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Technical Faculty in Bor
28th International Conference Ecological Truth
& Environmental Research

EcoTER'20

PROCEEDINGS

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Prof. Dr Snežana Šerbula

16 - 19 June 2020, Hotel Aquastar Danube, Kladovo, Serbia

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DETERMINATION OF PHTHALATES IN PVC MEDICAL DEVICES BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Abstract

The aim of this work was to determine phthalates in PVC medical devices using the FTIR spectroscopy, as a rapid pre-screening test. Phthalates were isolated from the PVC samples by tetrahydrofuran and then plastic is precipitated by the addition of an excess of methanol. The FTIR spectrum of PVC samples were recorded and on the basis of specific absorbance bands occurring in the spectra, the existence of phthalates in the PVC samples was checked. The characteristic adsorbance bands for phthalates in FTIR spectrum were at 743 cm^{-1}, 1579 cm^{-1} and 1599 cm^{-1}. Based on the intensity of absorption for three investigated PVC samples, it could be concluded that tubing for infusion set contains the most phthalates, following by tubing for dialysis set and dialysis bag, respectively. The absence of these characteristic peaks in the FTIR spectra obtained by the precipitation method demonstrated the effectiveness of this method in the removal of phthalates. Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

Keywords: phthalates, PVC, FTIR, precipitation

INTRODUCTION

Phthalates are the esters of 1,2-benzene dicarboxylic acid that are formed by the addition of an aliphatic or aromatic alcohols to phthalic anhydride in the presence of a catalyst. The resulting ester groups are in the *ortho*- position. Phthalates are a family of chemicals used to make plastics (primarily polyvinyl chloride - PVC) more flexible, elastic and soft, and for this reason phthalates are also called plasticizers. Because of that, phthalates are used in hundreds of products in households, hospitals and other spheres. Since phthalates are not chemically bonded to PVC, they can leach out of plastic under appropriate conditions. The consequences of phthalate migration from PVC are: the plastic becomes rigid and brittleand the phthalates reaches the environment. Due to their properties (non-polar molecules, easily soluble in fats), they are easily dissolved in food, dairy products, beverages, blood, urine, *etc*. This way

human are exposed to the harmful effects of phthalates. Research has shown that phthalates cause infertility in men, cause testicular cancer, and affect the secretion of glands, thereby classifying phthalates as endocrine disruptors [1–3].

In order to determine phthalates in various media due to their harmful effects, different methods have been developed, among which gas chromatography-mass spectrometry (GC/MS) is the most common used method for this analyse [4]. Phthalate structure with the ester groups in the *ortho*- position has great importance for the further phthalates determination by Fourier Transform Infrared Spectroscopy (FTIR). FTIR method as non-destructive, reliable, rapid, not expensive, without the need of special sample preparation, can be considered as significant in the pre-screening for phthalate determination in PVC [5].

The aim of this work was the qualitative determination of phthalates in medical devices, made of PVC. By removing phthalates from the plastic packaging materials by the dissolution/precipitation method, the phthalate content qualitatively checked in phthalates free – plastic and phthalate plastic by FTIR technique, while phthalate content in THF/methanol system was checked by GC/MS technique.

Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

MATERIALS AND METHODS

Chemicals and reagents

The tetrahydrofuran (THF) with HPLC purity was purchased from Fischer scientific (USA). The methanol with HPLC purity was purchased from Carlo Erba (France).

Medical devices made of PVC was taken from local Clinical Center Niš, Serbia. Dialysis bag with coupled dialysis tubing which constitute a set for peritoneal dialysis (Baxter, USA) and tubing for infusion set (Mediaset, Spain) were used for analysis.

FTIR technique

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

The manual hydraulic press (Graseby Specac) was used to create pellet samples for further analytical determination by analytical equipment such as FTIR.

Amalgamator (Wig-L-Bug) was used for mixing precipitates from this analysis with appropriate substance.

Gravimetric technique

Methanol was used to produce the PVC precipitate from THF 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.

Sample preparation

Dissolving PVC sample in THF

Accurately weighed mass of PVC medical equipment (0.01 g) was dissolved in 4 ml of THF. This was the first step in qualitative phthalates determination using the FTIR instrument. Dissolution of PVC was accelerated by heating, with caution not to evaporate THF. The next step was to evaporate THF solution in order to form a polymer film of PVC. The formed Phthalate-PVC polymer (PPVC) filmon the evaporating dish was mounted on an IR cell holder on FTIR instrument and FTIR spectrum was scanned. Each analysis was repeated three times.

Precipitation of PVC by methanol

The same mass of the sample (0.01 g) as in the previous experiment was dissolved in 4 ml of THF. After dissolution, 10 ml of methanol was added to form PVC precipitate without phthalates (P-free PVC), leaving dissolved phthalates in the supernatant above the precipitate. The P-free PVC precipitate was separated by centrifugation (3500 rpm). In order to confirm the complete release of phthalates from PVC samples by THF/methanol, the analysis was conducted in three directions:

(1) P-free PVC precipitate (pre-dried at 80°C in the oven) was mixed with KBr to form pellets using manual hydraulic press and amalgamator and scanned on FTIR instrument.

(2) P-free PVC precipitate was dissolved in THF. After evaporation of THF, the obtained polymer film was scanned on FTIR instrument.

(3) Evaporation of the dissolved phthalates supernatant into evaporating dish was done. Obtained disk was gravimetrically measured. The weight of the disk represented mass of the phthalates in PVC. In this way the mass percentage of phthalates in PVC samples was calculated.

Safety precautions and reduction of sample contamination by phthalates

Due to the volatility and flammability of the used solvents, care must be taken. Evaporation of THF must be done in the digester due to the toxicity of THF. Only glassware equipment was used, because THF dissolves PVC and in order to reduce laboratory phthalates contamination. 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 [6].

RESULTS AND DISCUSSION

Characterization of FTIR spectra of PVC samples

Given that the phthalates aromatic ring was substituted in the *ortho*- position, the expected absorbance band at 743 cm^{-1}, characteristic of that group appeared on the FTIR spectrum. This strong absorbance band at 743 cm^{-1} identifies the phthalates. On the FTIR spectrum doublet bands at 1599 cm^{-1} and 1579 cm^{-1} appeared as a result of the aromatic ring quadrant stretching vibration and also were useful for infrared analysis of phthalates. Frequency and intensity of these bands depends on the aromatic ring substitution. Other useful and

characteristic FTIR spectra absorption bands for PVC are: 2960 cm^{-1} (for -C-H bond), 1718 cm^{-1} (for the phthalate ester), 1450 cm^{-1} (for $-CH_2-$ and $-CH_3$), 1278 cm^{-1} (for $-CH_2-$), 1073 cm^{-1} (for $-CH_3$). In Figure 1 FTIR absorption spectrum of dialysis bag was given.

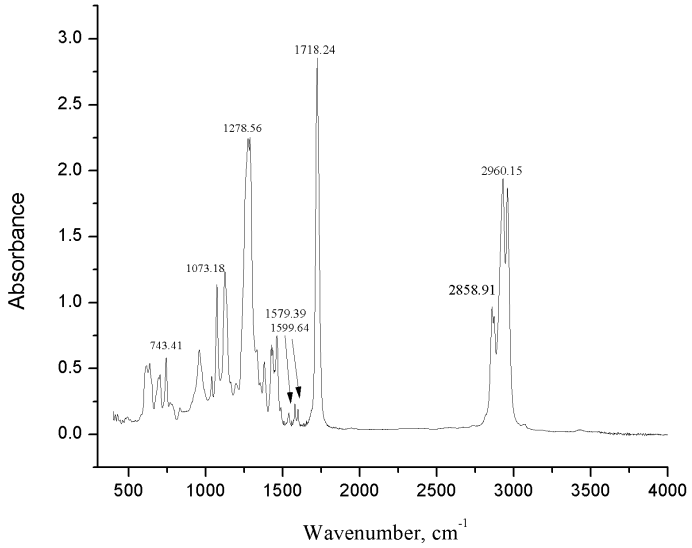

Figure 1 *The FTIR spectrum of dialysis bag with qualitative bands identified*

In Figure 2 two regions of the FTIR spectra of the investigated medical devices were given, region from 730 to 760 cm^{-1} and region from 1590 to 1610 cm^{-1}. Based on the graphs *Absorbance=f (Wavelength)*, it can be concluded which PVC sample contains the most phthalates. The tubing for infusion set contains the most phthalates, followed by tubing for dialysis set and dialysis bag, respectively.

a) *b)*

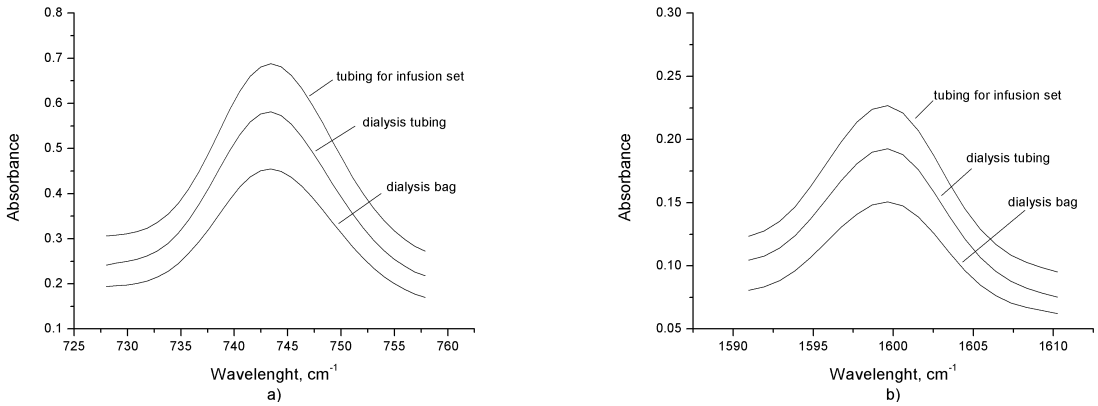

Figure 2 *The FTIR spectrum of PVC samples: a) region 730-760 cm^{-1} b) region 1590-1610 cm^{-1}*

Characterization of FTIR spectra of P-free PVC sample

Prepared the KBr pellets, were scanned on FTIR instrument to confirm complete release of the phthalates into methanol-THF aliquot and given spectra show absence of characteristic

absorbance bands for phthalates at 743 cm^{-1}, 1579 cm^{-1} and 1599 cm^{-1}. In Figure 3 FTIR spectrum of KBr pellet was given. The absence of these absorbance bands showed that the precipitation method by methanol completely released phthalate from PVC samples. The same FTIR spectrum was obtained by recording a polymer film obtained by evaporation of the dissolved P-free PVC precipitate in THF.

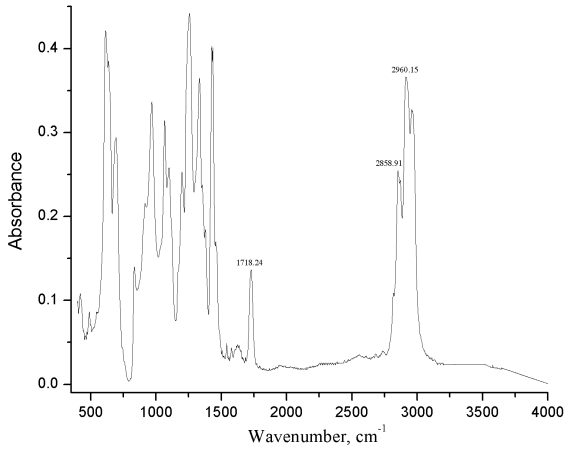

Figure 3 *The FTIR spectrum of dialysis bag without phthalates*

Determination of dissolved phthalates in methanol-THF supernatant

Analysis of methanol-THF supernatant given the following results. The weight of polymer film obtained after evaporation of THF/methanol was measured. The weight of this polymer film represented the total mass of phthalates in the sample. Obtained calculated mass percentage of phthalates in investigated PVC samples was given in Table 1.

Table 1 *Mass % of phthalates of PVC sample*

Sample	Mass % of phthalates
Tubing for infusion set	25.96±0.53
Tubing for dialysis set	20.95±0.41
Dialysis bag	19.2±0.36

Qualitative comparison of obtained polymer films

In this investigation two different polymer films were obtained. The PPVC polymer film with phthalates, obtained by evaporation of THF from the THF solution of PVC, was elastic and flexible, because phthalates have the function of plasticizers in PVC plastic. The P-free PVC polymer film, obtained by evaporation of THF-methanol, was rigid and brittle, which was a consequence of removal of phthalates from the PVC sample.

CONCLUSION

Considering the impact of phthalates on human health, determination of phthalates in various food, beverage, plastic packaging, medical equipment, etc. is of great importance. Given that determination methods generally are expensive and complicate, it is important to develop a method that is fast, reliable and inexpensive. Such a method uses FTIR technique described in this paper. The disadvantage of this method is that it is not specific method, because the obtained characteristic absorbance band at 743 cm^{-1} and absorbance doublet at 1579 cm^{-1} and 1599 cm^{-1} in FTIR spectra are characteristic of each phthalate. However, this method is useful, because it can be used in pre-screening, after which the GC/MS analysis can be performed.

Also, the precipitation method was used in this work to remove phthalates from plastic, and evidence of the removed phthalates was provided by the FTIR method. The free phthalates-plastic film was brittle and rigid, unlike the phthalate-containing plastic that was flexible and elastic. Comparison of obtained amount of phthalates in tetrahydrofuran/methanol solution, PVC precipitate and in PVC sample showed that FTIR method can be used as a rapid pre-screening test for qualitative determination of phthalates.

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