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# Analysis of mono- and diesters of *o*-phthalic acid by solid-phase extractions with polystyrene–divinylbenzene-based polymers

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## Abstract

Retention mechanisms of an unmodified and a hydroxylated polystyrene–divinylbenzene polymer were studied by solid-phase extraction of *o*-phthalic acid and some of its mono- and diesters from purified water and then analysing by GC–MS. The monoesters and phthalic acid were retained only when protonated (i.e. acidified with HCl to pH 0.9). Of all elution solvents tested, ethyl acetate gave the best overall recoveries (61–89%) with both polymers. Applicability to complex matrixes (e.g. acidogenic landfill leachates) was examined by introducing a washing step with acetone in acidified water (pH 0.9) to eliminate volatile fatty acids (C<sub>2</sub>–C<sub>6</sub>) from the cartridge. Finally, the method was tested on real samples. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Retention mechanism; Poly(styrene–divinylbenzene); Phthalates; Fatty acids

## 1. Introduction

Chemically, phthalates are di- and monoesters of *o*-phthalic acid. The diesters are widely used in various products, and it is well known that they are contaminants in the environment [1–3]. For example, these compounds have been found for decades in landfill leachates [1,4], whereas the presence of monoesters and phthalic acid in this type of medium is a more recent discovery [5]. Analysis of phthalic acid diesters in various aqueous media has been done using liquid–liquid extraction (LLE) with hexane [6–8], diethyl ether [5,9], dichloromethane [10], or mixtures of solvents such as hexane and diethyl ether [11] and GC together with electron capture detection (ECD) or flame-ionisation detection (FID), or mass

selective (MS) detection. GC–MS is useful in that it combines the high resolving power of GC with the selectivity of MS. Also, development of solid-phase extraction (SPE) procedures has provided an efficient new tool for environmental analysis that enables selective extractions, that is, samples are retained on the adsorbent and tailored washing procedures remove impurities from the final extracts. Initially, the adsorbents most widely used in SPEs were silica-based polymers. Holadová and Hajšlová [6] employed silica-based C<sub>18</sub> and C<sub>8</sub> to extract phthalic acid diesters from drinking water and ethyl acetate as the elution solvent. More recently, organic polymers such as crosslinked polystyrene–divinylbenzene (PS–DVB) have been developed. Davi et al. [12] found that a wide range of organic compounds (including phthalic acid diesters) in drinking and surface water could be adsorbed on a hydroxylated PS–DVB cartridge and then eluted with acetone–ethyl acetate. Suzuki et al. [13] also

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used hydroxylated PS–DVB to analyse di- and monoesters of phthalic acid in acidified river water.

The objective of the present study was to examine the use of SPE with an unmodified and a hydroxylated PS–DVB polymer to remove phthalates from media that also contained high concentrations of volatile fatty acids. This was done, since it is known that biological processes increase the levels of fatty acids (especially acetic and butyric acid) and ethanol in acidogenic landfills [14].

We chose to use the PS–DVB polymers in the tests, because the loading properties of organic carbon are superior to those of silica-based adsorbents. The following compounds were analysed: dimethyl, diethyl, dibutyl, butylbenzyl, and di(2-ethylhexyl) phthalate (respectively designated DMP, DEP, DBP, BBP and DEHP), and their corresponding monoesters monomethyl, monoethyl, monobutyl, monobenzyl, and mono(2-ethylhexyl) phthalate (MMP, MEP, MbutP, MbenzP and MEHP, respectively), as well as *o*-phthalic acid. The retention mechanisms were compared with LLEs.

## 2. Experimental

### 2.1. Chemicals and materials

As solvents we used acetone, acetonitrile, diethyl ether, ethyl acetate, dichloromethane, hexane, methanol, toluene and *tert*-butylmethyl ether (TBME), which were all 99.8% pure and were obtained from Sigma–Aldrich (Stockholm, Sweden). The diesters and phthalic acid (all >98% pure) were purchased from Merck Eurolab (Stockholm, Sweden), and the monoesters were synthesised [15] with a purity of 69–98%. SPEs were carried out with two hypercrosslinked PS–DVB cartridges packed with Isolute 101 and Isolute ENV+ (IST, UK; 200 mg), the latter of which is a hydroxylated moiety; both were purchased from Sorbent (Stockholm, Sweden). The internal standard (I.S.) 3-bromobenzoic acid (3-BrBA; Merck Eurolab, Stockholm, Sweden) and the synthesised I.S. *n*-didecyl phthalate (DDP, a gift from Neste Oxo, Stenungsund, Sweden), respectively, designated I.S.1 and I.S.2, were both >98% pure. The purity of the synthesised phthalates was shown

by GC–FID. The standard solution was prepared by dissolving the analytes in acetone (1.5–5.1  $\mu\text{g}/\mu\text{l}$ ) and was stored in a freezer ( $-18\text{ }^\circ\text{C}$ ). Since diesters are present as background contaminants, blanks were analysed to ensure that the results were accurate. The volatile fatty acids (>98% purity) were purchased from Merck Eurolab.

### 2.2. Solid-phase extraction

The cartridges were solvated with 5 ml of ethyl acetate followed by 5 ml of methanol and conditioned with 5 ml of acidified water before introducing samples. As sample matrix, and for preparing the washing solutions, we used purified, organic-free Milli-Q (Millipore) water containing 0.28 *M* HCl, which gave a pH of 0.9. The samples were acidified to prevent ionisation of the monoesters and phthalic acid. Individual cartridges were loaded with 3.0–8.6  $\mu\text{g}$  of each analyte, along with 4.0  $\mu\text{g}$  of 3-BrBA as I.S., and were subsequently vacuum dried for at least 30 min before elution. Two 1.0-ml portions of each of the solvents tested were used to elute the phthalates, and the cartridges were dried between the solvent additions. All flow-rates were less than 2 ml/min. The collected extracts were evaporated with nitrogen to 200  $\mu\text{l}$  at ambient temperature, after which 10  $\mu\text{g}$  of DDP was added as a second I.S. Finally, the extracts were silylated with 40  $\mu\text{l}$  of reagent and analysed by GC–MS. The derivatising reagent was prepared from TMCS (chlorotrimethylsilane) and BSTFA [bis(trimethylsilyl)-trifluoroacetamide] in pyridine (1:10:10). The derivatised phthalates were analysed as silylesters by GC–MS in the selective ion monitoring (SIM) mode. The mass fragments used for quantification and qualification are presented in Table 1, and a SIM chromatogram of the phthalates is shown in Fig. 1.

Removal of volatile fatty acids from the plain PS–DVB cartridge was tested by performing a washing step before eluting the phthalates. Ethanol and acetic, propionic, isobutyric, *n*-butyric, isovaleric, *n*-valeric and isocaproic acids (410–880  $\mu\text{g}$  each) in 5 ml of acidified water were added to the cartridges. The washing tests consisted of three 2.5-ml portions of identical washing solutions consisting of 0–20% acetone in acidified water. The same

Table 1

Retention times and mass fragments ( $m/z$ ) used for SIM analysis of the silylated phthalates; the most abundant  $m/z$  were used for quantification

Compound	Abbreviation	Retention time (min)	Mass fragments $m/z$	Proportions of the fragments
Dimethyl	DMP	9.79	163, 194, 133	100/7/6
Monomethyl	MMP	13.28	237, 163, 221, 252	100/59/11/3
Diethyl	DEP	13.62	149, 177, 222	100/26/2
Monoethyl	MEP	14.47	251, 223, 149, 221	100/86/40/36
Phthalic acid	PA	15.26	147, 295, 221,	100/26/7
Monobutyl	MButP	17.77	223, 221, 149, 279	100/47/40/10
<i>n</i> -Dibutyl	DBP	20.31	149, 223, 205	100/5/4
Mono(2-ethylhexyl)	MEHP	22.65	221, 223, 149, 239	100/65/47/26
Monobenzyl	MBenzP	24.30	91, 179, 222	100/61/47
Butylbenzyl	BBP	26.60	149, 91, 206, 238	100/56/25/4
Di(2-ethylhexyl)	DEHP	29.08	149, 167, 279	100/29/14
Didecyl	DDP (I.S.2)	36.60	149, 307	100/9
3-Brombenzoic acid	3-BrBA (I.S.1)	10.46	259, 257	100/98

solutions were used to test for losses of the phthalates during the washing procedure. The phthalates were eluted with two 1-ml portions of ethyl acetate.

Acid landfill leachates were used after lowering the pH to 0.9 with HCl and then spiking with phthalates. The analytes were adsorbed on solvated and conditioned plain PS–DVB cartridges, which were subsequently dried for 1 h and washed with two portions of 5% acetone in water (pH 0.9). Elution and detection of the phthalates were performed as described for the purified water.

### 2.3. Liquid–liquid extraction

For LLEs, 5-ml water samples were prepared as for the SPEs and then extracted for 2 min with 2 ml of solvent. The organic phases were dried with  $\text{Na}_2\text{SO}_4$ , and further evaporated and analysed using the same chromatographic parameters as for SPE. The results are presented in Table 3.

### 2.4. Instrumental parameters

#### 2.4.1. Phthalates

The phthalates were analysed with a Hewlett-Packard 6890 GC connected to a Hewlett-Packard 5973 MS system, with the latter in the SIM mode. The dwell time was 100  $\mu\text{s}$ , and the electron multiplier voltage was set at 1575 V. Pulsed splitless autoinjection (1  $\mu\text{l}$ ) was done on a BPX5 5% phenyl column (30 m $\times$ 0.25 mm I.D., 0.25  $\mu\text{m}$  film thickness; SGE, Scantec, Stockholm, Sweden). Helium was used as carrier gas at a constant flow-rate of 1.2 ml/min. Temperature programming was 100  $^\circ\text{C}$  initially, increasing by 5  $^\circ\text{C}/\text{min}$  to a final temperature of 290  $^\circ\text{C}$ . The injector, interface, ion source, and quadrupole temperatures were 250, 280, 230 and 150  $^\circ\text{C}$ , respectively. The quantification limit for the phthalates was  $180 \pm 80$  ng/l, corresponding to  $0.9 \pm 0.4$  ng in the samples performed with purified

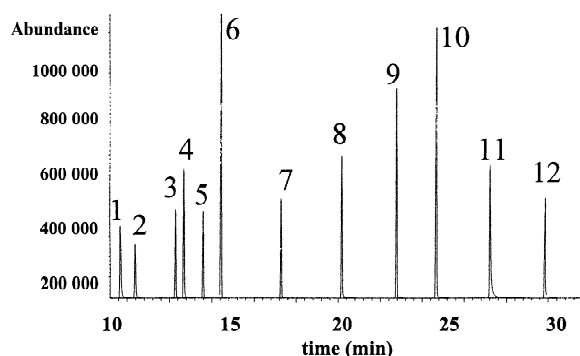


Fig. 1. Total ion current chromatogram of the selected  $m/z$  fragments chosen for SIM analysis of the phthalates: (1) DMP, (2) 3-BrBA (I.S.1), (3) MMP, (4) DEP, (5) MEP, (6) PA, (7) MbutP, (8) DBP, (9) MEHP, (10) MbenzP, (11) BBP, and (12) DEHP.

water. Real samples increased the limit of quantification to approximately 1 µg/l.

#### 2.4.2. Volatile fatty acids

The volatile fatty acids were analysed by GC–FID as follows: 400 µl of the water sample was acidified with 40 µl of 25% formic acid containing 52 µg of crotonic acid as I.S., and a 1-µl aliquot was injected with a split flow of 30 ml/min on a BP21 polyethylene glycol column (30 m×0.32 mm I.D., 0.25 µm film thickness; SGE, Scantec). The temperature program was 80 °C for 0 min, thereafter increasing by 3 °C/min to 175 °C. Helium was used as carrier gas and the analyses were performed at a constant pressure of 83kPa (1.9 ml/min). The quantification limit for the fatty acids was 7.9±1.3 mg/l, corresponding to 39±6 µg in the samples.

### 3. Results and discussion

The results of elution of plain and hydroxylated PS–DVB cartridges are presented in Table 2. Recoveries were not improved by acetonitrile but were slightly better with so-called two-step solvation of the adsorbents with ethyl acetate followed by methanol. Therefore, methanol is preferable due to the

toxicity of acetonitrile. The solvation improved the recovery of the more polar compounds, especially phthalic acid, but not the diesters, and this was more pronounced for the plain than for the hydroxylated polymer. All phthalates must have been fully adsorbed on the polymers, since they were not detected in the water phase that had passed through the cartridges. Accordingly, it was not necessary to add salt to increase the ionic strength as a means of augmenting the hydrophobic interactions [16]. Calculating area ratios, the relative standard deviation was <5% (*n*=3) when DDP was used as the I.S. and was added to the final extract, and was <1% when 3-BrBA was the I.S. and was added to the original water sample. The relative standard deviation increased, but did not exceed 7%, when real samples were analysed.

#### 3.1. Plain PS–DVB

Hexane, the most hydrophobic solvent tested, desorbed the diesters in good yield (66–83%) from the plain PS–DVB, with higher yields for the most hydrophobic moieties, whereas it eluted the monoesters in very low yield or not at all (0–10%). Toluene, which is more polar than hexane, desorbed both mono- and diesters very well (65–85%) but phthalic

Table 2

Recoveries of the phthalates by elution of plain and hydroxylated PS–DVB cartridges with different solvents. The sorbents were solvated with ethyl acetate and methanol and conditioned with acidified water before application of the phthalates

Phthalate	Recovery (%)													
	Plain PS–DVB							Hydroxylated PS–DVB						
	Hexane	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	TBME <sup>a</sup>	Diethyl ether	Ethyl acetate	Ethyl acetate <sup>b</sup>	Hexane	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	TBME <sup>a</sup>	Diethyl ether	Ethyl acetate	Ethyl acetate <sup>b</sup>
DMP	66	74	70	67	72	75	65	–	63	62	–	70	61	54
DEP	72	76	73	71	78	79	71	–	64	68	2	73	66	62
DBP	83	82	73	73	83	81	80	–	69	74	11	80	69	77
BBP	80	85	74	73	80	82	80	–	65	68	–	96	73	80
DEHP	75	75	69	67	81	80	74	2	73	76	84	85	69	77
PA	–	5	9	62	84	86	13	–	–	8	54	12	68	48
MMP	–	65	62	60	83	88	35	–	–	44	38	46	75	53
MEP	1	74	69	66	83	89	68	–	–	57	41	52	76	61
MbutP	10	77	73	65	84	85	80	–	9	76	47	44	66	63
MbenzP	1	83	83	67	82	89	87	–	–	61	1	29	82	71
MEHP	3	79	77	64	79	81	80	–	–	70	72	45	70	68

–, Below limit of quantification.

<sup>a</sup> *tert*-Butylmethyl ether.

<sup>b</sup> Elution with ethyl acetate, but no solvation of the cartridges.

acid very poorly (5%). Dichloromethane gave the same elution pattern as toluene. TBME, diethyl ether, and ethyl acetate desorbed all phthalates (72–89%), including phthalic acid. Introduction of 20, 40 and 60% acetone in ethyl acetate did not improve the recovery of any of the phthalates.

### 3.2. Hydroxylated PS–DVB

The only phthalate eluted from the hydroxylated PS–DVB with hexane was DEHP (2%). Toluene desorbed the diesters (63–73%) and MbutP (9%), but not the other monoesters or phthalic acid. Using dichloromethane, recovery increased with increasing hydrophobicity of the phthalates (phthalic acid 8% and the other compounds 44–76%), and was most efficient for the diesters. Elution with diethyl ether gave results similar to those obtained with dichloromethane (phthalic acid 12%, the other compounds 29–96%). Only a minor fraction (0–11%) of the diesters DMP, DEP, DBP and BBP were eluted with TBME, whereas 84% of DEHP was desorbed with this solvent. Elution of the monoesters with TBME increased from 38 to 72% with increasing hydrophobicity of these phthalates. The benzylic esters BBP and MbenzP were not desorbed (0–1%) by TBME. Ethyl acetate gave the best overall recovery of the analytes (61–82%).

### 3.3. Retention mechanisms

All phthalates contain a structural element comprising a benzene ring with ester or carboxylic groups. Moreover, these compounds show decreasing polarity with increasing length of the ester chains ( $C_1$ – $C_8$ ), and the branched chains in DEHP and MEHP make the chemical backbone bulkier. Other aromatic structures, such as the benzyl groups in BBP and MbenzP, also differ with regard to the alkyl ester chains. All these disparities in molecular structure influence adsorption and desorption properties and these differences were covered by the solvents included in our study, which ranged from nonpolar hexane to polar ethyl acetate and aromatic toluene, and the bulky TBME.

The only way to extract organic compounds from water is to appeal to their hydrophobic properties, which means that the analytes were adsorbed to the

PS–DVB polymers by hydrophobic interactions. Suzuki et al. [13] found that the adsorbing properties of phthalic acid monoesters dramatically decreased with increasing pH of water samples. Therefore, when phthalic acid and monoesters and diesters are to be analysed simultaneously, we suggest that water samples to be acidified to pH 0.9 to prevent ionisation (the lowest  $pK_a$  of phthalic acid is 2.9). With both types of cartridges used in our study, this resulted in hydrophobic interactions that were strong enough to achieve complete adsorption of the phthalates from the aqueous phase, as indicated by the absence of phthalates in samples that had passed through the extraction cartridges. If hydrophobic interactions constituted the only sorption mechanism, hexane would have been an excellent elution solvent for all phthalates. The results presented in Table 2 indicate that this was not the case. For the hydroxylated PS–DVB, the only phthalate eluted with hexane was the most hydrophobic analyte (i.e. DEHP). However, for the plain PS–DVB, hexane successfully desorbed the diesters and accordingly, the yields were higher for the most hydrophobic moieties, whereas this solvent gave unsatisfactory yields of the monoesters and phthalic acid. This means that, with nonpolar solvents, not only hydrophobic but also polar interactions had substantial effects on sorption to both of the PS–DVB polymers. Borén et al. [17] have found that toluene improved the yield of aromatic compounds when the sorbent was activated carbon, a substance that involves only hydrophobic mechanisms. In our experiments with PS–DVB, toluene did not increase the recovery of the more aromatic MbenzP and BBP, and this was especially pronounced for the hydroxylated polymer, which indicates that polar interactions were stronger than the influence of the aromatic element. Considering the branched and bulky TBME, the most marked effect was seen with the hydroxylated PS–DVB. More precisely, the branched and bulky MEHP and DEHP was more fully desorbed whereas most of the other mono- and diesters were not, especially not the flat-structured MbenzP and BBP, for which the structure of the bulkiness of TBME was too cumbersome. Phthalic acid was still discriminated when the hydroxylated PS–DVB was desorbed with the more polar solvent diethyl ether, whereas ethyl acetate eluted all phthalates, including phthalic acid, from

Table 3  
Recoveries of the phthalates by liquid–liquid extraction with different solvents

Compound	Recovery (%)				
	Hexane	Toluene	CH <sub>2</sub> Cl <sub>2</sub>	Diethyl ether	Ethyl acetate
DMP	57	67	80	70	79
DEP	73	70	86	73	82
DBP	87	77	88	80	91
BBP	77	74	73	96	91
DEHP	93	77	84	85	92
PA	1	7	16	12	60
MMP	–	14	42	46	80
MEP	–	23	63	52	83
MbutP	24	63	94	44	89
MbenzP	1	61	71	29	87
MEHP	41	70	80	45	85

–, Below limit of quantification.

both polymers. By comparison, slightly better recoveries were achieved with the plain PS–DVB, and as expected, the polar interactions were weaker with this polymer than with the hydroxylated PS–DVB. The chromatogram in Fig. 1 shows the studied phthalates analysed by GC–MS in SIM mode.

The PS–DVB polymers are manufactured as general sorbents, but our results show that they can also be used for selective elution. More precisely, when the hydroxylated PS–DVB cartridges were eluted with toluene, we found that the polar interactions were strong enough to retain phthalic acid and its monoesters, while the diesters were smoothly desorbed (Table 2). Moreover, after complete elution of the diesters, the monoesters and phthalic acid were successfully eluted with ethyl acetate.

LLEs were also performed with different solvents

(Table 3), and the results were more similar to the extraction pattern obtained with the plain PS–DVB than with the hydroxylated polymer. Hence, we believe that the efficiency with which any analytes are eluted by from the plain polymer by different solvents can be predicted from the extraction properties of traditional LLEs.

### 3.4. Elimination of volatile fatty acids

The results presented in Table 4 show the recovery of the fatty acids in the eluted washing solutions when using the plain PS–DVB polymer. All fatty acids but propionic acid was completely adsorbed to the cartridges (i.e. 20% propionic acid was recovered in the water sample that had passed through the cartridges). The ethyl acetate and methanol used to

Table 4

Plain PS–DVB cartridges were rinsed with a 2.5-ml portion of each of three washing solutions (A, B and C) containing different concentrations of acetone in water (pH 0.9). The values represent recoveries of ethanol and volatile fatty acids from the water phase of the eluate

Fatty acid	% Acetone																				
	0			2			5			7.5			10			15			20		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Propionic acid	51	18	–	62	–	–	61	–	–	59	–	–	78	–	–	73	–	–	70	–	–
Isobutyric acid	3	7	16	15	65	17	43	50	1	58	34	–	76	36	–	61	–	–	95	–	–
<i>n</i> -Butyric acid	2	5	13	12	75	8	50	51	–	60	32	–	77	23	–	60	–	–	95	–	–
Isovaleric acid	–	–	–	–	–	–	2	11	25	–	25	41	–	40	45	21	58	13	37	57	–
Valeric acid	–	–	–	–	–	–	–	5	11	–	12	34	–	25	50	10	58	24	22	69	–
Isocaproic acid	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	6	–	10	45

–, Below quantification limit.

solvate the cartridges coeluted with ethanol and acetic acid in the GC analyses, thus it was not possible to quantify ethanol and acetic acid. However, the trend seen in Table 4 indicates that they would probably be completely eluted even when using acetone-free acid water, since they are both more hydrophilic than propionic acid, which was almost completely desorbed by acidified water, even in the absence of acetone. So, the less volatile fatty acids ( $C_4$ – $C_6$ ) were completely adsorbed to the polymer during application. Though, the most hydrophobic acid in our study (isocaproic acid) was not completely desorbed, even when the washing solution was 20% acetone. Nonetheless, acetic and butyric acid, which are the most significant important fatty acids in acidic landfill leachates, were completely desorbed by 5 ml of 5% acetone.

The mechanisms of adsorption of the phthalates were also studied using the same washing solutions employed to remove the fatty acids. The results show that none of the phthalates, except phthalic acid and MMP was affected, not even by 20% acetone (Fig. 2). Phthalic acid and MMP were influenced by acetone concentrations above 5 and 12.5%, respectively. The presence of acetone decreased the polarity of the acid washing solution. Thus, increasing concentrations of acetone therefore desorbed analytes with decreasing polarity. That is, 100% acetone eluted not only all fatty acids, but also all phthalates.

Compounds such as fatty acids can compete for the sorption sites on the polymer and for the

derivatising agent added to the extract to make the monoesters and phthalic acid amenable to GC analyses, hence they may have an adverse effect on the chromatographic separation. Accordingly, it is necessary to decrease the concentrations of fatty acid in the final extracts.

### 3.5. Analysis of acidogenic landfill leachates

Notably, when real samples were analysed by the procedure applied to purified water, phthalic acid was almost completely eliminated from the final extract. We assume that the presence of ethanol in real samples would have little effect on the retention of the phthalates on plain PS–DVB, because all phthalates were retained on the polymer when the sample contained as much as 7% ethanol (data not shown). Thus, even if the analytical procedures were tailored with respect to competitive compounds such as ethanol and volatile fatty acids, it was not feasible to adjust for all possible disturbances from the matrix. Though, when we used acidic water without any acetone as washing solution to remove volatile fatty acids, we achieved recoveries that were reproducible and similar to those achieved with purified water. The recovery of phthalic acid showed that retention of this analyte was complete but adsorbance to the polymer was weaker than in pure water. In summary, calibrations should always be done in the same matrix as the samples that are to be analysed.

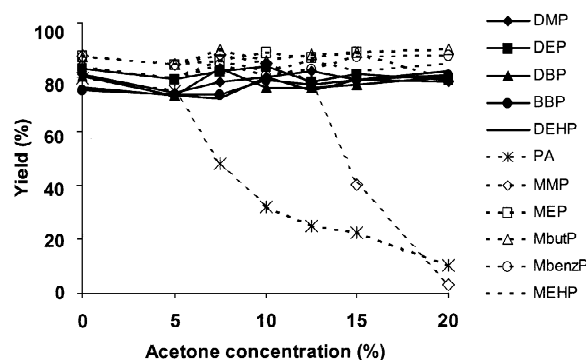


Fig. 2. Recoveries of the phthalates upon elution of plain PS–DVB cartridges that had been washed with two 2.5-ml portions of washing solution containing different concentrations of acetone in acidified water (pH 0.9).

## 4. Conclusions

We used two polystyrene–divinylbenzene polymers to examine the sorption properties of phthalates, including *o*-phthalic acid and its mono- and diesters, in the presence of volatile fatty acids and ethanol, and we came to the following conclusions:

- Both the plain and the hydroxylated PS–DVB polymer satisfactorily retained the phthalates when the water samples were acidified to pH 0.9, which is two pH units below the  $pK_a$  of phthalic acid.
- More polar solvents gave better recovery of all the phthalates, because these compounds have polar as well as nonpolar elution properties.

Highest recoveries for both polymers were achieved using ethyl acetate as mobile phase, and recoveries were slightly better with the plain than with the hydroxylated polymer.

3. Careful choice of eluants allowed selective desorption of the phthalates from these two general PS–DVB sorbents. More precisely, with the hydroxylated PS–DVB, an initial elution with toluene desorbed the diesters, and subsequent elution with ethyl acetate desorbed the monoesters and phthalic acid.
4. Analysis of real samples (i.e. acidic landfill leachates), showed that it was necessary to use acidified water (pH 0.95) without acetone as washing solution to prevent desorption of phthalic acid, because the matrix had a negative effect on the phthalic acid and enforced the desorption at any of the acetone concentrations used. Nonetheless, in experiments using pure water and washing with 5% acetone the most volatile fatty acids (C<sub>2</sub>–C<sub>4</sub>) were successfully removed, with minimal loss of the phthalates.
5. We believe that the phthalates and the fatty acids can be used as model compounds when predicting the retention mechanisms of plain and hydroxylated PS–DVB polymers. We also claim that analyte recoveries from LLEs can be used as guidelines for elution of the plain PS–DVB.

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