of PVC. First, a qualitative analysis will be performed using FTIR technique, after which the phthalate will be removed from the PVC by precipitation method, which will also be verified using the FTIR technique.

MATERIALS AND METHODS

Chemicals and reagents

The tetrahydrofuran (HPLC grade) was purchased from Fischer scientific (USA). The *n*-hexane (HPLC grade) was purchased from Carlo Erba (France).

Medical equipment made of PVC was taken from local Clinical Center Niš, Serbia. Transfusion set with transfer bag, quadrupole blood bag, Sag-M bag and transfusion tubing (TIANHE Pharmaceutical, Chine) was used for analysis.

FTIR technique

FTIR spectra were recorded on a laser Fourier Transform Infrared Spectroscop (BOMEM Hartman & Braun — Michelson MB series 100).

The manual hydraulic press (Graseby Specac) was used. This hydraulic press is designed fundamentally to create pellet samples which can then be processed using analytical equipment such as FTIR and provide high optical throughput for precise and efficient analysis.

Amalgamator (Wig-L-Bug) was used for mixing a variety of materials including precipitates from this analysis.

Gravimetric Techniques

n-Hexane was used to produce the PVC precipitate from tetrahydrofuran solution. The centrifuge (Jouan C4I Benchtop, Termo Fisher) was used to separate precipitates from the aliquot. Mass of PVC precipitate after drying was measured on the analytical balance with accuracy of ± 0.00001 g.

PVC sample dissolve in THF

The noted medical equipment (plasticized PVC) was used as sample for this investigation. 0.01 g of sample was weighted and transferred into 8 mL vial. After that, 4 mL of tetrahydrofuran was added in vial. In order to quickly dissolve the plastic into tetrahydrofuran the vial was placed on the hot plate and obtained covered with glass to prevent evaporation and loss of tetrahydrofuran. After dissolving PVC, the obtained solution was poured into evaporating dish. After evaporation of the tetrahydrofuran for 30-40 minutes, a polymer film was formed. The polymer film was created on the evaporating dish and was mounted on an IR cell holder on FTIR instrument and FTIR spectrum was scanned. Each analysis is repeated three times.

PVC sample dissolve in THF and precipitation by *n*-hexane

The mass of the sample of 0.01 g was dissolved in 4 ml of tetrahydrofuran. After dissolution, 10 ml of *n*-hexane was added to the obtained solution. The PVC precipitate without phthalates was obtained, while dissolved phthalates were found in the aliquot above the precipitate.

The PVC precipitate was separated from the aliquot by centrifugation (3500 rpm). In the oven at 80°C the PVC precipitate was dried. After that, PVC precipitate was mixed in amalgamator with KBr and pellets were formed by manual hydraulic press. FTIR spectrum was recorded to confirm completely release of phthalates from PVC sample. In order to confirm the complete removal of phthalates from PVC sample by *n*-hexane precipitation, the following was done. Phthalates-free PVC precipitate was dissolved in tetrahydrofuran, after which the obtained solution was poured into evaporating dish, left for tetrahydrofuran evaporation and obtained polymer film that did not contain phthalates was scanned on FTIR instrument.

The aliquot with dissolved phthalate was placed into evaporating dish and after evaporation obtained disk was gravimetrically measured. These was the plasticizers from the PVC sample. The weight of the film represented mass of the phthalates in PVC, so the mass percentage of phthalates in PVC samples was determinate.

Safety precautions and reduction of sample contamination by phthalates

Used solvents are volatile and flammable, therefore, care must be taken. Tetrahydrofuran is toxic by inhalation and ingestion and the evaporation must be done in the digester. In order to reduce laboratory phthalates contamination, and since tetrahydrofuran dissolves PVC, only glassware equipment was used. All glassware was washed with soap, tap water and ultrapure water, then washed with acetone and *n*-hexane and dried at 200 °C in the oven for 4 hours [7].

RESULTS AND DISCUSSION

Characterization of IR spectra of PVC sample dissolved in tetrahydrofuran

The strong absorbance band at 743 cm^{-1} in the infrared spectrum identifies the phthalates, due to their ortho substituted aromatic ring. Other useful bands for infrared analysis of phthalates are the doublet bands at 1599 cm^{-1} and 1579 cm^{-1} . These bands appear as a result of the aromatic ring quadrant stretching vibration, and their frequency and intensity depends on the aromatic ring substitution. Also, the characteristic FTIR spectra absorption bands for PVC were: 2960 cm^{-1} (for -C-H bond), 1718 cm^{-1} (for the phthalate ester), 1450 cm^{-1} (for -CH₂- and -CH₃), 1278 cm^{-1} (for -CH₂-), 1073 cm^{-1} (for -CH₃). In the figure 2 IR absorption spectrum of PVC sample is given.

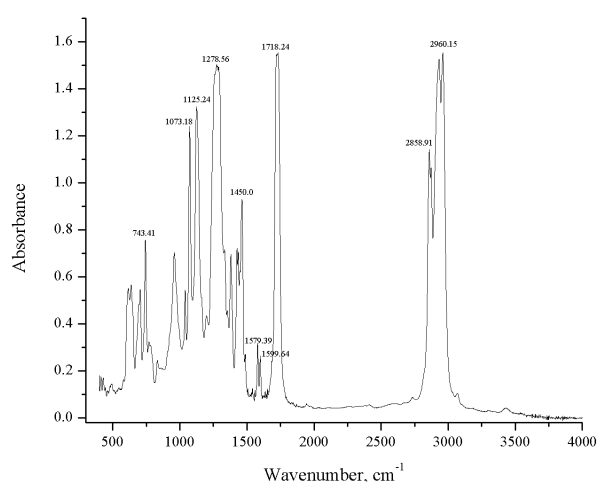


Figure 2 The FTIR spectrum of transfusion tubing, with qualitative bands identified

In the Figure 3 two regions of the IR spectra of PVC samples were given. Based on the given spectra it can be concluded which PVC sample contains the most phthalates. The tubing for transfusion contains the most phthalates, followed by quadrupole blood bag, transfer bag and Sag-M bag.

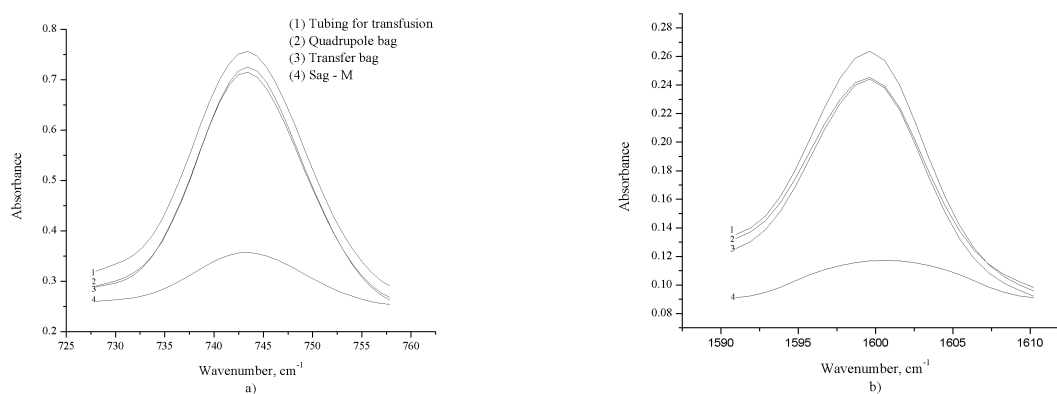


Figure 3 The FTIR spectrum of PVC samples: a) region $730\text{--}760\text{ cm}^{-1}$ b) region $1590\text{--}1610\text{ cm}^{-1}$

Characterization of IR spectra of PVC sample dissolved in tetrahydrofuran and precipitated by *n*-hexane

Obtained KBr pellets were recorded by FTIR instrument and given spectra show absence of characteristic absorbance bands (743 cm^{-1} , 1579 cm^{-1} , 1599 cm^{-1}) for phthalates. In Figure 4 FTIR spectrum of one KBr pellet is given. These data indicate that the precipitation method of PVC by *n*-hexane completely releases phthalate from PVC samples. Identical FTIR spectra was obtained by recording a plastic film obtained by evaporation of the dissolved precipitate in tetrahydrofuran.

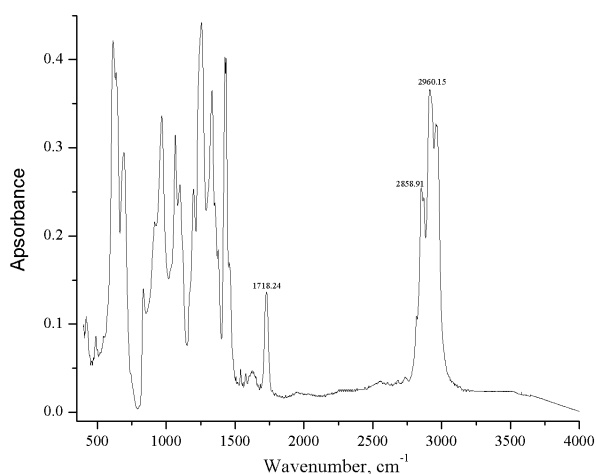


Figure 4 The FTIR spectrum of transfer bag without phthalates

Analysis of aliquots above precipitates, with dissolved phthalates, give the following results. The weight of polymer film after evaporation of *n*-hexane-tetrahydrofuran give the total mass of phthalates in the sample. Obtained calculated mass percentage of phthalates in PVC samples is given in Table 1.

Table 1 Mass % of phthalates of PVC sample

Sample	Mass % of phthalates
Tubing for transfusion	29.25±0.31
Quadrupole bag	25.51±0.06
Transfer bag	25.11±0.10
Sag-M	5.50±0.09

During this analysis, two polymer films were obtained. The first polymer film was obtained by evaporation of solvent from the solution of dissolving PVC with phthalates in tetrahydrofuran was elastic and highly flexible, which is related to the effect of phthalates. The second polymer film was obtained by evaporation of solvents from the *n*-hexane-tetrahydrofuran solution of the PVC precipitates without phthalates was non-flexible, which showed that the phthalates are removed from the PVC sample.

CONCLUSION

Bearing in mind structure of phthalates and their ortho substituted aromatic ring, expected characteristic absorbance bands in FTIR spectra occurred. In this way pre-screening of phthalate content in PVC samples can be done, because this method is a rapid and efficient, after which the GC-MS analysis can be performed. For the phthalate analysis the precipitation technique and evaporation method of the aliquot above precipitate can also be used. A more efficient method for recording FTIR spectra of PVC-free phthalates, give the same results, is the method of making KBr pellets, because it is rapidly than the method of re-dissolving the precipitates in tetrahydrofuran.

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