

## **Deskstudy**

# **PHTHALATES**

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## SUMMARY

The report first gives a short overview of the chemistry, environmental fate and toxic effects of phthalic acid esters. The importance of single phthalates is discussed on the basis of production volumes and occurrence in environmental samples. This is followed by an extended review of 31 different analytical methods for the detection of phthalates, mainly in environmental samples, which discusses various aspects of the methods, such as scope, matrix, extraction, cleanup, detection and limit of detection/quantitation.

A broad scope of matrices has been investigated with the considered methods including solid matrices like soils, sewage sludge, biowaste, sediments and liquid matrices like water, ground water, and leachates as well as related matrices. For some solvents the efficiency of the extraction procedure was evaluated. It was concluded that a single solvent is preferable to solvent mixtures in order to reduce contamination risk. The moderately polar solvent ethyl acetate was shown to be optimal for the phthalates.

Most of the methods used GC/MS for detection and quantification of the phthalates, because it is a common technique with high sensitivity.

From the production volumes of phthalates and from analyses of environmental samples a set of compounds was identified that should be considered in the future method. Dibutyl phthalate (DBP) and di (2-ethylhexyl) phthalate (DEHP) are included.

Recommendations are given for a method that should be straightforward, inexpensive and done with common analytical instrumentation.

The following steps in the analytical work are necessary:

- Evaluation and adoption of the suggested procedure to different matrices (soil, biowaste, sediments, and special sludge).
- Determination of kind and number of the phthalates to be investigated by the proposed method.
- Comparative evaluation of the different solvent used in the methods.
- Evaluation of the need for future investigation of phthalates with long side chains including the determination of the necessary internal standards.

As prenormative investigations the following items have been identified:

- Partition behaviour of different solid matrices (sludge, soil, biowaste, and sediment).
- Influx of phthalates into the environment.
- Estimation of the endocrine effects and environmental risk, limit values.
- The role of suspended particles as carrier.

The intended activities are meant to answer the question of the necessity of a limit value for sewage sludge and its level.





## **1. INTRODUCTION**

Activities of the European Commission regarding the actualisation of the sewage sludge directive forced the respective work for preparing analytical methods which are recommended for regulation in the future directive. Besides PAH, PCB, nonylphenol and LAS, phthalates were also proposed as compounds to be regularly analysed in sewage sludge when an application on agricultural land takes place. It is known that phthalates play an important role in many applications in industry and in our life. Phthalates can be found in many different matrices in our environment and therefore a standardised analytical methods must be available and applicable. The chemical and toxicological behaviour and the relevance of the different phthalates have to be considered when we select the phthalates which we have to observe in the future.

### **1.1 CHEMISTRY AND USE**

Plasticisers are used to improve or even make possible the processing of plastics, their flexibility or elasticity by decreasing the glass transition temperature of the respective polymer. They are liquid or solid compounds with low vapour pressure, mostly esters that do not react with the polymer but interact with it only physically to produce a homogeneous system. An ideal plasticiser should be odourless, colourless, resistant against water, light, cold and heat, neutral, not toxic and it should offer low inflammability and low volatility.

Plasticisers are found in plastics, varnishes, coatings, sealants, rubbers, adhesives, they are often applied as mixture in order to optimise the properties of the resulting plastic.

Chemically most of the compounds are esters, monomeric as well as polymeric, very often of dicarboxylic acids, but also of phosphoric acid. The use of polychlorinated biphenyls as plasticisers has been stopped (Römpp 2003).

Of the several hundreds of different plasticisers the most important group are the esters of 1,2-benzenedicarboxylic acid, the phthalic acid esters. The alcohol moiety consists mostly of linear or branched alkyl chains, usually saturated, and to a lesser extent also of phenyl, cycloalkyl, or alkoxy groups. The phthalates are mainly used as softeners in polyvinyl chloride (PVC) which can contain up to 60% plasticiser, preferably the mid- to high molecular weight esters. 87% of the total production and 95% of di (2-ethylhexyl) phthalate are applied for this (UK Marine SAC 2001). Di-n-butyl phthalate is mainly used in epoxy resins and in cellulose esters and as solvent for many purposes. Dimethyl and diethyl phthalate have similar applications (Staples et al. 1997).

The annual global production of phthalates in the 1990s was approximately 4 million tonnes (Lin et al. 2003) and about one million tonnes are produced each year in Western Europe, of which

approximately 900,000 tonnes are used to plasticise PVC. The most common are: di (2-ethylhexyl) phthalate (DEHP, sometimes also referred to as DOP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP) (ECPI, 2003 a) representing more than 85% of the total volume of phthalate esters produced in Western Europe (Ecobilan 2001). Of this amount di (2-ethyl hexyl) phthalate (CAS No 117-81-7) accounts for 50% of all plasticiser usage (ECPI, 2003 b).

As the plasticisers are only physically bound they are able to migrate within the polymer and also to leave the polymer and thus enter the environment.

The properties and the distribution of the phthalates in the environment are controlled by their physical properties such as partition coefficients and vapour pressure/boiling point which are mainly determined by the length of the alkyl chain.

The determination of the water solubility of the more hydrophobic phthalates is difficult. They easily form colloidal emulsions and thin films at the air-water interface as they are slightly less dense than water. Experimental difficulties led to values for the solubility and for  $k_{ow}$  that differed by several orders of magnitude. More recent measurements gave values that agreed better with theoretically predicted values. The short chain phthalates show solubilities of up to 4000 mg/L (dimethyl phthalate), and compounds with long alkyl chains are virtually insoluble ( $< 1\mu\text{g/L}$  for C9 and longer) while the  $\log k_{ow}$  increases from 1.6 (dimethyl phthalate) to more than 8 (for C9 and longer) (Staples et al. 1997).

The better solubility and thus the higher availability of the phthalates with short alkyl chains leads to a higher toxicity. Concurrently they are available for degrading microorganisms and therefore not persistent. The compounds with higher molecular weight and a low solubility are strongly adsorbed to soil and to suspended particulate matter in water. Therefore they are not very accessible to biochemical processes leading to degradation.

The phthalates enter the environment during production and manufacture (minor pathway) and by leaching, migration and volatilisation (major pathway) during use and after disposal of the products. It is presumed that about 100 million tonnes of DEHP were present in the technosphere at the end of the 1990s (Furtmann 1994). Only two of the phthalates are regularly found in environmental samples, primarily DEHP and to a much lesser degree DBP.

There are not many data on those phthalates that are technical mixtures of isomers, mostly compounds with more than 8 C-atoms in the side chains. Especially DiNP and DiDP are economically important, but their concentrations in environmental matrices have been only very rarely determined. The quantification is difficult because the total amount is spread across several peaks, thus lowering the determination limit, and standards are not available (Lin et al. 2003).

## **1.2 FATE OF THE PHTHALATES**

### **1.2.1 PHTHALATES IN THE ENVIRONMENT**

The phthalates that are found ubiquitously are primarily DEHP and in much lower concentrations DBP and BBzP. The few reports on the occurrence of isomeric mixtures of long chain phthalates suggest that the importance of this group is underestimated. Berset and Etter-Holzer (2001) presented a list with data from the literature for DEHP concentrations in sewage sludge which ranged from almost zero to 160 mg/kg dry matter. Sewage treatment plant effluents contain very low DEHP concentrations compared to raw sewage because DEHP readily adsorbs to the solid particles of the sludge. Effluents contained only a few µg/l of DEHP, i.e. concentrations similar to those found in river water (Martinen 2003). Vikelsøe et al. (2002) reported levels of up to 2 mg DEHP/kg d.m. in soil which had been amended with a large amount of sewage sludge, and also detected DBP and nonyl phthalates in considerable amounts. McDowell and Metcalfe (2001) reported levels of up to 30 mg DEHP/kg d.m. in harbour sediment.

In river water DEHP, DBP, DiBP, and DEP were found in all samples, with DEHP as the dominant compound with concentrations of up to 10 µg/l and a mean value of ca 1 µg/l for the river Rhine (Furtmann 1994). Tan (1995) reported levels from Malaysia of up to more than 60 µg/l in river water and of up to 15 mg/kg in sediment.

Aquatic organisms bioconcentrate the phthalates. The bioconcentration factors (expressing the partition coefficient of a chemical between test organism and water at steady state, Staples et al. 1997) range from ca. 3500 for algae to 200-300 for fish indicating a higher ability of the metabolism of higher organisms for biotransformation.

Plant uptake of DEHP from soil was not observed, nor was foliar uptake or accumulation. The latter was not observed in terrestrial animals either which are able to limit bioaccumulation by metabolism.

It has been calculated that waste for landfill may contain approx. 1 kg phthalate per tonne of dry waste (0,1%), of which 1 g phthalate per ton may be leached. Thus landfills form a reservoir for decades. It is estimated that in Western Europe an annual amount of ca. 250 t of DEHP is leached from landfills into groundwater (Bauer and Herrmann 1997/ ECPI 1994).

Legal regulations for phthalates exist in Europe only for DEHP. Denmark has established a limit value of 50 mg/kg d.m. in sewage sludge while a draft for a European sewage sludge regulation sets a limit value of 100 mg/kg d.m. (Braun et al. 2001).

## **1.2.2                    DEGRADATION OF PHTHALATES**

Phthalates are mainly set free by volatilisation. In the atmosphere they are photodegraded with predicted half-lives of ca. 1 day while their photodegradation half life in water is much longer (Staples et al. 1997). Abiotic hydrolysis under environmental conditions is also insignificant. In acidic media the phthalates are so stable that a even cleanup with concentrated sulphuric acid was possible (Thurén and Södergren, 1987).

Biodegradation has been investigated often and in detail. Staples et al. (1997) gave an extensive survey of the work done up to 1997. As diesters the phthalates are hydrolysed in two steps forming the respective alcohols and phthalic acid which is further degraded either aerobically or anaerobically. Most of the reported investigations deal only with primary degradation by measuring the remaining fraction of the compound of interest, a smaller number of studies describes the ultimate degradation to carbon dioxide. The degradation rates in several environmental media and in some artificial media have been determined. Though the results vary very much they tend to indicate a reduced degradability for long chain phthalates under aerobic as well as under anaerobic conditions. Degradation seems to be limited by accessibility of oxygen. Temperature and nutrient content also influence the degradation rate.

Accordingly the half-lives vary widely, e.g. for DEHP in soil they range from a few days to several months for primary degradation. This is attributed mainly to different test conditions and different microbial communities. Less data are available for sediments.

## **1.2.3                    TOXIC EFFECTS OF PHTHALATES**

Most of the toxicological investigations were performed with rats, mice and other rodents. These animal species seem to be more sensitive to toxic effects of phthalates than humans. The critical organs are liver, kidney and testis.

The risk assessment report on DEHP as demanded by regulation 793/93 of the EU (Existing Substances Regulation) gives as consumer exposure to DEHP values in the  $\mu\text{g}/\text{kg}\cdot\text{day}$  range. Occupational exposure and exposure from medical products are in the low  $\text{mg}/\text{kg}\cdot\text{day}$  range. The NOAEL for kidney and testicular toxicity in rats is also in the low  $\text{mg}/\text{kg}\cdot\text{day}$  range while it is much higher in other animals than rodents (CSTEE 2002).

In spite of their moderate acute toxicity it is important to control the phthalates because of their high production volumes and their ubiquitous occurrence.

For some wild animals it has been found that dibutyl phthalates may act as endocrine disruptors thus influencing reproduction. These findings as well as the relevance of phthalates in this case are still under discussion. The Scientific Committee on Toxicity, Ecotoxicity and the Environment

(CSTEE) of the EU has established a tolerable daily intake value for DEHP of 37 µg/kg body weight and day and the EPA recommended a “reference dose” of 20 µg /kg\*day (Koch et al. 2003). It is estimated that these values are almost reached or even exceeded today under common living conditions.

### **1.3 DISCUSSION OF RELEVANCE**

In 1993 the Existing Substances Regulation (ESR) (Council Regulation (EEC) 793/93) was adopted, with the intention to evaluate and control the risks posed by existing chemicals. Existing chemicals, i.e. chemicals produced/ imported between March 1990 and 1994, were divided into two groups: high production volume chemicals (HPVC), produced or imported in quantities exceeding 1000 tonnes per year, and low production volume chemicals (LPVC), produced or imported in quantities between 10 and 1000 tonnes per year (ECB 2003).

The list of HPVCs includes 22 phthalic acid esters (from a total of 2704 items), both single compounds and technical mixtures with different isomers. A further 11 phthalates are compiled in the list of LPVC (from a total of 7842 items).

The HPVCs underwent a ranking process, the EURAM (EU Risk Ranking Method). The results of the EURAM formed the basis for the discussions on the selection of high priority substances for further work. These efforts have resulted up to now in four priority lists of chemicals which are expected to exhibit the greatest risk to man or the environment. A total of 141 compounds are included in these lists, and 8 of them are phthalates. Not included in the HPVC though in the priority list is di-n-octyl phthalate (CAS-No. 117-84-0). These phthalates are listed in table 1 separately from the HPVC and LPVC.

Staples et al. (1997) identified 28 major phthalates, some of which are not included in the HPVC or LPVC list of the EU (table 1).

Only six phthalates have been designated as priority pollutants by the EPA: DMP, DEP, DBP, BBzP, DnOP, and DEHP (Furtmann 1994). There are no substances among the phthalates that are classified as persistent, bioaccumulative and toxic chemicals (PBT).

In 1997 the OECD drew up a list of high production volume chemicals. This list contains those chemicals which are produced or imported at levels greater than 1,000 tonnes per year in at least one Member country. It has been compiled based upon submissions from 20 Member countries and by combining it with the European Union’s HPVC list according to EC Regulation 793/93. It is used by Member countries in choosing chemicals on which to make an initial assessment of their potential to exert a risk to man or the environment (TSG 2002). There are some differences to the list of European HPVCs and LPVCs.

The EPA listed several phthalates in method 8061A (revision 1, December 1996) which is designed to be used for phthalate analysis in various environmental media. In addition Table 1 also includes those phthalates which Furtmann (1993) identified as relevant to water based on his own experience with the analysis of numerous water samples. The limitation to aqueous samples excludes largely phthalates with long alkyl chains which are almost insoluble in water and preferably adsorbed to solids.

The drafts for ISO standards for the analysis of phthalates in water and soil contain some compounds that are not included in other methods and vice versa (ISO/CD 18856, CEN/TC 308). All methods omit the isomeric mixtures of esters of long chain alcohols in spite of their economic importance because of practical difficulties.

The six EPA phthalates are included in all lists. Additional emphasis should be put on the esters with long alkyl chains. Many of them are listed as HPVC in the European Union and they tend to readily adsorb to the organic fraction in soils and sludges where they can accumulate. In those cases where these esters have been quantified their concentrations range just behind that of DEHP (Kolb et al. 1997, Lin et al. 2003).

If the long chain phthalates cannot be included in regular testing, e.g. due to the absence of standards, they should at least be kept in mind and solid matrices should be investigated more frequently for these compounds.

Table 1 gives a summary of data mainly from European sources, but also from the American EPA. It contains those compounds that are mentioned in at least one list of industrially important chemicals or which have been found to occur in the environment. Besides the "official" lists two publications have been included that give an overview of phthalates in the environment (Furtmann 1993, Staples et al. 1997).

Table 1: Compilation of industrially and environmentally important phthalic acid esters

<b>Compound</b>	<b>CAS-No.</b>	<b>OECD</b>	<b>HPVC ECB</b>	<b>LPVC ECB</b>	<b>priority list EU</b>	<b>EPA priority pollutants</b>	<b>Furtmann Staples</b>	<b>ISO drafts water and soil</b>	<b>EPA 8061</b>
Dicyclohexyl phthalate .....	84- 61- 7	x					F	x	x
Diethyl phthalate .....	84- 66- 2	x	X			x	FS	x	x
Di- iso- butyl phthalate .....	84- 69- 5	x	X				FS	x	x
Dibutyl phthalate .....	84- 74- 2	x	X		x	x	FS	x	x
Dihexyl phthalate .....	84- 75- 3						S		x
Dinonyl phthalate.....	84- 76- 4								x
Phthalic acid, didecyl ester .....	84- 77- 5	x						x	
Butyl benzyl phthalate .....	85- 68- 7	x	X		x	x	FS	x	x
Butyl 2-ethylhexyl phthalate .....	85- 69- 8						S		
Bis (2- ethylhexyl) phthalate .....	117- 81- 7	x	X		x	x	FS	x	x
Di (2-methoxyethyl) phthalate .....	117- 82- 8			x					x
Di (2-butoxyethyl) phthalate .....	117- 83- 9			x					x
Diocetyl phthalate .....	117- 84- 0	x			x	x	FS	x	x
Ditridecyl phthalate .....	119- 06- 2	x		x			S		
Dimethyl phthalate .....	131- 11- 3	x	X			x	FS	x	x
Dipropyl phthalate .....	131- 16- 8						FS	x	
Diallyl phthalate .....	131- 17- 9	x		x			S		
Dipentyl phthalate .....	131- 18- 0			x					x
Bis(4-methyl-2-pentyl) phthalate .....	146- 50- 9								x
Bis(2-ethoxyethyl) phthalate .....	605- 54- 9								x
Di-undecyl phthalate .....	3648- 20- 2	x	X				S	x	
Di-heptyl phthalate .....	3648- 21- 3	x		x					
Diocetadecyl phthalate .....	14117- 96- 5			x					
2,2,4-Trimethyl-1,3-pentanediol 1-isobutyrate benzyl phthalate ..	16883- 83- 3	x							
Butyl isobutyl phthalate .....	17851- 53- 5						F		
Bis (2-ethylhexyl) tetrabromophthalate .....	26040- 51- 7			x					
Di- iso- decyl phthalate .....	26761- 40- 0	x	X		x		S		
Di- iso- tridecyl phthalate .....	27253- 26- 5	x	X						

Table 1 (continued)

<b>Compound</b>	<b>CAS-No.</b>	<b>OECD</b>	<b>HPVC ECB</b>	<b>LPVC ECB</b>	<b>priority list EU</b>	<b>EPA priority pollutants</b>	<b>Furtmann Staples</b>	<b>ISO drafts water and soil</b>	<b>EPA 8061</b>
Di- iso- octyl phthalate .....	27554- 26- 3	x	x				S		
Decyl hexyl phthalate .....	25724- 58- 7						S		
Dimethyl cyclohexyl phthalate .....	27987- 25- 3			x					
Di- iso- nonyl phthalate .....	28553- 12- 0	x	x		x		S		
Phthalic acid, mixed cyclohexyl and 2-ethylhexyl esters .....	68130- 49- 4			x					
Phthalic acid, mixed cetyl and stearyl esters .....	68442- 70- 6	x	x						
Phthalic acid, benzyl C7- 9- branched and linear .....	68515- 40- 2	x	x						
Phthalic acid, di- C7- 9- branched & linear esters .....	68515- 41- 3	x	x						
Phthalic acid, di- C7- 11- branched and linear alkyl esters.....	68515- 42- 4	x	x						
Phthalic acid, di- C9- 11- branched & linear alkyl esters .....	68515- 43- 5	x	x						
Phthalic acid, diheptyl ester, branched and linear .....	68515- 44- 6						S		
Phthalic acid, dinonyl ester, branched and linear .....	68515- 45- 7						S		
Phthalic acid, di- C11- 14- branched alkyl esters C13 rich.....	68515- 47- 9	x	x				S		
Phthalic acid, di- C8- 10 branched alkyl esters C9 rich .....	68515- 48- 0	x	x		x		S		
Phthalic acid, di- C9- 11 branched alkyl esters C10 rich .....	68515- 49- 1	x	x				S		
Phthalic acid, dihexyl, branched & linear esters .....	68515- 50- 4	x					S		
Phthalic acid, di- C6- 10- alkyl esters .....	68515- 51- 5	x	x				S		
Phthalic acid, mixed decyl, hexyl and octyl diesters .....	68648- 93- 1	x							
Phthalic acid, mixed decyl, lauryl and octyl diesters .....	70693- 30- 0	x							
Phthalic acid, di- C8- 10- alkyl esters .....	71662- 46- 9	x	x						
Phthalic acid, di- C6- 8 branched alkyl esters C7 rich .....	71888- 89- 6	X	x						
Hexyl 2-ethylhexyl phthalate .....	75673- 16- 4								x
Diundecyl phthalate, branched and linear esters .....	85507- 79- 5	X							
Phthalic acid, di-C16-18-alkyl esters .....	90193- 76- 3			x					
Phthalic acid, mixed decyl, lauryl and myristyl diesters .....	90193- 92- 3	X							
Phthalic acid, heptyl- nonyl, branched & linear esters .....	111381- 89- 6	X					S		
Phthalic acid, heptyl- undecyl, branched & linear esters .....	111381- 90- 9	X					S		
Phthalic acid, nonyl- undecyl, branched & linear esters .....	111381- 91- 0	X					S		



## **2. EXISTING STANDARDS OR DRAFT STANDARDS**

At first a general description of the analytical procedures in the context of selecting a favourite method for the analysis of phthalates will be given. An overview of the available different procedures for the measurement of phthalates is presented in table 2.

### **2.1 ANALYSIS**

Residue analysis in environmental matrices usually only considers the concentration of the original molecule, the monoesters of phthalic acid as products of the primary degradation step are of no interest except e.g. in medical and dietary products (Shintani 2000) though they are present in leachate from municipal wastes in concentrations several orders of magnitude higher than the diesters themselves (Jonsson et al. 2003). This group of compounds is suspected of being responsible for the toxic effects of phthalates.

Nevertheless all references cited below present methods for the determination of phthalic acid diesters. For this short review only publications from 1990 or younger (with one exception) have been evaluated.

Up to now no decision has been made on a standard method for the quantification of phthalates in solid matrices. Two drafts are available. One method is designed to detect solely DEHP among other soil and sludge contaminants (CEN/TC 292), the other method includes several phthalates (CEN/TC 308).

Most of the more detailed studies have recognized the importance of avoiding contamination of the samples in the laboratory during cleanup. The samples may be contaminated in all steps of preparation. Glassware, solvents, materials for columns like silica or alumina or simply the laboratory air may act as sources for phthalates (e.g. Lopez-Avila et al. 1990). Therefore many authors propose to heat the thoroughly cleaned glassware to 400°C and deactivate the glass surface afterwards with an appropriate solvent. In spite of all efforts Vikelsøe et al. (1998) still found DBP in significant amounts on their laboratory glass, so that they decided later on to use only new and annealed glassware for phthalate analysis (Vikelsøe et al. 2002).

Therefore regular blanks are absolutely necessary for controlling contamination. Additionally it is desirable to reduce the cleanup effort as far as possible.

The following discussion of the various steps of sample preparation concentrates on those methods that describe the handling of solid samples, therefore solid phase extraction, liquid-liquid extraction and similar will not be regarded.

## **2.2 SAMPLES**

Generally such methods have been taken into account that deal with highly polluted waters such as sewage and landfill leachate or with sludge, sediment and soil with emphasis on the latter as the focus should be on solid matrices or matrices with an elevated content of dry matter. Some methods which analyse other complex matrices like e.g. blood or milk, have been included because they represent methods that may be applicable also for the solid matrices of interest.

The methods discussed differ very much in scope. Some methods concentrate on the most important compound, DEHP (Shintani, 2000; Kambia, 2001; Sharman, 1994; Merkel and Appuhn 1996; CEN/TC 292), some methods test for 10 or more phthalates (Furtmann 1994; Berset and Etter-Holzer, 2001; Lin et al. 2003; Lopez-Avila et al. 1991, ISO 18856, EPA 8061A, CEN/TC 308). While every method includes DEHP, only one method was used to also analyse isomeric mixtures of phthalates with long alkyl chains (Lin 2003), and some methods also take at least defined single compounds of this group into account (Kolb et al. 1997, McDowell and Metcalfe 2001, Vikelsøe et al. 2002, Fauser et al. 2003).

### **2.2.1 SAMPLE PREPARATION**

If there is any preparation the sludge, soil, and sediment samples are homogenized and dried. If the samples are dried this may be done either by air-drying (Möder et al. (1998) for sludge, McDowell and Metcalfe 2001), by lyophilization which is mostly used for sludges (e.g. Merkel and Appuhn 1996, Kolb et al. 1997, Petrovic and Barceló 2000, CEN/TC 308, Marttinen et al. 2003) or by mixing with baked sodium sulphate until a free-flowing powder is obtained (Lin et al.(2003) for sediment and biota samples, CEN/TC 308). The latter method should be preferred because the risk of contamination is smaller.

### **2.2.2 EXTRACTION**

Mostly the solid samples are extracted with ethyl acetate, usually as pure solvent, or with dichloromethane alone or in mixture with other solvents . Besides these diverse mixtures of hexane with other solvents are applied for extraction. Out of these extractants dichloromethane (DCM) is

suspected of being carcinogenic to humans and it is strongly water-polluting. As part of European efforts to avoid the use of chlorinated hydrocarbons it is to be expected that the application of this solvent will be limited in the near future (Joint Committee PCB 2003). Ethyl acetate is less toxic, not carcinogenic and it is readily degradable. Hence the use of ethyl acetate seems to be more favourable than that of a chlorinated solvent. Moreover its higher boiling point makes ethyl acetate more suitable for ultrasonication if a thermostatic ultrasonic bath is not available.

The Soxhlet apparatus is only occasionally used for extraction, sometimes it is included for comparison with other methods. Preferably the extraction is performed by simply shaking the sample with solvent or by ultrasonication. Kolb et al. (1997) and McDowell and Metcalfe (2001) extracted sludge and sediment, resp., by supercritical fluid extraction (SFE) with carbon dioxide. In both cases the samples did not require further cleanup. Because SFE is not very common it is not appropriate for wide-spread application.

Accelerated solvent extraction (ASE) for phthalates has been described only once with very few data given on method performance (Ventura and Adam 2000). ASE may be worth looking into in more detail. Although the equipment is quite expensive, it is a fast method with little solvent consumption.

Microwave assisted extraction (MAE) was compared to conventional Soxhlet and ultrasonic extraction by Chee et al. (1996). MAE allows a larger sample throughput, but like ASE it is expensive and not very widespread.

### **2.2.3 CLEANUP**

As any additional step of handling increases the risk of sample contamination, further purification steps should be avoided as far as possible, but as extracts from sludge and soil samples may contain large amounts of co-extractives a purification step is often inevitable. In many cases this is done by adsorption chromatography on small columns of silica, aluminium oxide or Florisil, sometimes by (alone or preceding) gel permeation chromatography fractionating the extract according to molecule dimensions. The columns which fractionate the samples by adsorption have the advantage of requiring less solvent which, too, may be a source of sample contamination.

The choice of method depends on the kind of sample and co-extractives. Pre-packed columns of all kinds are available. As the columns are usually made of plastic (which must be avoided) glass columns are recommended. They can be baked at high temperatures like the filling material for the columns.

If a cleanup step for sludge and soil samples is omitted the crude extracts will rapidly contaminate the column for GC or LC. Berset and Etter-Holzer (2001) had to cut the retention gap after 10-15 samples to restore the initial chromatographic performance.

## 2.3 CHOICE OF INSTRUMENTATION

The most widely used separation technique is gas chromatography with capillary columns. Liquid chromatography such as HPLC is used less, one reason being the much better chromatographic resolution of single compounds with capillary columns compared to HPLC. Another reason is the common use of mass selective detectors in GC while these detectors are not used as frequently in HPLC.

Typically used are columns with a 5% phenyl methyl siloxan film, but resolution of certain pairs of phthalates is not satisfying (e.g. dihexyl phthalate and BBzP, DEHP and DCHP). Berset and Etter-Holzer (2001) recommend the use of a HT-8 column (a high temperature phase with 8% phenyl groups), which has a better performance.

Mass specific detection in conjunction with selected ion monitoring seems to be the method of choice after chromatographic separation either by GC or LC. As all phthalates except DMP form the ion with  $m/e$  149 the esters are easy to identify. With the exception of barbiturates and cholesterol derivatives almost no other compounds exhibit this fragment ion (Furtmann 1993). However the method only permits a general identification as phthalate. Further information can only be obtained from the retention time. All other detectors (FID, ECD, FT-IR) are less sensitive and lack the necessary specificity to find the right peaks among all the other peaks from the background that can be expected in samples of organically rich matrices like soils, sediments, and sludges, when cleanup is largely dispensed with.

Berset and Etter-Holzer (2001) compared EI and CI. They found that EI-MS was the most sensitive detection technique. PCI was helpful for identification due to the formation of molecular ions, and NCI gave only small molecular ion peaks and was less sensitive.

## 2.4 INTERNAL STANDARDS

Several methods (e.g. Berset and Etter-Holzer 2001, Lin et al. 2003) use isotope labelled (deuterated) phthalates as internal standards which are quite expensive. EPA method 8061A uses esters that either are not in industrial use or are esters of isophthalic acid. Though it is desirable to use internal standards that are chemically almost identical to the analytes, it may be necessary for reasons of costs to prefer other compounds. Possible internal standards for early eluting phthalates are dimethyl isophthalate (Bauer and Herrmann 1997) or diallyl phthalate (Kolb et al. 1997, Furtmann 1993, ISO18856). Dioctyl isophthalate may be preferred for later eluting compounds.

## **2.5 LIMITS OF DETECTION/DETERMINATION, STANDARD DEVIATIONS**

The data for limits of detection, limits of determination, and limits of quantification vary considerably. It is not always explicitly mentioned whether or not the values were obtained from real samples. Determined limits are generally higher in the analysis of highly polluted samples and for those phthalates that are regularly found as background. The values range from ca. 5 µg/kg to ca. 50 µg/kg, in cases with background problems the values are up to 800 µg/kg (McDowell and Metcalfe 2001).

Although some authors give no data on recovery it can be assumed that in these studies it was as satisfactory as demonstrated in others. Only with the phthalates with short side chains the recovery is sometimes lower. All the published figures are within the range that is common in residue analysis. The data on precision are not complete either and often they do not refer to real samples so that a comparison is not possible.

Table 2 gives a synopsis of several analytical methods for the determination and quantification of phthalic acid esters. It is divided into multi-substance methods that analyse phthalates among other compound classes and phthalate methods. Emphasis has been put on environmental matrices, other matrices such as blood or milk are included as examples of related samples having a similarly complex matrix.



Table 2: Compilation of methods for the quantitative determination of phthalic acid esters

matrix	compounds	extraction	cleanup	Method	% recovery	Analytical quality	reference
MULTI METHODS							
-effluent, landfill leachate, sewage, - sludge	DMP, DEP, DBP, BBzP, DEHP, DOP, PAH, dinitro toluene	- DCM - sonication/DCM	Florisil	GC/MS HP-5	---	LOQ: 1 µg/L (phthalates)	Martinen et al. (2003)
waste water, sludge	DPP, DBP, BBzP, DEHP, DnOP, DnNP, nonyl phenols, LAS	shaking with DCM/HCl	---	HRGC/MS DB-5MS		3-9 ng/L, DBP 30 ng/L, DEHP 25 ng/L	Fausser et al. (2003)
sewage sludge	anionic and non-ionic surfactants, BPA, DEP, DBP, DEHP	Ultrasonic extr. MeOH/DCM	concentrate, redissolve in water, SPE (C18)	LC-APCI-MS and LC-NI-ESI-MS, RP18 column	87%(DEP), 91%(DBP), 78%(DEHP)	LOD (instr.): 0,5 ng (DEP), 1,0 ng (DBP), 1,5 ng (DEHP) LOD (sludge): 15 ng/g (DEP), 25 ng/g (DBP), 50 ng/g (DEHP)	Petrovic and Barceló (2000)
sewage sludge, sediment	DBP, DEHP, fatty acids, non-ion. surfactants, carbohydrate derivatives	SPME (carbowax) from aqueous suspension of dried samples	---	HPLC/ESI/MS RP8 column	---	LOD 50 ng/mL (DEHP), 30 ng/mL (DBP)	Möder et al. (1998)
Air	DEP, DBP, BBzP, DCP, DEHP, Phosphate esters	adsorption on charcoal	extraction with toluene/ultrasonication	GC/MS HP-5	68-100%	MDL: between 0,11 µg (DEP) and 0,51 µg (BBzP)	Otake et al. (2001)

Tab. 2 (continued)

matrix	compounds	Extraction	cleanup	method	% recovery	Analytical quality	reference
- water, STP influent, STP effluent, liqu. manure, - sewage sludge, sediment	BPA, BPF, DBP, BBzP, DEHP	- water: steam distillation/solvent extraction - dried sediment: soxhlet (chx/ethyl acetate)	- ---  - GPC and silica column	GC/MS DB-XLB	82-110 % (water)  71-117% (sediment)	detection limit: 0,02-0,03 µg/L in water, 0,02-0,05 mg/kg d.m. in sediment	Fromme et al. (2002)
soil sludge	DBP, DPeP, BBzP, DEHP, DOP, DNP, DiNP, nonylphenol	shaking with DCM	---	HRGC/MS DB5-MS	DBP:ca.85% BBzP:ca.80% DEHP ca. 60%	lim. determ., low contam./ soil, 0,1-1µg/kg (DBP: 1,5µg/kg), high contam. 0,8-1 µg/kg (DBP 40 µg/kg, DiNP 10 µg/kg) sludge (low contam.): 8-60 µg/kg	Vikelsøe et al. (2002); NERI Report 268 (1999)
PHTHALATE METHODS							
surface water	DMP, DEP, DBP, BBzP, DEHP, DOP, DPP, DMPP, BMPP, DCHP	C18 cartridge	aluminium oxide (only when necessary)	GC/MS HP-1	91-108%	Detect. lim. 0,01-0,02 µg/L, 0,03 µg/L for BBzP Determ. lim. 0,02-0,03 µg/L, 0,04 µg/L for BBzP, 0,05 µg/L for DEHP	Furtmann (1994)
- aqueous solution - soil	DEP, DEHP	- shaking with n-hexane - ultrasonic extr. ethyl acetate	- none  - centrifugation	- HPLC/UV C <sub>18</sub> column - GC/FID BP5	-60%(DEP), 67%(DEHP) -94%(DEP), 73%(DEHP)	- detec. lim. 1 µg/mL  - detec. lim. 0,1 µg/mL extract	Cartwright et al. (2000)

Tab. 2 (continued)



matrix	compounds	extraction	cleanup	method	% recovery	Analytical quality	reference
- water - suspended particulate matter (SPM)	DMP, DEP, DBP, BBzP, DEHP, DOP	- SPE C8 column  - shaking with ac/water/hx	- none  - centrifugation	GC/ECD GC/MS Sil-5	water (spike level 300-500 ng/L) 83-97% SPM: 82-93% except DEP (67%), DMP (26%)	detect. lim.: water: 0,01 µg/L (DMP, DEP, BBzP) 0,1 µg/mL (DBP, DEHP, DOP) ; SPM: 0,01-0,1 mg/kg, except DEHP: 1 mg/kg	R. Ritsema et al. (1989)
Bioreactor leachate, fractions of household wastes	DMP, DEP, DEHP, DBP, BBzP	Leachate: shaking with hx/diethyl ether Solids: ultrasonication with diethyl ether/hx	Filtration through alumina	GC/MS DB-1			Bauer, Herrmann (1997)
Sewage sludge	DMP, DEP, DBP, BBzP, DEHP (separation from PCB, PAH, pesticides)	a) Ultrasonication (DCM) b) Soxhlet (DCM)	aluminium oxide followed by Florisil	GC/ECD	98-103%	---	Zurmühl (1990)
- soil - plants	DBP, BBzP, DEHP	- shaking with ac/hx - Ultrasonication (ac/hx)	- GPC  - GPC, silica column	HPLC/UV C <sub>18</sub> column	- 90-95%  - 80-90%.	- detect. lim.: 0,005 mg/kg  - detect. lim.: 0,74 mg/kg d.m. (DEHP), 3,4 mg/kg d.m. (DBP), 1,0 mg/kg d.m. (BBzP)	Müller, Kördel (1993)
sewage sludge	DBP, BBzP, DEHP, DiNP, DiDP	SFE (CO <sub>2</sub> ), shaking with ethyl acetate	--- centrifugation	GC/MS HP5	85-100% for SFE and shaking	detect. lim. between 0,005 mg/kg d.m. (DBP) and 0,062 mg/kg d.m. (DiDP); LOQ: 0,015 and 0,212, resp.	Kolb et al. (1997)

Tab. 2 (continued)

matrix	compounds	extraction	cleanup	method	% recovery	Analytical quality	reference
sewage sludge	16 phthalates (same as EPA 8061A)	Shaking of dried sample with ethyl acetate	centrifugation	GC/EI/MS GC/CI/MS (HT-8 column)		LOD: 0,08 µg/mL (DEHP, DiBP) to 3,8 µg/mL (bis(methoxyethyl)phthalate) for standards 10 µg/kg d.m. (DMP) to 632 µg/kg d.m. (BBzP) for sludge samples	Berset, Etter-Holzer (2001)
- water - sediment	DMP, DEP, DBP, DiBP, DEHP, DOP, DOiP	- DCM  - multi step solvent extraction with DCM/petroleum ether, acetonitrile	Florisil	GC/FID SPB-608	- 60-80%, DMP 37% - 40-80%, DMP 26%	Detec.lim. (S/N 3/1): 0,01 ng (DMP, DEP, DBP), 0,05 ng (DOP), 0,1 ng (DEHP, DiBP), 0,4 ng dioctyl isophthalate	Tan (1995)
sediment, biota	DMP, DEP, BBzP, DBP, DEHP, DnOP, 5 isomeric mixtures	Dried samples: ultrasonication (DCM/hx)	Alumina  Alumina and Florisil	HPLC/ESI/MS C <sub>8</sub> column GC/MS, DB-5	71-106% (individual compounds), 89-102% (mixtures)	0,3-1,1 ng/g (single comp./GC), 3,3 ng/g (DEHP/GC), 0,5-4,2 ng/g (LC) no reproducible results for mixtures with GC, 0,5-3,0 ng/g with LC	Lin et al. (2003)
sediment	DEP, DBP, BBzP, DEHP, DiNP	SFE (CO <sub>2</sub> )	Silica column, elution with DCM, change to hexane	GC/MS DB-5	85% (DBP), 88% (DEHP)	DEHP 0,81, DBP 0,30, DEP 0,18, BBzP 0,11, DiNP 0,09 [µg/g] for 0,2 g sample	McDowell, Metcalfe (2001)
- water leachate, sludge, - sediment, soil	16 phthalates	- separatory funnel, C8 and C18 membrane disks - soxhlet (hx/ac) ultrasonication (DCM/ac)	Florisil, aluminium oxide (recommended), removal of sulfur	GC/ECD GC/FID; DB-5, DB-1701	a)	2-10 µg/L (1 L sample, 2 mL final volume), 6-60 µg/kg (30 g sample, 2 mL final volume)	Lopez-Avila et al. (1991)

Tab. 2 (continued)

matrix	compounds	extraction	cleanup	method	% recovery	Analytical quality	reference
- sewage sludge, - soil	DEHP	ac/petroleum ether/NaCl solution	- Florisil, aluminium oxide ---	GC/FID GC/ECD		LOQ: 1 mg/kg d.m (sludge), 0,1 mg/kg (soil)	Merkel, Appuhn (1996)
soil, sediment	DEP, DBP, BBzP, DEHP	ASE (hx)	---	GC/MS DB-5	“complete”	---	Ventura, Adam (2000)
soil, sediment	DMP, DEP, DAP, DBP, BBP, DEHP	microwave assisted with ac/hx	centrifugation	GC/MS HP-5	70-91%	---	Chee et al. (1996)
blood products	DEHP (and mono-EHP)	SPE	---	HPLC (C <sub>18</sub> column), UV	98-102%	---	Shintani (2000)
- parenteral nutrition, - plasma	DEHP	vortex with NaOH and hexane as above after protein precipitation	- centrifugation - centrifugation	HPLC (C <sub>18</sub> column), UV		LOQ: 20 ng/mL for spiked samples	Kambia (2001)
milk and milk products	DEHP	Shaking with hx/MeOH/KOH	SEC on bio beads (fatty samples)	GC/MS CPSIL5CB	100±7%	---	Sharman et al. (1994)
OFFICIAL METHODS OR DRAFTS							
water	11 phthalates	SPE (C18)	Alumina if necessary	GC/MS, 5% phenyl methyl siloxan	75-110%, 60-75% (DOP, DUP)		ISO 18856 (DRAFT) 2001
sludge	DEHP, PAH, NPE, LAS	ultrasonic bath (DCM)	Dried and concentrated	GC/MS, HP-5	70 - 130 % (required)	for DEHP: 0,5 mg/kg d.m. (required)	NERI 2003
groundwater, leachate, sludge, sediment, soil	16 phthalates	Shaking with DCM, or C18 disk DCM/ac	If necessary: methods 3610 (alumina), 3620 Florisil), 3640 (GPC), or 3660 (sulfur removal)	GC/ECD			EPA method 8061 A

Tab. 2 (continued)

matrix	compounds	extraction	cleanup	method	% recovery	Analytical quality	reference
waste water, solid waste, sediment, soil	semivolatile organics incl. 6 EPA phthalates	EPA methods 3510 (separatory funnel), 3520 (cont liq.-liq. Extraction), 3540/ 3541 (Soxhlet), 3550 (ultrason.), or 3580, (dilution with solvents)	If necessary: GPC (method 3640)	GC/FT-IR DB-5  GC/MS DB-5 or equivalent		Identification limit 2,5-5 µg/L  Estimated quant. limits: 10 µg/l (ground water) 660 µg/kg (low contamination)	EPA method 8410  EPA method 8270
sludge, sediment, soil	11 phthalates	Shaking with ethyl acetate	alumina	GC/MS, 5% phenyl methyl siloxan			CEN/TC 308/WG 1/TG 4 N 0052

- a) Water (spike level 10 µg/L): separation funnel: 73-110%; C<sub>18</sub> disk 67-98%. Loamy sand (spike level 1 µg/g): soxhlet 54-135%, sonication 63-112%. For further recoveries from Florisil and alumina with and without interferences see reference (Lopez-Avila et al. 1991).

## 2.6 PHTHALATES WITH LONG SIDE CHAINS

Largely unsolved remains the problem of phthalic acid esters with isomeric mixtures of long chain alcohols. Especially the C9- and C10- but also the C11-phthalates are economically and technically important. These compounds are separated by GC to a pattern of different peaks whose assignment to certain compounds is not possible because the retention time windows of the single groups overlap and the EI usually gives no molecular ions by which the peaks could be identified.

This group of phthalates is rarely included in investigations. Kolb et al. (1997) analysed C9- and C10-isomeric mixtures, Braun et al. (2001) proposed a method for their rough quantitation. McDowell and Metcalfe (2001) included C9-phthalates but did not detect them. Vikelsøe et al. (2002) determined C9-phthalates in concentrations comparable to those of DBP but they were not part of further considerations .

Kolb et al. (1997) reported that though GC did not completely separate the isomers of DiNP and DiDP, an assignment of the single peaks to the compounds groups is clearly possible in the scan mode with the spectra library NBS 54 K 1.

As the total amount of isomers is spread over many compounds the determination limit of mixtures is higher than for single compounds. Braun et al. (2001) tested a method for their determination and stated that they were not (yet) found in most of environmental samples.

Lin et al. (2003) used HPLC for the separation of these mixtures, which does not resolve the isomers, and they used ESI to produce molecular ions and thus got information about the identity of the respective molecules. Nevertheless HPLC does not have as high a resolution power as GC, therefore it will be disadvantageous for the other phthalates.

However, if the peak patterns are usually the same for a commercial plasticiser or at least company specific, it may be possible to use a few of the larger peaks for identification and quantification as done e.g. in case of the PCB.

In spite of the mentioned restraints GC should be the method of choice because of its much better resolution power for the phthalates with shorter alcohol chains. A mass selective detector should be recommended as detector because it gives some specificity by the detection of the ion with  $m/e$  149 thus eliminating most of the background and it is quite common in many laboratories.

### 3. EVALUATION OF A DRAFT FOR A HORIZONTAL STANDARD

A straightforward and low cost method with common instrumentation should meet a number of criteria. Some of the points which have to be taken into account are: use of ethyl acetate as low toxic solvent, extraction only by shaking or ultrasonication, a single step cleanup to protect the analytical column, and detection with GC/MS. In addition the method should be validated for a variety of phthalates in order to have also the less frequent compounds under observation.

Methods that meet these criteria are compiled in Table 3. The mentioned criteria are fulfilled by the methods by Kolb, Berset, Chee, and Ventura who dropped all cleanup steps and by Bauer and CEN/TC308 who added a column cleanup. They all used ethyl acetate or n-hexane (also as mixture with ethyl ether) and GC/MS. If dichloromethane is accepted as solvent in connection with the complete omission of cleanup the Danish methods also meet the mentioned criteria more or less.

The method by Ventura has the disadvantage that the description is not very exhaustive. The methods by Fauser, Vikelsoe and CEN/TC292 are all based on the same Danish source. While Fauser and Vikelsoe included several phthalates the method of CEN/TC 292 includes only DEHP. These methods have the disadvantage that they require relatively large volumes of DCM while the others use smaller volumes of less toxic solvents. The method by Berset is very similar to CEN/TC308, but due to the fact that it omits further cleanup of the samples it is necessary to shorten the GC column after every 10-15 sample injections which seems not to be practicable for routine use. It cannot easily be decided whether or not only a pure solvent should be taken instead of a mixture. If the solvent needs purification, a single solvent would be more convenient.

The extraction times are mostly in the range of 1-2 h except for the microwave method of Chee et al. (1996) and the CEN/TC308 draft method.

Regarding these considerations the CEN/TC308 method seems to fulfil the criteria discussed above more than the other methods mentioned in table 3. However, the list of proposed phthalates should be revised to include some of the most important high production volume phthalates (DiNP, DiDP).

Tab. 3: Selected methods

author/ method	matrix	method	solvent	volume [mL]	time [h]	cleanup	measure- ment
Fauser (2003)	sludge	shake	DCM	100	4	-	GC/MS
Vikelsøe (2002)	soil	shake	DCM	100	1	-	GC/MS
Bauer (1997)	waste	ultrasonica- tion	hx/ ether	30		alumina	GC/MS
Kolb (1997)	sludge	shake	EA	20	1,5	-	GC/MS
Berset (2001)	sludge	shake	EA	7	1	-	GC/MS
Chee (1996)	soil, sediment	microwave	ac/hx	30	0,2	-	GC/MS
Ventura (2000)	soil, sediment	ASE	hx	50	1,5	-	GC/MS
CEN/TC292	sludge	ultrasonic.	DCM	150	2	-	GC/MS
CEN/TC308	soil, sludge, sediment	shake	EA	20	0,3	alumina	GC/MS

## **4. CRITICAL POINTS AND RECOMMENDATIONS**

### **4.1 Prenormative investigations**

When preparing a standard method some general consideration have to be made concerning the relevance of matrices and the distribution of the target compounds.

#### **■ Partitioning behaviour of phthalates to SPM**

As the phthalates tend to adsorb to solid particles (Ritsema et al. 1989), it is necessary to investigate the amount, size, size distribution, and composition of SPM and the dependence on these parameters of the partitioning of the phthalates between the solid and the aqueous phase. The different solubilities of the phthalates result in a different partition behaviour.

#### **■ The role of suspended particles as carrier**

In the effluent of STPs the phthalates are due to their mostly low solubility in water adsorbed to suspended fine particles and thus transported into the environment. If sludge treated soil is eroded by surface water this material could trigger endocrine effects in aquatic organisms if deposited into small streams.

#### **■ Influx of phthalates into the environment**

The range of total flow of phthalates from the production into the environment via sewage water, sewage sludge, composts, and related sources has to be evaluated. The effective concentration of the phthalates also depends on the prevailing conditions in the solid matrix. The presence or absence of oxygen (aerobic/anaerobic), pH, and other parameters of the matrix will influence the degradation and thus the effective concentrations. Partition coefficients are a measure for the availability of phthalates for degradation processes.

#### **■ Estimation of the endocrine effects and environmental risk, limit values**



The transfer of phthalates from sewage and effluents of STPs to the soil and the effective concentrations in soil has to be estimated for evaluating the environmental risk. Also the occurrence of endocrine effects has to be considered and the concentration at which they might be observed. This is a preliminary activity for the assessment of limit values. It has especially to be checked how far the endocrine effects that are observed in aquatic environments are also relevant in terrestrial environments.

## 4.2 Method

- Investigation of further matrices

The proposed method has been applied mainly for sewage sludge. Extended investigations of other matrices are still lacking. Therefore fundamental work is inevitable to gain also information on the behaviour of different soils and sediments, biowastes and other related matrices.

- Validation of the extracting agent

Though the application of ethyl acetate as extracting agent seems to be a good choice from a technical and toxicological point of view its applicability has to be validated. Other solvents have to be checked and eventually validated which reduce the amount of co-extractives with matrices like e.g. biowastes and composts.

- Designation of target compounds

As the use pattern of phthalates changes by the time, e.g. due to modified technical demands, it is necessary to have data as actual as possible as a basis for the designation of relevant phthalates. Screening analyses of the matrices mentioned above are needed to determine the current inventory of phthalates. This is a prerequisite for the selection of those compounds that shall be included in the method.

- A method for isomeric mixtures is still lacking

The proposed method does not include isomeric mixtures of long chain phthalic acid esters. Their detection limits are much higher than those for short chain single compounds because the

total detector signal is spread over many single peaks. As the isomeric mixtures are becoming more important (in recent years), the method has to be adopted to these compounds. It may also be necessary to develop a separate method for them.

■ Choice of internal standards

Though the deuterium labelled phthalates are the optimal internal standards, they are very costly. Several other compounds have been used, too. For a broad application of horizontal standard methods it may be advantageous to have less expensive validated internal standards and also method performance standards. Table 4 compiles the compounds from the references cited in table 2. Some of these potential standard compounds should be checked thoroughly, especially the isophthalates because they resemble the target compounds very much.

Table 4: Internal and method performance standards

<b>compound</b>	<b>CAS No.</b>	<b>reference</b>
DMP- D <sub>4</sub>	93951-89-4	Lin et al. 2003
Dimethyl isophthalate	1459-93-4	Zurmühl 1990 Bauer and Herrmann 1997
DEP-D <sub>4</sub> (P.S.)	93952-12-6	Lin et al. 2003
Diallyl phthalate	131-17-9	Kolb et al. 1997 ISO CD 18856
DBP-D <sub>4</sub>	93952-11-5	Berset and Etter-Holzer 2001 Otake et al. 2001 Fromme et al. 2002 Lin et al. 2003 ISO CD 18856 CEN/TC 308
BBzP-D <sub>4</sub> (I.S., P.S.)		Vikelsøe et al. 1998 Fromme et al. 2002
di- n heptyl phthalate	3648-21-3	Kambia et al. 2001
DnOP-D <sub>4</sub> , (DEHP-D <sub>4</sub> )	93952-13-7	Vikelsøe et al. 1998 Berset and Etter-Holzer 2001 Otake et al. 2001 Fromme et al. 2002 Lin et al. 2003 CEN/TC 308
Benzyloxy benzoate (I.S.) Diphenyl phthalate (P.S.) Diphenyl isophthalate (P.S.) Dibenzyl phthalate (P.S.)	120-51-4 84-62-8 744-45-6 523-31-9	EPA 8061A
Diethyl terephthalate 9-bromophenanthrene	6422-86-2 ? 573-17-1	Bauer and Herrmann 1997

The name dioctyl phthalate is sometimes used for di-n-octyl phthalate and for di (2-ethylhexyl) phthalate. In the table it is not differentiated between these compounds.

## **5. DRAFT STANDARD (CEN TEMPLATE)**

A first raw proposal for a draft standard is in preparation and will be discussed in the ad hoc group Phthalates in the TG 4 of CEN TC 308 WG 1 (see Doc N 0052).

## 6. ACRONYMS

The short cuts for the phthalate esters are not standardized. In this text the proposals of Furtmann (1993) were followed where possible, the other variants are added in brackets.

### Phthalates

BMPP (BiBP): butyl-iso-butyl phthalate, butyl-methylpropyl phthalate

BBzP (mostly BBP): butyl benzyl phthalate

DBP: dibutyl phthalate

DCHP (DCP): dicyclohexyl phthalate

DEHP (occasionally DOP): di (2-ethylhexyl) phthalate

DEP: diethyl phthalate

DiBP: see DMPP

DiDP: di-isodecyl phthalate

DiNP: di-isononyl phthalate

DMP: dimethyl phthalate

DMPP (DiBP): di-isobutyl phthalate, di-methylpropyl phthalate

DNP (DnNP): di-n-nonyl phthalate

DOP (DnOP): di-n-octyl phthalate, see also DEHP

DPeP: dipentyl phthalate

DPP: dipropyl phthalate

DUP: diundecyl phthalate

### Miscellaneous

ac: acetone

ASE: accelerated solvent extraction

BPA: bisphenol A

BPF: bisphenol F

chx: Cyclohexane

CI: chemical ionisation

d.m.: dry matter

DCM: dichloromethane

EA: ethyl acetate

EI: electron impact ionisation

ESI: electro spray ionisation

FT-IR: Fourier transform infrared spectroscopy

GPC: gel permeation chromatography

hx: n-hexane

I.S.: internal standard

LAS: linear alkylbenzene sulphonates

LOD: limit of detection

LOQ: Limit of quantitation

MAE: microwave assisted extraction

MDL: method detection limit

NCI: negative chemical ionisation

NOAEL: No observed adverse effect level

NPE: nonylphenols ethoxylates

PAH: polycyclic aromatic hydrocarbons

PCB: polychlorinated biphenyls  
PCI: positive chemical ionisation  
P.S.: method performance standard  
SEC: size exclusion chromatography  
SFE: supercritical fluid extraction  
SPM: suspended particulate matter  
STP: sewage treatment plant

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