



The Sensitive Method of Determination of Hazardous Phthalates in Polymeric Building Materials by High Performance Liquid Chromatography

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Abstract: Polymeric building materials and equipment for indoor use in spaces intended for people may, in an essential way, contribute to the deterioration of wholesome quality of life. Phthalates, present in many products, constitute an omnipresent group of compounds used widely as plasticisers. The research results show that these substances may negatively impact human health, and thus European Union has implemented several regulatory measures restricting their use. Manufacturers and suppliers must comply with these regulations. As a result, it is necessary to investigate and determine the contents of phthalates in these materials. This paper presents the analytic profile of the method of marking phthalates extracted from polyvinyl chloride using HPLC chromatography with UV-VIS detection and selected results obtained in examinations of materials used in interior design. The results of described examinations of phthalates content indicate that not all materials recommended by manufacturers may be used indoors in spaces intended for people. The method was verified for its suitability for routine analyses of materials made of PVC and submitted for attestation. The elaborated method can be used to determine the banned phthalates' presence in PVC. The method allows for detecting these phthalates at the level required by the REACH regulation, and its validation parameters are highly satisfactory considering a very complex matrix.

Keywords: Liquid chromatography HPLC, phthalates, REACH, PVC

1. Introduction

Phthalates, i.e. esters of phthalic acid, are widely used in the production of plastics and as solvents in hygiene products, cosmetics and pharmaceutical preparations. They are commonly used as standard plastic plasticisers and as raw materials for producing phthalate-glycerine resins, varnishes, paints, laminates, eco-



leathers, stretch ceilings, wallpapers, photo wallpapers, floor coverings, rubbers, foams, welding curtains, water pipes, sewerage and other products. Phthalates acting as plasticisers do not form chemical bonds with polymer molecules but fill intermolecular spaces, decreasing hardness and glass transition temperature and increasing flexibility. Under the influence of some factors, such as high or low temperature, they can be released from the polymer matrix. As a result, phthalates can be released from plastics into the air, dust, water, soil, sewage and sewage sludge, thus leading to human exposure to the toxic effects of these substances (Chmielewski et al. 2019).

Unfortunately, as proven by many years of research, these compounds pose a threat to human health and life, as they potentially increase the risk of developing asthma and cancer and adversely affect the mechanism of certain hormones action, thus contributing to the development of numerous chronic severe diseases such as, e.g. diabetes. Phthalic acid esters introduced into the body directly affect its hormonal balance and the nervous and immune systems.

The phthalates listed in Table 1 are included in the lists of hazardous substances in Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 (REACH) (Regulation as amended).

Table 1. Phthalates and their hazardous properties (summary)

No	Name	Synonym	CAS Number	EC Number	*Hazard statements
1	Dibutyl phthalate	DBP	84-74-2	201-557-4	H317, H372, H335, H360Df, H411
2	Benzyl butyl phthalate	BBP	85-68-7	201-622-7	H335, H360Df, H400, H410
3	Dipentyl phthalate	DAP	131-18-0	205-017-9	H360Df, H400
4	Diethyl phthalate	DHP	84-75-3	201-559-5	H360Df, H400
5	Dicyclohexyl phthalate	DCP	84-61-7	201-545-9	H317, H360D
6	Bis(2-ethylhexyl) phthalate	DEHP	117-81-7	204-211-0	H360Df
7	Di-n-octyl phthalate	DNOP	117-84-0	204-214-7	H319, H361Df, H335

*Hazard statements:

H317 May cause an allergic skin reaction

H319 Causes severe eye irritation

H335 May cause respiratory irritation

H360D May damage the unborn child

H360Df May damage the unborn child. Suspected of damaging fertility

H361Df Suspected of damaging fertility. Suspected of damaging the unborn child

H372 Causes damage to organs through prolonged or repeated exposure (state all organs affected, if known) through prolonged or repeated exposure (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)

H400 Very toxic to aquatic life
H410 Very toxic to aquatic life with long-lasting effects
H411 Toxic to aquatic life with long-lasting effects
H335 May cause respiratory irritation

Studies have shown that phthalates can cause reproductive system concerns (e.g. increasing the risk of infertility or teratogenicity), destroy nervous tissue, and cause various allergic reactions. Due to the widespread use of hazardous phthalates as plasticisers in popular plastics, they pose a justified risk to human health. Therefore, it is necessary to test the content of particularly hazardous to human health phthalates in plastics, including polyvinyl chloride. Many of phthalates are listed as hazardous substances in Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Regulation as amended. Since 7 July 2020, trading bans were introduced for BBP, DBP, DEHP and DIBP in materials with the addition of plasticisers >0.1% individually or in combination. Additionally, these phthalates are listed on the SVHC list. Suppliers of materials with SVHC content exceeding 0.1% are obliged to provide the recipient of such material with adequate information to enable the safe use of the product. The minimum requirement is listing the name of a given SVHC substance.

The literature describes two general approaches to extracting phthalates from plastic matrices: dissolution or precipitation process and solvent extraction. The separation of plasticisers in polyvinyl chloride (PVC) tubes used in medical applications is described (Wang & Storm 2005). The studies were conducted with the use of various solvents and compared by examining the residual PVC after separation by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), as well as by examining the extracted low molecular weight plasticisers by gas chromatography/mass spectroscopy (GC/MS) and GC/FID. Simple extraction in chloroform at room temperature presented the best results in separating plasticisers from the PVC matrix.

Quantification is usually done by flame ionisation gas chromatography (GC-FID) or mass detection (GC-MS). The possibility of extracting plasticisers at different temperatures and times with methanol, diethyl ether, dichloromethane, and chloroform separately and in a mixture was tested. Extraction can be performed at room or elevated temperatures with a Soxhlet extractor (Monteiro et al. 2011). The results of extraction with methanol in a Soxhlet extractor for 6 hours were comparable to those obtained by dissolving in THF for 24 hours, followed by precipitation with methanol. Other researchers recommend the method of extraction with dichloromethane for 6 hours in a Soxhlet extractor at a temperature

of 60-80°C with the use of GC-MS (Zou & Cai 2013). Good recoveries were obtained for all investigated phthalates. The literature describes a method for routine analysis involving extraction of THF (tetrahydrofuran) and precipitation with hexane, followed by GC-MS analysis. (Test Method: CPSC-CH-C1001-09.3).

According to the test procedure based on the Polish standards, PN-EN 15777:2009 and PN-EN ISO 14389:2014-07 phthalates were determined by gas chromatography in combination with mass spectrometry detector (GC-MS) and flame ionisation detector (GC-FID). Methods were developed for qualitative and quantitative analysis of phthalic esters (Mrozińska & Niedźwiedzki 2016). Another standard test method provides a procedure to identify and quantify phthalates by thermal desorption (TD), gas chromatography (GC), mass spectrometry (MS) (ASTM D7823 – 20). HPLC with UV detection technique has been successfully used to separate and identify phthalates (Ranganadham 2017).

Phthalates tend to migrate into the environment, leading to their accumulation in several matrices such as soil, seawater, sediments, sludge, and surface waters, among others. Thus, monitoring their levels is imperative due to the possible implications for human health. These compounds are usually extracted from the matrices using several extraction procedures. Efficient pre-concentration and clean-up procedures are necessary to guarantee the quality of the analytical methods due to the predictable low concentration of these target analytes in samples and the sample complexity (Haji Harunarashid N.Z.I. et al. 2017). It is possible to observe that the most common extraction techniques used to extract phthalates from environmental and food samples are LLE, SPE, SPME, QuEChERS-dSPE.

The study described by Korkmaz S.D. and Küplülü Ö. (2019) allowed the qualitative and quantitative determination of phthalates in yoghurt samples. The phthalates were extracted with methanol and hexane and analysed by LC-MS/MS. Jun Jiang et al. (2019) described extraction with acetonitrile (n-hexane saturated) combined with RC and Gas chromatography – electron ionisation quadrupole mass spectrometry (GC – EIMS) for quantification of 16 phthalate esters in suet oil. Quing et al. (2017) present a method for the determination of migration of six phthalate esters in plastic toys based on gas chromatography-tandem mass spectrometry (GC-MS/MS) coupled with solid phase extraction using cucurbiturils (CB6-8) as adsorbent. Phthalates were migrating in simulated saliva.

In contrast to LLE, soxhlet, and SPE, SPME comprises sampling, extraction, purification, concentration, and injection into a single procedure. This extraction procedure is solvent-free and does not need previous sample preparation, and consequently, the risk of cross-contamination from solvents, samples, and glassware was reduced SPME.

Solid phase microextraction coupled with the flash evaporation gas chromatography method was applied to determine phthalate esters. Polysulfone hollow fibre at 1 cm length was employed as an extraction element to adsorb directly. The extracted analytes were thermally desorbed at 300°C in a pyrolyser and then entered into a column for separation. The results demonstrated that this was a simple, environmentally friendly and accurate method for determining in bottled water (Huang et al. 2020). Hollow fibre and monolithic fibre were fabricated based on metal-organic solvents/molecularly imprinted polymers and were used for the microextraction of phthalate esters, followed by gas chromatography-flame ionisation detection. The procedure was successfully applied with satisfactory results in determining phthalate esters in yoghurt, water, and soybean oil samples. (Mirzajani et al. 2020).

Headspace solid-phase microextraction (HS-SPME) combined with gas chromatography-mass spectrometry (GC-MS) was optimised through the multivariate optimisation process and validated to evaluate the occurrence of four common phthalates in different food packaging. The best extraction efficiency was achieved using the polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibre at 80°C for 30 min. (Perestrelo et al. 2021).

The Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method is a simple and straightforward extraction technique involving an initial partitioning followed by an extract clean-up using dispersive solid-phase extraction (d-SPE). Socas-Rodríguez et al. (2018) present a new method for determining 14 phthalic acids in different baby foods. Separation was carried out by gas chromatography triple quadrupole tandem mass spectrometry, while the previous extraction of the samples was carried out using the QuEChERS method.

An innovative, modern and sensitive analytical method has been developed, allowing for the simultaneous determination of 7 phthalates listed on the REACH and SVHC lists in various polymers (polymer matrices, plastics). This paper presents the characteristics of the phthalate separation method from the PVC and the results obtained after analysing the extracts using the HPLC technique with UV detection. The dissolution parameters of other plastics will be covered in a separate publication: Use of a medium for dissolving plastics, Polish Patent Registration 436003 of 18 November 2020.

The innovation of the method is based on the analysis of products/plastics, and not water, in which higher phthalate plasticisers dissolve very poorly (examples of water solubility: according to Summary Risk Assessment Report – DEHP 3 µg/l at 20°C; according to TCI specification, DNOP – 3 mg/l at 25°C).

2. Experimental Section

2.1. Apparatus and Reagents

A Summit PAN High Performance Liquid Chromatograph (Dionex, Germany) with a diode array detector was used to determine phthalates. Separations were carried out on an RP C18 column (150×4.6 mm, 4 μm) (Dionex) under gradient conditions (Table 2), with an injection volume of 10 μl, at a temperature of 20°C. The separations were carried out; data were collected at different wavelengths. The best shapes and heights of the phthalate peaks were obtained at 210 nm.

Because in the case of a complex matrix, interactions hindering the interpretation of results may occur, analytical data were collected at different wavelengths, while the method was also validated at 3 wavelengths: 210, 230 and 254 nm. The results presented in this study were obtained at 210 nm wavelength.

Table 2. Gradient elution conditions (acetonitrile (ACN) : water)

Time [min]	ACN [%]	Flow [ml/min]
0-10	60	0.5
10-18	60-75	0.5
18-20	75	1.0
20-27	75-95	1.0
27-29	60	0.5
29-40	60	0.5

For the purpose of identification, for preparation of calibration solutions, stock solutions of phthalates in methanol (Merck), obtained after dissolving the exact amount of phthalate standards (TCI EUROPE N.V. – single standards of purity from 97.8% to 99.6%) were prepared. Under the described chromatographic analysis conditions, the analyte signals' retention times were: BBP 7.8; DBP 8.5; DCP 15.7; DAP 16.3; DHP 21.5; DEHP 23.5 and DNOP 25.3 min. A sample chromatogram is shown in Figure 1.

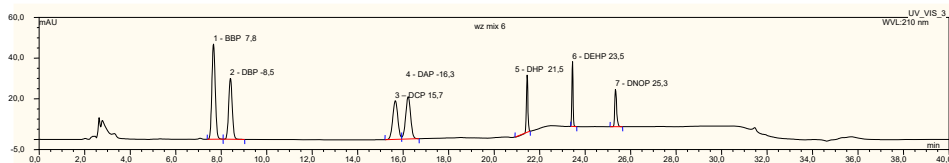


Fig. 1. An exemplary chromatogram of a standard solution of phthalates (concentration each of phthalates is 6.0 $\mu\text{g/ml}$) recorded by high-performance liquid chromatography with UV detection

Calibration based on five calibration solutions in methanol (concentration levels in the range of 0.6-15.0 $\mu\text{g/ml}$) was performed each time on the test day. Additionally, the level of the blind was controlled. The obtained correlation coefficients were not lower than 0.99.

2.2. Preparation of samples

Phthalates are common pollutants. Even a low level of contamination can affect the quantitative results. Thus only scrupulously cleaned glassware was used in the experiment. All solvents were checked for the content of the tested phthalates. No plastic laboratory equipment was used.

For validation of the method, the determination of phthalate content was carried out for phthalates-containing PVC granulate samples. For validation purposes, polyvinyl chloride (Sigma Aldrich) with molecular weights of 43.000 and 233.000 was used. Except that PVC plastics containing precisely defined contents of 7 tested phthalates were obtained. For verification of the method's trueness and routine analysis solutions with concentration of 25 mg PVC plastics in 1 ml of THF (Merck) were prepared, and methanol was added for precipitation. The solution was cooled for one hour in a refrigerator, and after cooling it was centrifuged for 5 min at 4000 rpm. An aliquot of sample was collected and diluted with methanol to 10 ml in total. The final concentration of PVC plastic is 1 mg in ml. Before the chromatographic analysis – to remove polymers and mineral fillers such as CaCO_3 , TiO_2 , BaSO_4 , and $\text{Al}(\text{OH})_3$ – it was filtered through a membrane filter with a diameter of 25 mm and a pore diameter of 0.45 μm . The parameters characterising the method obtained during the validation are presented in Table 3.

Table 3. Selected parameters characterising the method for the determination of phthalates in polyvinyl chloride

Phthalate/ Retention time [min]	LOD [$\mu\text{g}/\text{ml}$]	LOQ [$\mu\text{g}/\text{ml}$]	Trueness [%]	Recovery [%]**	Precision [%]**	Expanded uncertainty [%]**
BBP 7.8	0.16	0.33	5.15	82.00	0.6	12.01
DBP 8.5	0.20	0.39	7.20	84.58	1.0	12.09
DCP 15.7	0.21	0.42	7.95	78.00	3.1	12.84
DAP 16.3	0.28	0.56	10.45	80.59	1.2	12.23
DHP 21.5	0.35	0.70	10.02	97.00	5.1	14.61
DEHP 23.5	0.15	0.291	9.67	94.00	4.1	13.31
DNOP 25.3	0.22	0.44	7.78	88.03	2.4	12.61

**Refers to a level of 1 $\mu\text{g}/\text{ml}$ corresponding to 0.1%.

The method for phthalates determination was validated at 3 concentration levels. The presented results refer to a level of 1 $\mu\text{g}/\text{ml}$, which corresponds to the phthalate content in the product at the level required by the legislation, i.e. 0.1%. The following validation parameters were obtained: limit of detection from 0.15 to 0.35 $\mu\text{g}/\text{l}$, limit of quantification from 0.30 to 0.70 $\mu\text{g}/\text{ml}$. The precision and uncertainty budget for the 3 concentration levels were estimated. The precision at the level of 1 $\mu\text{g}/\text{ml}$ ranges from 0.6 to 5.1%. The mean recovery of the method is between 78% and 97%. For the 1 $\mu\text{g}/\text{ml}$ level, the overall uncertainty ranges from 12.1% to 14%. The developed method is characterised by high sensitivity. It enables the determination of trace amounts of phthalates in PVC with satisfactory precision.

3. Results

The method's suitability for phthalates determination was checked by analysing the extracts of samples obtained from construction products after dissolving and PVC precipitating following the described methodology. Figure 2 shows the chromatograms corresponding to the sample of the PVC (without the plasticiser) from the analysis. A peak at about 14th min comes from the stabiliser added to THF. Figures 3, 4, and 5 show the results of actual samples obtained after dissolving PVC following the described method.

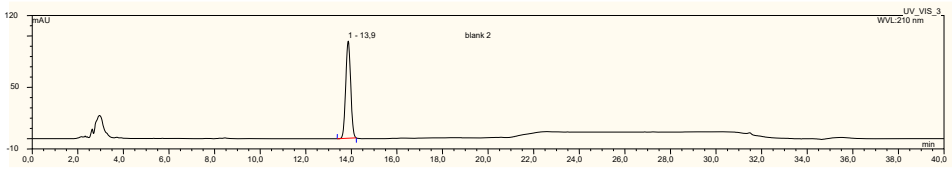


Fig. 2. Chromatogram of the blank samples received after analysis

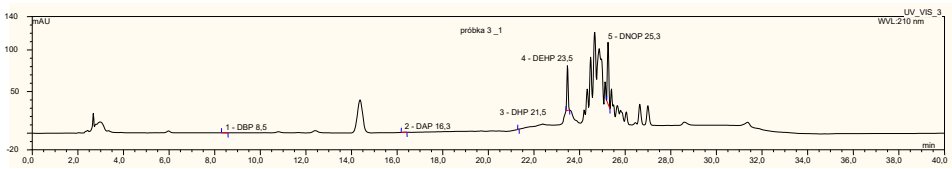


Fig. 3. Chromatogram of the actual sample – welding foil

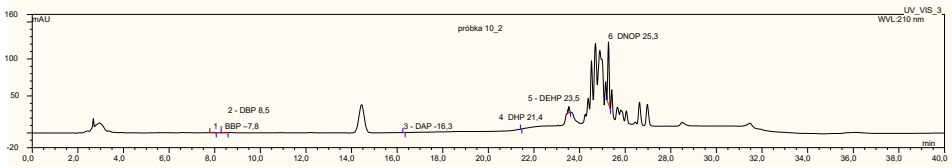


Fig. 4. Chromatogram of the actual sample – suspended ceiling

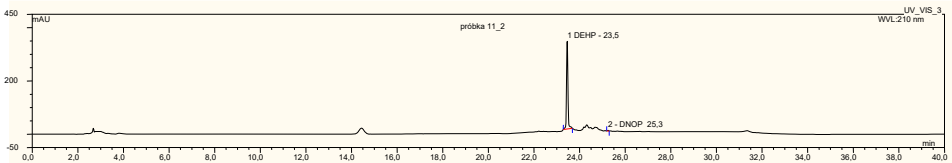


Fig.5. Chromatogram of the actual sample – curtain

The research was carried out on domestic and imported materials, such as synthetic floor coverings, wallpaper, and suspended ceilings, available on the domestic market. A total of 12 products of this type were tested. Exceedances were found in 6 samples, four of which the levels were exceeded drastically. The results are summarised in Table 4.

Table 4. Results of the phthalate content test in selected materials subject to assessment

Product	BBP [%]	DBP [%]	DCP [%]	DAP [%]	DHP [%]	DEHP [%]	DNOP [%]	Total [%]
Welding foil 1	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	–
Welding foil 2	<LOD	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOD	–
Welding foil 3	<LOD	<LOQ	<LOD	<LOQ	0.24	0.98	1.65	2.87
Veneer for furniture 1	<LOQ	<LOD	<LOD	<LOQ	<LOD	<LOD	0.044	0.044
Veneer for furniture 2	<LOQ	<LOQ	<LOD	<LOQ	<LOD	<LOD	<LOQ	–
Curtain 1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
Wallpaper 1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	1.02	1.02
Wallpaper 2	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOQ	0.45	0.45
Upholstery material	<LOD	<LOD	<LOD	<LOQ	<LOQ	0.12	<LOD	0.12
Curtain 2	<LOQ	<LOQ	<LOD	<LOQ	0.11	0.12	1.89	2.12
Suspended ceiling	<LOD	<LOD	<LOD	<LOD	<LOD	6.29	0.065	6.36
Eco-leather	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	–

4. Conclusions

Legal acts binding in the European Union specify the permissible content of individual phthalates not only in toys and childcare articles (DIDP, DINP and DNOP) but also in building materials and elements of equipment used indoors in spaces intended for people. From 7 July 2020, it is prohibited to market BBP, DBP, DEHP and DIBP in materials with the addition of plasticisers in an amount >0.1% individually or in combination.

Additionally, the phthalates in question are listed on the SVHC list. Suppliers of articles containing SVHC in a concentration higher than 0.1% are required to provide the recipient with sufficient information to enable the safe use of the article. The minimum requirement is an indication of the name of the SVHC substance.

The method developed by our team for the simultaneous determination of 7 phthalates in PVC is selective. It is suitable for routine analyses and presents good linearity in the range of 0.6-15.0 µg/ml. It enables the determination of selected phthalates in PVC with satisfactory precision and recovery.

The results obtained from 12 samples showed that manufacturers/importers still use/sell banned phthalates on the market despite the ban. The permissible phthalate content in the tested samples was exceeded. The results of the

phthalate content studies described here indicate that not all materials recommended by their manufacturers can be used in spaces intended for people.

The phthalate content in the sample taken from the stretch ceiling was exceeded 63 times. Therefore, one may assume that the decisive role is played by economic factors – using cheaper plasticisers instead of safe but more expensive ones diminishes production costs and – in the absence of control – leads to the availability of such products to consumers despite the ban.

Exceedances concern DEHP and DNOP, and in one case, DHP. The remaining tested phthalates were not present in the tested materials or were present in amounts below the limit of quantification. The presence of DCP was not detected in any of the tested samples. As a result of this work, a reliable method of quality control of building and furniture materials was established.

The new research method for determining the content of phthalates in materials used in the construction and furniture industries will expand the service offered by the Environmental Health and Safety Department.

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