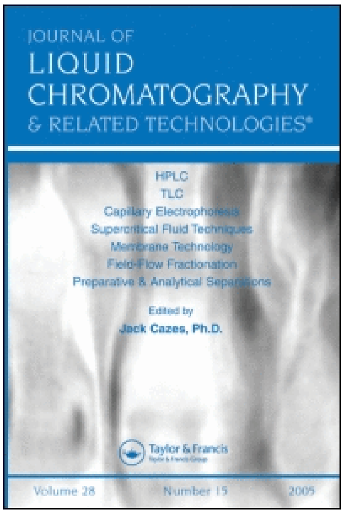

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MIXED-MODE S.P.E. OF POLLUTANTS IN WATER ON MECHANICALLY BLENDED SILICA-BASED BONDED PHASES. II. INFLUENCE OF MULTIPLE PARAMETERS†

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ABSTRACT

We have studied the retention of aromatic environmental pollutants of neutral, very weakly acid or weakly basic types, in solid-phase extraction in aqueous media, by mixed phases prepared by dry mechanical blending of a silica-bonded C_{18} phase and a silica-bonded propylsulfonic phase. The relations : percent recovery = f(mass % of C_{18} phase) were quasi-linear over a wide composition range. This enables the predominant type of mechanism operating for each compound to be deduced.

The effect of the configuration of the mixed phase and the effect of the total mass of adsorbent show the superiority of mechanical blending over other arrangements : tandem combinations, and in particular, the type of phase having functional groups carried by the same particle. This is still better illustrated by the effect of sample volume when this is very rich in water, the flow rate variations having no impact on the results; and especially, by the effect of type of water simulating sample matrix as well.

INTRODUCTION

Solid-Phase Extraction (S.P.E.) is a modern technique for preparing samples for chromatographic analysis. A recent review article[1] has described the latest developments and applications in various different fields. However, it is in the environment field that this technique has revealed its potential, since it can be used to concentrate organic compounds which are very often present at only trace levels. Aqueous samples taken from the environment are also characterized by high complexity since a large variety of pollutants, with very different polarities, are present simultaneously, in addition to the matrix components. In order to trap a maximum of these components, it is necessary to make use of multiple interactions, which is achieved with « mixed-mode » extraction, of which there are two types characterized by different combinations of phases.

Firstly, there is the type with two cartridges in tandem. The first cartridge, used for the isolation, contains a non-selective adsorbent which receives the aqueous sample. The second cartridge, containing a selective adsorbent which generally receives the organic solvent which has eluted the first cartridge, is used to purify (fractionate). This second cartridge retains the compounds of interest,[2-6] but can also be used to retain unwanted interferences.[7] With this tandem combination, isolation of the most polar compounds on the non-selective adsorbent is not guaranteed ; also, comparisons between different adsorbents have been carried out,[8] and adsorbents based on slightly modified polymers have been proposed.[9,10]

Secondly, there is the type where different functional groups are together in the same cartridge, the strategy being to make use of multiple interactions to achieve total retention. There are two sub-categories of this type :

a) the particle contains two chemical functions obtained by bonding,[11-13] one of which may also be present as a surface impurity;[14]

b) each particle carries only a single functional group and the different particles are mechanically blended.[13]

We are interested in this latter sub-category because of its very great simplicity. We have recently shown[15] that the speed of preparation of dry-blended phases is accompanied by better reproducibilities of the percent recoveries than those obtained from a phase of the first sub-category.

An application of blended phases has recently been reported,[16] and since they seem to us to have a huge potential, arising particularly from great flexibility in composition, we have studied different variables so as to determine the advantages and disadvantages compared with other mixed phases.

MATERIALS

Solvents, reagents, compounds analyzed, and solutions of these, cartridges and accessories, and the equipment used for the extraction and H.P.L.C. analysis, respectively, have been previously described in detail.[15] Another commercial mixed phase was tested, Bond Elut THC (Analytichem International, Harbor City, CA, U.S.A.), for which we were not able to obtain any specifications.

METHODS

The preparation of the dry-blended phases, and the extraction procedure, were based on those previously described,[15] with modifications according to the variables studied.

For the tandem configuration studied, each cartridge contained a certain mass of the individual phase corresponding to a given mass ratio, plus a given total mass of adsorbent.

The system of two cartridges connected to one another by an adapter was placed in a « Visiprep » and the extraction procedure referred to above was used.

The quantitative analysis by H.P.L.C. has been described.[15] Every relative standard deviation is calculated from four extraction procedures. Every extract was repeatedly injected three times.

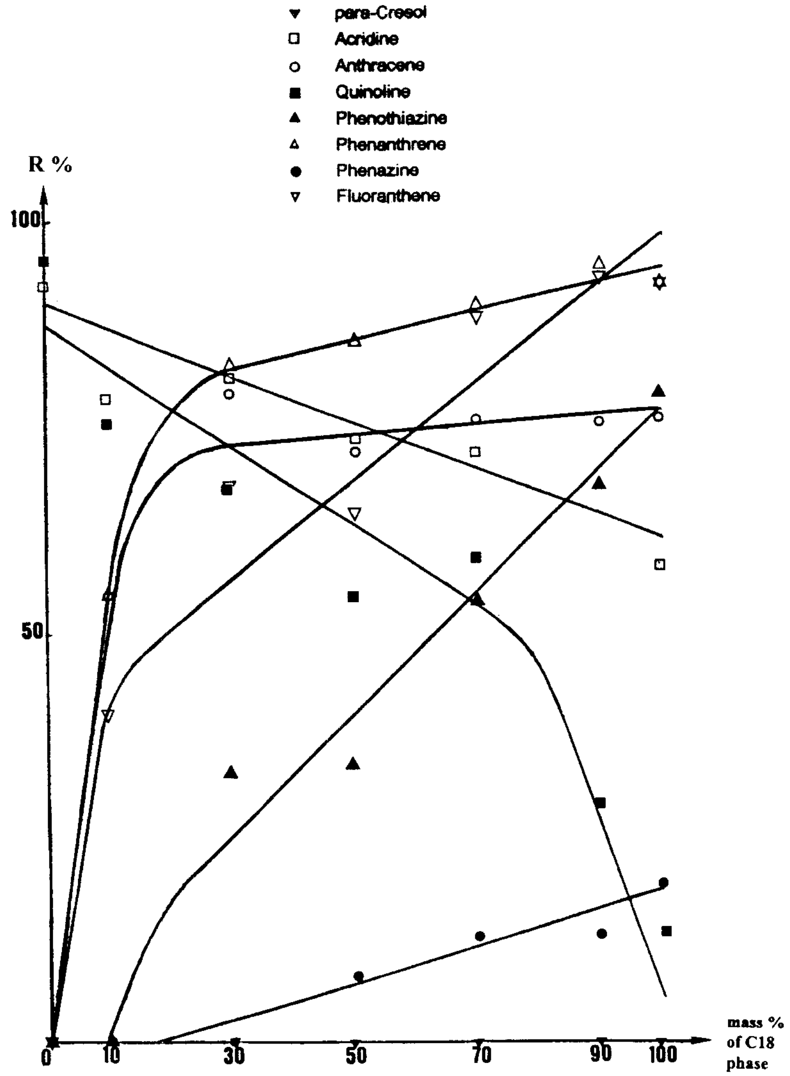

Figure 1. Effects of the variation in composition by mass of the C18 phase of blended mixed phases on the percent recoveries. (≠) Conditions : solid phase : total weight : 50 mg ; sample : total weight : 0.072 mg, solution volume : 50 mL of deionized water / acetonitrile (85/15 v/v), flow-rate : 1 mL.min^{-1} ; elution : solvent : acetonitrile with 2 % ammonium hydroxyde, flow- rate : 1 mL.min^{-1}. (≠) Each result is the mean of 4 extractions, each extract having been injected 3 times.

RESULTS AND DISCUSSION

The studies were performed with an essentially aqueous sample matrix in which the water used was of two types : one of H.P.L.C. quality (§ A, B, C, D) and one of tap water taken at the Faculty of Sciences of Tours (§ E). The amount of material analyzed, a mixture of aromatic pollutants which were neutral : anthracene, phenanthrene, fluoranthene, or very weakly acidic : phenothiazine, p-cresol, or weakly basic : phenazine, quinoline, acridine, was always constant.

The two adsorbents used to make the blended phases contained, respectively, octadecyl (C_{18}) and propylsulfonate (PRS) groups bonded onto silica.

Effect of the Mass Composition of the Stationary Phase

The variable was the mass percent of the C_{18} phase, the total mass of the stationary phase being kept constant. The composition, volume and flow rate of the sample and eluent respectively were also kept constant.

Under these conditions, the first conclusions were drawn from Figure 1 :

a) For all the compounds analyzed, except for p-cresol which was not retained by any phase, the percent extractions varied quasi-linearly with the mass percent of the C18 phase over the range 20-80 %.

b) In the extreme ranges, i.e. 0-20 % or 80-100 %, we observed some sharp variations in the percent extractions, except for acridine and phenazine.

With some compounds a sharp increase in lost fraction of overall sample is noticed which means that breakthrough volume is reached.

c) There was a variation of the percent extractions giving graphs with slopes of opposite signs. The following can be distinguished :

The family of polycyclic aromatic hydrocarbons (P.A.H.), characterized in its linear regions by positive slopes. This is the case for phenanthrene and anthracene giving rise to curves of the same shape, as well as fluoranthene. The interactions are of the hydrophobic type with the C_{18} phase.

It is noticeable that the recovery of anthracene was clearly weaker than that of phenanthrene, both with the C_{18} phase alone and with the different mixed phase compositions. This phenomenon was reduced by optimizing the volume of organic eluent to 8 mL.[15] The choice of eluent, acetonitrile, was influenced by several considerations : all the components of the mixture are soluble in it ; in addition, the miscibility of this solvent with water allows the subsequent H.P.L.C. analysis to be performed without a solvent evaporation step, and encourages the extraction of the molecules from the pores of the particles which are still hydrated if the drying operation has not been performed to completion.

Phenothiazine can also be included in this family. Its property as proton acceptor being very weak, it cannot allow cation exchange. On the order hand, its hydrophobic character is still significant judging by the value of the partition coefficient calculated according to Rekker[17] : $\log P_{calc.} = 3.87$.

Lastly, to a small extent phenazine, $pK_a = 1.2$,[18] is also included in this family despite the presence of two nitrogen atoms in its structure. In fact, being also in molecular form, is still has some hydrophobic character : $\log P_{calc.} = 2.75$,[17] whose lower value compared particularly to that of phenanthrene : $\log P_{calc.} = 4.68$[17] justifies a markedly lower retention.

In addition, as for triazines,[13] the polar and weakly basic characters of phenazine suggest a possible interaction by hydrogen bonding with the exchanger. However, considering the absence of recovery on the PRS phase, this latter interaction would here be of very low energy, the hydrophobic interaction remaining predominant.

The family of aromatic bases characterized in its linear regions by negative slopes. This is very clearly the case for quinoline, $pK_a = 4.94$,[18] which is positively charged, and thus, essentially retained by cation exchange. Acridine, $pK_a = 5.60$,[18] has a slightly greater partial positive charge. In addition, considering its strong hydrophobic character : $\log P_{calc.} = 3.39$,[17] compared with that of quinoline for which $\log P_{calc.} = 2.10$,[17] a double mechanism with more balanced interaction forces could be operating. This would justify, for all adsorbent compositions, a high retention which is not affected when the percentage of C_{18} phase approaches 100.

Table 1

Effects of the Variation of the Total Mass of Adsorbent on the Percent Recoveries and R.S.D. (%), using Various Types of Mixed Phases

Phase Type	**Bond Elut Certify**			**Bond Elut THC**			**C_{18}**		
Phase Mass	**50 mg**	**100 mg***	**200 mg**	**50 mg**	**100 mg**	**200 mg**	**50 mg**	**100 mg***	**200 mg**
Compound									
para-Cresol	0	0	0	0	0	0	0	0	0
Quinoline	48 ± 4	98 ± 3	107 ± 7	0	0	21 ± 7	14 ± 7	30 ± 6	102 ± 8
Phenazine	20 ± 8	58 ± 16	96 ± 1	0	0	0	19 ± 1	33 ± 9	77 ± 10
Acridine	93 ± 8	97 ± 4	99 ± 2	0	0	36 ± 2	58 ± 4	99 ± 4	101 ±3
Phenothiazine	39 ± 6	74 ± 13	85 ± 18	0	0	0	74 ± 5	101 ± 7	103 ± 13
Fluoranthene	56 ± 3	92 ± 2	90 ± 3	0	7 ± 8	14 ± 6	94 ± 7	103 ± 2	100 ±1
Anthracene	60 ± 2	82 ± 1	90 ± 5	0	9 ± 4	19± 5	77 ± 2	76 ± 5	98 ±3
Phenanthrene	75 ± 9	91 ± 2	89 ± 1	0	13 ± 7	24 ± 5	93 ± 2	95 ± 7	100 ± 3

Phase Type	**C_{18}/PRS 90/10**			**C_{18}/PRS 70/30**			**C_{18}/PRS 50/50**		
Phase Mass	**50 mg**	**100 mg**	**200 mg**	**50 mg**	**100 mg**	**200 mg**	**50 mg**	**100 mg***	**200 mg**
Compound									
para-Cresol	0	0	0	0	0	0	0	0	0
Quinoline	29 ± 2	81 ± 5	96 ± 8	59 ± 3	92 ± 7	106 ± 9	54 ± 4	98 ± 4	93 ± 15
Phenazine	13 ± 4	24 ± 3	70 ± 4	13 ± 2	23 ± 4	45 ± 6	8 ± 2	14 ± 4	34 ± 6

(continued)

Table 1 (continued)

Phase Type	C_{18}/PRS 90/10			C_{18}/PRS 70/30			C_{18}/PRS 50/50		
Phase Mass Compound	50 mg	100 mg	200 mg	50 mg	100 mg	200 mg	50 mg	100 mg*	200 mg
Acridine	68 ± 6	95 ± 4	98 ± 2	72±3	95 ± 3	97 ± 2	74 ± 2	101 ± 4	99 ± 3
Phenothiazine	66 ± 7	96 ± 10	103 ± 11	55 ± 8	85 ± 5	100 ± 15	34 ± 11	66 ± 8	80 ± 12
Fluoranthene	94 ± 5	95 ± 10	101 ± 3	89 ± 4	96 ± 6	107 ± 6	65 ± 3	86 ± 10	103 ± 6
Anthracene	76 ± 12	76 ± 13	92± 5	76 ± 6	77 ± 2	91 ± 3	72 ± 5	81 ± 4	93 ± 5
Phenanthrene	95 ± 4	96 ± 5	93 ± 4	90 ± 2	98 ± 2	96 ± 3	86 ± 1	93 ± 2	96 ± 7
Phase Type	C_{18}/PRS 30/70			C_{18}/PRS 10/90			PRS		
para-Cresol	0	0	0	0	0	0	0	0	0
Quinoline	68 ± 14	103 ± 5	104 ± 2	76 ± 5	98 ± 2	97 ± 2	95 ± 6	101 ± 5	100 ± 2
Phenazine	0	11 ± 9	16 ± 2	0	0	0	0	0	0
Acridine	81 ± 4	94 ± 3	101 ±3	79 ± 8	102 ± 1	94 ± 3	92 ± 2	109 ± 4	103 ± 3
Phenothiazine	33 ± 8	85 ± 16	64 ± 16	0	38 ± 1	45 ± 5	0	0	0
Fluoranthene	68 ± 14	68 ± 2	96 ± 4	40 ± 7	64 ± 2	77 ± 3	0	4 ± 6	4 ± 2
Anthracene	79 ± 8	69 ± 1	97 ± 2	55 ± 9	66 ± 7	78 ± 8	0	14 ± 5	15 ± 4
Phenanthrene	83 ± 5	95 ± 5	95 ± 1	55 ± 1	81 ± 1	81 ± 7	0	5 ± 7	5 ± 5

Conditions: identical to those described under Figure 1, with only the total mass of the solid phase varying. * Results taken from reference 15.

Effect of the Total Mass of Adsorbent, Comparison with Commercial Mixed Phases

The variable was now the total mass of adsorbent, and the variation of the results obtained was compared within each mixed phase and between the different mixed phases.

Examination of Table 1 shows :

a) Whatever the phase tested : commercial mixed, or mechanically blended, and whatever the mass composition in the latter case, we observed an increase in percent extractions with an increase in the total mass of the solid phase. The anomaly affecting anthracene appeared again with a higher mass (100 mg). However, for a still higher mass (200 mg) the percent extractions became identical to those obtained for phenanthrene. The hypothesis of « sorption » on the walls of the extraction system, which would be specific to anthracene when the number of particles of the solid phase is low, is not entirely satisfactory. Further work is needed.

b) Using a sample solution volume of 50 mL, we studied a given mass, m, of the commercial mixed phase Bond Elut Certify. The percent extractions obtained with a mass 2m of one or other of the mechanically blended phases with C_{18}/PRS composition 90/10 or 70/30 were in general better, for a significantly lower cost.

c) The other commercial phase tested, Bond Elut THC, only gave very low percent extractions. However, the recoveries obtained on 200 mg of this phase seemed to prove that it was operating with a double mechanism, cation exchange, and hydrophobic interaction, judging by the results for quinoline and acridine on the one hand and the P.A.H. on the other.

Effect of the Configuration of the Mixed Phase

The variable now was the relative arrangement of the C_{18} and PRS phases. Thus, for a fixed total mass of adsorbent, m = 100 mg, we compared for the same mass composition the blended mixed phases (Table 1) with the mixed phases arranged in tandem, for which two configurations were studied : the C_{18} phase on top, then below (Table 2). We did not follow the normal tandem strategy;[2-7] on the contrary, we performed sample deposition continuously on the two linked cartridges. We obtained the following information :

Table 2

Effects of the Configuration of Mixed Phases of Different Compositions, Arranged in Tandem on the Percent Recoveries and R.S.D. (%)

Phase Type	**C_{18}/PRS 90/10**		**C_{18}/PRS 70/30**		**C_{18}/PRS 50/50**	
Phase Arrangement Compound	**C_{18} On Top**	**C_{18} Below**	**C_{18} On Top**	**C_{18} Below**	**C_{18} On Top**	**C_{18} Below**
para-Cresol	0	0	0	0	0	0
Quinoline	78 ± 9	68 ± 26	81 ± 16	121 ± 23	89 ± 2	94 ± 2
Phenazine	32 ± 6	32 ± 3	32 ± 5	30 ± 35	15 ± 11	18 ± 7
Acridine	95 ± 9	103 ± 3	93 ± 2	104 ± 11	92 ± 9	100 ± 4
Phenothiazine	92 ± 21	78 ± 27	75 ± 14	97 ± 28	70 ± 11	67 ± 29
Fluoranthene	90 ± 4	98 ± 4	81 ± 10	102 ± 11	88 ± 3	88 ± 6
Anthracene	73 ± 14	79 ± 14	74 ± 9	84 ± 7	70 ± 1	70 ± 15
Phenanthrene	88 ± 4	93 ± 4	85 ± 8	96 ± 9	87 ± 4	89 ± 5

Phase Type	**C_{18}/PRS 30/70**		**C_{18}/PRS 10/90**	
para-Cresol	0	0	0	0
Quinoline	102 ± 5	121 ± 11	92 ± 1	97 ± 7
Phenazine	13 ± 5	12 ± 13	6 ± 16	7 ± 9
Acridine	98 ± 3	110 ± 7	96 ± 2	90 ± 3
Phenothiazine	61 ± 3	54 ± 27	27 ± 20	29 ± 24
Fluoranthene	86 ± 3	99 ± 15	61 ± 11	43 ± 2
Anthracene	64 ± 3	70 ± 18	59 ± 12	52 ± 2
Phenanthrene	89 ± 1	100 ± 13	73 ± 10	52 ± 1

Conditions: identical to those described under Figure 1 except that the total mass of adsorbent was 100 mg.

a) There was no significant change in the percent recoveries.

b) On the other hand, the tandem arrangement was prejudiced by much poorer reproducibilities, particularly when the PRS phase was above.

Effects of the Flow Rate and Volume of the Sample Solution

The total mass of adsorbent was fixed. The variables were the flow rate and concentration of sample solution since for the latter only the volume varied.

The values given in Tables 3 and 4, to which we have added some taken from Table 1 (those corresponding to an adsorbent mass of 100 mg, to a sample volume of 50 mL deposited with a flow rate of 1 $mL.min^{-1}$), lead to the following conclusions :

Effects of the variation in flow rate

At a constant volume of 50 mL, we raised the sample introduction rate from 1 to 5, and then to 10 $mL.min^{-1}$.

In general, we did not observe any clear variation in either direction. At the most we sometimes observed a slight decrease in the percent recovery. It was notable that with the pure PRS phase, and for the P.A.H. alone, the percentages varied from low to zero. This could result from their poor mass transfer. Lastly, we emphasize that the reproducibilities were not affected.

Effects of the variation in volume

Since the concentration of the pollutants in actual samples of water of different origins is often very low, it is necessary to carry out extractions from very large volumes. Bearing in mind the possible application of blended mixed phases, we therefore studied this parameter :

> At constant flow rate of 10 $mL.min^{-1}$, we increased the sample solution volume from 50 to 100, 200, 500, and then 1000 mL, the acetonitrile volume remaining constant. We observed a number of effects. Thus for the higher volumes, and for all the sample components, the percent recoveries obtained with the blended phases of C_{18}/PRS mass composition 90/10 and 70/30 approached and then exceeded the corresponding percentages obtained with the Bond Elut Certify phase.
>
> As for the variations of percentages possibly affecting certain compounds, we observed two clearly contrary effects. It would be expected that a decrease of the eluent force of the organo-aqueous solution on the deposit would cause an increase in the retention by the C_{18} groups. This was the case for phenazine whose percent extractions increase sharply when the volume increased from 50 to 100, then to 200 mL, then stabilized for higher volumes. However, the opposite was the case for phenothiazine. This could be result of secondary mechanisms of different types.

Table 3

Effects of the Variation of the Introduction Flow Rate of a Constant Sample Volume on the Percent Recoveries and R.S.D. (%), Using Various Types of Mixed Phases*

Phase Type	**Bond Elut Certify**			**C_{18}**			**C_{18}/PRS 90/10**		
Flow Rate ($mL\ min^{-1}$) Compound	**1**	**5**	**10**	**1**	**5**	**10**	**1**	**5**	**10**
para-Cresol	0	0	0	0	0	0	0	0	0
Quinoline	98 ± 3	99 ± 12	101 ± 1	31 ± 6	33 ± 3	28 ± 3	81 ± 5	83 ±4	79 ± 1
Phenazine	58 ± 16	46 ± 4	66 ± 5	33 ± 9	34 ± 2	30 ± 7	24 ± 3	32 ± 7	34 ± 1
Acridine	97 ± 4	89 ± 11	92 ± 9	100 ± 4	99 ± 3	94 ± 1	95 ± 4	100 ± 6	100 ± 1
Phenothiazine	76 ± 13	71 ± 1	61 ± 14	102 ± 7	86 ± 4	76 ± 10	96 ± 10	84 ± 1	81 ± 2
Fluoranthene	92 ± 2	86 ± 6	101 ± 1	103 ± 2	95 ± 5	92 ± 2	95 ± 10	95 ± 6	94 ± 2
Anthracene	82 ± 1	70 ± 7	79 ± 1	76 ± 5	94 ± 5	87 ± 4	76 ± 13	96 ± 5	78 ± 1
Phenanthrene	91 ± 2	91 ± 7	98 ± 2	95 ± 7	96 ± 3	96 ± 3	96 ± 5	95 ± 9	90 ± 2
Phase Type	**C_{18}/PRS 70/30**			**C_{18}/PRS 50/50**			**C_{18}/PRS 30/70**		
para-Cresol	0	0	0	0	0	0	0	0	0
Quinoline	92 ± 7	88 ± 4	91 ± 5	98 ± 4	97 ± 3	90 ± 7	103 ± 5	103 ± 1	100 ± 3
Phenazine	23 ± 4	23 ± 10	26 ± 1	14 ± 4	13 ± 7	9 ± 9	11 ± 9	12 ± 5	0
Acridine	95 ± 3	99 ± 5	94 ± 1	101 ± 4	90 ± 6	96 ± 6	94 ± 3	90 ± 2	100 ± 4

Table 3 (continued)

Phase Type	C_{18}/PRS 70/30			C_{18}/PRS 50/50			C_{18}/PRS 30/70		
Flow Rate (mL min^{-1}) Compound	1	5	10	1	5	10	1	5	10
Phenothiazine	85 ± 5	83 ± 12	76 ± 4	66 ± 8	87 ± 3	70 ± 10	85 ± 16	70 ± 6	55 ± 5
Fluoranthene	96 ± 6	99 ± 7	87 ± 2	86 ± 10	94 ± 4	100 ± 4	68 ± 2	94 ± 5	87 ± 4
Anthracene	77 ± 2	93 ± 7	84 ± 1	81 ± 4	87 ± 4	89 ± 3	69 ± 1	72 ± 5	79 ± 1
Phenanthrene	98 ± 2	94 ± 9	92 ± 2	93 ± 2	97 ± 6	83 ± 4	95 ± 5	92 ± 3	92 ± 1

Phase Type	C_{18}/PRS 10/90			PRS		
para-Cresol	0	0	0	0	0	0
Quinoline	98 ± 2	97 ± 6	103 ± 3	101 ± 5	99 ± 6	106 ± 1
Phenazine	0	0	0	0	0	0
Acridine	102 ± 3	96 ± 1	103 ± 4	109 ± 4	97 ± 6	93 ± 5
Phenothiazine	38 ± 1	29 ± 6	40 ± 6	0	0	0
Fluoranthene	64 ± 2	76 ± 1	56 ± 10	4 ± 6	0	0
Anthracene	66 ± 7	69 ± 4	55 ± 8	14 ± 5	0	0
Phenanthrene	81 ± 1	80 ± 1	49 ± 11	5 ± 5	0	0

Conditions: identical to those described under Figure 1, except that the total mass of adsorbent was 100 mg and the sample deposition flow rate was variable.

Table 4

Effects of the Variation of the Volume of the Sample Introduced at Constant Flow Rate on the Percent Recoveries and R.S.D. (%) , Using Various Types of Mixed Phases*

Phase Type	**Bond Elut Certify**				**C_{18}**			
Volume (mL)	**100**	**200**	**500**	**1000**	**100**	**200**	**500**	**1000**
Compound								
para-Cresol	0	0	0	0	0	0	0	0
Quinoline	95 ± 2	91 ± 4	90 ± 3	88 ± 11	71 ± 3	69 ± 2	98 ± 2	73 ± 4
Phenazine	65 ± 2	82 ± 2	86 ± 5	51 ± 10	71 ± 2	73 ± 5	85 ± 2	78 ± 9
Acridine	92 ± 1	94 ± 5	102 ± 5	88 ± 9	93 ±4	82 ± 2	96 ± 3	112 ± 1
Phenothiazine	65 ± 1	64 ± 1	63 ± 10	42 ± 8	63 ±3	56 ± 10	57 ± 1	59 ± 5
Fluoranthene	90 ± 2	81 ± 2	93 ± 5	64 ±7	84 ± 2	84 ± 2	97 ± 3	89 ± 2
Anthracene	61 ± 7	59 ± 6	74 ± 2	66 ± 9	81 ± 2	44 ± 2	86 ± 9	88 ± 6
Phenanthrene	87 ± 2	97 ± 2	83 ± 1	80 ± 6	84 ± 4	90 ± 1	81 ± 4	87 ± 5
Phase Type	**C_{18}/PRS 90/10**				**C_{18}/PRS 70/30**			
para-Cresol	0	0	0	0	0	0	0	0
Quinoline	82 ± 5	82 ± 3	111 ± 6	95 ± 1	79 ± 4	98 ± 6	95 ± 2	97 ± 2
Phenazine	57 ± 1	82 ± 1	81 ± 1	77 ± 1	47 ± 5	75 ± 4	85 ± 7	77 ± 6
Acridine	83 ± 1	79 ± 1	104 ± 6	105 ± 2	81 ± 3	91 ± 4	103 ± 3	103 ± 1
Phenothiazine	61 ± 4	62 ± 1	59 ± 3	61 ± 2	62 ± 12	63 ± 9	58 ± 1	57 ± 1

Table 4 (continued)

Phase Type		C_{18}/PRS 90/10				C_{18}/PRS 70/30		
Volume (mL) Compound	100	200	500	1000	100	200	500	1000
Fluoranthene	76 ± 3	78 ± 1	90 ± 5	88 ± 8	72 ± 5	92 ± 7	95 ± 5	86 ± 6
Anthracene	68 ± 2	48 ± 2	83 ± 9	86 ± 12	53 ± 1	72 ± 11	70 ± 2	91 ± 9
Phenanthrene	81 ± 4	71 ± 3	85 ± 10	88 ± 1	84 ± 7	72 ± 2	88 ± 6	88 ± 5
Phase Type		**C_{18}/PRS 50/50**				**C_{18}/PRS 30/70**		
para-Cresol	0	0	0	0	0	0	0	0
Quinoline	94 ± 4	97 ± 4	92 ± 3	91 ± 1	99 ± 3	98 ± 5	95 ± 2	88 ± 6
Phenazine	36 ± 12	58 ± 2	54 ± 10	59 ± 4	24 ± 11	33 ± 7	51 ± 5	29 ± 4
Acridine	92 ± 4	91 ± 2	105 ± 5	96 ● 3	93 ± 2	85 ± 7	98 ± 6	91 ± 7
Phenothiazine	62 ± 10	53 ± 2	51 ● 13	40 ± 2	48 ± 1	40 ± 9	31 ± 2	28 ± 8
Fluoranthene	91 ± 4	96 ± 6	97 ± 7	86 ± 2	88 ± 3	96 ± 7	86 ± 2	69 ± 6
Anthracene	58 ± 12	76 ± 8	80 ± 9	89 ± 7	50 ± 3	87 ± 3	81 ± 1	67 ± 5
Phenanthrene	89 ± 4	76 ± 4	92 ± 7	83 ± 3	91 ± 4	81 ± 2	82 ± 6	55 ± 6

(continued)

Table 4 (continued)

Phase Type		**C_{18}/PRS 10/90**				**PRS**		
Volume (mL)	**100**	**200**	**500**	**1000**	**100**	**200**	**500**	**1000**
Compound								
para-Cresol	0	0	0	0	0	0	0	0
Quinoline	94 ± 8	97 ± 1	102 ± 5	89 ± 4	96 ± 9	100 ± 5	98 ± 7	76 ± 7
Phenazine	8 ± 12	13 ± 2	19 ± 1	11 ± 7	0	0	0	0
Acridine	93 ± 3	102 ± 9	97 ± 1	91 ± 3	96 ± 5	101 ± 6	96 ± 3	94 ± 6
Phenothiazine	38 ± 6	36 ± 12	28 ± 10	19 ± 6	0	0	0	0
Fluoranthene	76 ± 4	66 ± 4	68 ± 2	51 ± 4	0	0	0	0
Anthracene	69 ± 5	64 ± 4	65 ± 4	50 ± 7	0	0	0	0
Phenanthrene	79 ± 6	67 ± 2	68 ± 9	67 ± 5	0	0	0	0

Conditions: identical to those described under Figure 1, except that the total mass of adsorbent was 100 mg, the sample introduction flow rate as 10mL min^{-4} and the volume was variable.

Effects of Water Type

Our objective in replacing the unbuffered H.P.L.C. quality water by tap water in the sample matrix was to examine the possible constraints undergone by the two varieties of mixed phases arising from the matter dissolved in the tap water.

We took as variable the mass percent of the C_{18} phase, all other experimental conditions remaining constant. Comparison of the values given in Tables 4 and 5 led us to the following conclusions :

Variations using the blended phases

With increasing percentage of the PRS phase in the blends, we observed with the tap water, and in each mass composition, that the recovery of quinoline was much lower. It even became zero for the blend with 90 % of the PRS phase.

For acridine, we noted the same tendency when we studied blends with high PRS percentages. These trends were confirmed with the PRS phase alone, with which, in tap water, the recoveries of these two pollutants were zero. This demonstrates that ion exchange is suppressed with the tap water.

Only hydrophobic interaction remained, since with the C_{18} phase alone the acridine recovery still remained total, as did that of the P.A.H. However, with the C_{18} phase alone, the recovery of quinoline still decreased. Some attenuation of the hydrophobic power of the C_{18} groups can occur, mainly affecting the least hydrophobic substances.

With phenazine, we observed a tendency for the recovery to improve slightly in tap water. Considering the preceding results, the weakening of the hydrophobic interactions with the C_{18} groups would be more than compensated by the strengthening of another type or interaction, almost certainly of a polar type.

Finally, for phenothiazine, there was no recovery in tap water, for any phase. It may suggest that interactions with some components from the tap water may occur.

There is no ozone in the water, whereas 0.01 $mg.l^{-1}$ of chlorine can be detected. By-products from phenothiazine oxidation does not seem possible. Scanning of chromatograms at different wavelengths does not evidence any by-products from phenothiazine.

Table 5

Effects of the Tap Water on the Percent Recoveries and R.S.D. (%), Using Various Types of Mixed Phases*

Phase Type **Compound**	**Bond Elut Certify**	**C_{18}**	**C_{18}/PRS 90/10**	**C_{18}/PRS 70/30**	**C_{18}/PRS 50/50**	**C_{18}/PRS 30/70**	**C_{18}/PRS 10/90**	**PRS**
para-Cresol	0	0	0	0	0	0	0	0
Quinoline	6 ± 6	37 ± 10	44 ± 7	32 ± 1	28 ± 8	12 ± 5	0	0
Phenazine	44 ± 8	96 ± 1	88 ± 5	78 ± 2	65 ± 3	43 ± 3	14 ± 3	0
Acridine	81 ± 3	108 ± 2	93 ± 3	92 ± 2	104 ± 5	86 ± 3	41 ± 2	0
Phenothiazine	0	0	0	0	0	0	0	0
Fluoranthene	87 ± 4	96 ± 6	94 ± 5	97 ± 3	99 ± 3	90 ± 2	55 ± 6	0
Anthracene	82 ± 9	88 ± 8	79 ± 2	73 ± 1	76 ± 3	79 ± 11	52 ± 3	0
Phenanthrene	101 ± 4	97 ± 5	89 ± 1	96 ± 1	98 ± 4	90 ± 2	63 ± 5	0

Conditions: identical to those described under Table 4, with a value of 1000 mL for the sample volume.

The tap water utilized in experiments contains inorganic cations. Water hardness (10 to 14° F) prevents cation exchange from both quinoline and acridine which are partly ionized.

Mn^{2+} and Fe^{3+} cations which can be detected at 0.02 $mg.l^{-1}$ and 0.04 $mg.l^{-1}$ respectively both enhance the phenomenon. Moreover it is well known that phenothiazines may be involved in coordination bonds especially with ferric ion.[19]

Spring waters utilized to produce drinking water may contain 2 to 6 $mg.l^{-1}$ of dissolved organic carbon (D.O.C.), 85 - 95 % of which come from « humic substances ».[20] Water treatment does reduce D.O.C. to 1.6 - 1.8 $mg.l^{-1}$ but « humic substances » are not totally eliminated. This may participate in charge transfer complexes with phenothiazine since this species is electron donating owing to the presence of an atom of sulfur. In the same way, thiobencarb recovery decreases when distilled water is spiked up to 10 $mg.l^{-1}$ with humic acid.[21]

Comparison between blended phases and the commercial mixed phase

In this case, for a given total mass of adsorbent, not only were the blended phases of C_{18}/PRS mass composition 90/10 and 70/30 very superior to the Bond Elut Certify phase, but those of composition 50/50 and 30/70 were also superior, particularly with respect to quinoline, phenazine, and to a lesser degree acridine.

This suggests that some masking of the sites is occuring. The proximity of the C_{18} and sulfonic groups in the Bond Elut Certify phase, where they are present on the same particle, effectively hinders access to the two functional groups since one of them may be masked.

The proximity of two types of functional groups could give an apparent advantage to the commercial phase.[13] In a non-chemically pure water we now emphasize its undeniable handicap.

CONCLUSION

The variation in composition between 20 and 80 % by mass of the C_{18} phase in the blended phases studied led to a quasi-linearity of the percent recoveries. From the sign of the slope of the straight line obtained, we deduced the principal retention mechanism operating for each pollutant.

Replacement of the mechanically blended phases by a tandem configuration with continuous sample deposition on the two types of adsorbent offered no advantages. However, the effect of volume showed that it is advantageous to use the mechanically blended phases when the percentage of water in the sample was high, since some C_{18}/PRS compositions give percent extractions, practically insensitive to flow rate variations, which are higher than those obtained with the mixed phase with two functional groups on the same particle.

When tap water is utilized instead of pure distilled water there is no reason to use the commercially available solid support. First of all observed recoveries, starting with same amount, are less than those obtained from mixed phases and then the cost for sample is higher. The main advantage of mixed phases lies in the wide possible selection of different supports which can be easily handled.

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