

<https://doi.org/10.3176/oil.1997.4S.10>

## CONCENTRATION OF OIL SHALE ORIGINATED PHENOLS BY SPE

I. JOHANNES  
L. MÖLDER  
L. TIIKMA

Institute of Chemistry  
Tallinn, Estonia

*The solid phase extraction (SPE) efficiency of 5-methylresorcinol on a variety of cartridges is compared. On the best cartridge found, Bakerpond SDB 1, the SPE characteristics for hydroxybenzene, resorcinol, 5-methylresorcinol and 2,5-dimethylresorcinol are evaluated. Distribution factors and sorption rate factors for these systems are estimated. The effect of NaCl on the SPE efficiency is interpreted.*

### Introduction

Oil shale retorting products are the main source of phenolic pollutions in Estonia. Specific to "kukersite", 80-90 % of the water-soluble phenols belong to the resorcinol (1,3-benzenediol) series dihydric phenols and only 10-20 % to the widely known monohydric phenols. The minimal detection limit for hydroxybenzene and resorcinol series phenols under direct colorimetric method is 0.1 ppm [1, 2] and under GC method 1 ppm [3].

To observe the distribution of hydroxybenzene and resorcinol series compounds in ground water or in the Gulf of Finland, their preconcentration should take place. A new technique, solid phase extraction (SPE) [4-7], seems to be attractive for that purpose. This simple procedure involves passing a definite volume of the sample through a sorbent layer and eluting the trapped sorbate from the cartridge with a small volume of an appropriate solvent.

Many papers, e.g. [8-13], dealing with preconcentration of monohydric phenols by SPE prior GC and LC analysis have been published. Only our study [4] deals with SPE of a dihydric phenol, resorcinol. The recovery of hydroxybenzene series phenols on ethyl-, butyl-, octyl-, cyclohexyl- and phenyl-bonded silica phase sorbents as well on styrene-divinylbenzene series copolymers has been studied.

In papers [8, 9] on the 1.2 g of cyclohexyl bonded silica phase over 80 % recovery of 2-methylphenol, 2,4- and 3,5-dimethylphenols, 2,3,5-trimethylphenol and pentachlorophenol from 50-100 cm<sup>3</sup> of water was obtained. Only hydroxybenzene (phenol), the most water-soluble compound in the series, retained poorly (24-37 %). Addition of NaCl to the sample increased to some extent the recovery of phenols. At lower concentrations the recovery decreased.

At a concentration of 1 ppb the recovery of hydroxybenzene on an octadecylsilane-bonded phase from the 25-30 cm<sup>3</sup> sample volume was 76 %. The corresponding distribution factor was 55.4 [10].

When 300 mg of the sorbent Bakerbond C18 Polar Plus was used [11], the recovery of 10 ppb hydroxybenzene from 250 cm<sup>3</sup> solution of 20 % NaCl was 78 %.

Sorbent Bakerbond SDB 1 seems to have the best affinity with hydroxybenzene. According to the "Service Method Instruction" [12], on 200 mg of this sorbent the recovery of 11 phenolic compounds (hydroxybenzene and its chloro- and nitro-derivatives, á 20 ppm) was 89-100 %, having been preconcentrated from 75 cm<sup>3</sup> of the sample at a flow rate of 30 (!) cm<sup>3</sup>/min.

In all methods described above, the efficiency of SPE was evaluated by recovery percentage. As a matter of course, before breakthrough, this quantity has to be 100 % and further to depend on the solution volume passed. So, the recovery percentage describes a definite procedure but cannot predict the extraction efficiency under different conditions.

Recently we have modified the Bochart-Adams equation into bed depth-service volume (BDSV) model [4]. It was deduced that when the external diffusion is the limiting factor for the sorption rate, the breakthrough volume could be approximated to a linear relationship with the reciprocal of the influent concentration

$$V(\text{max}) = A - B/C_0 \quad (1)$$

with

$$A = k G/d \quad (2)$$

and

$$B' = (S/f) \ln [C_0/C(\text{max}) - 1] \quad (3)$$

where  $C_0$  - influent concentration,  $\mu\text{g}/\text{cm}^3$

$C(\text{max})$  - maximal admissible effluent concentration,  $\mu\text{g}/\text{cm}^3$

$G$  - mass of sorbent, g

$k$  - dynamic distribution factor,  $(\mu\text{g}/\text{cm}^3)_s / (\mu\text{g}/\text{cm}^3)_l$

$d$  - density of sorbent layer,  $\text{g}/\text{cm}^3$

$S$  - cross-section area of cartridge,  $\text{cm}^2$

$f$  - sorption rate factor,  $\text{cm}^2/\mu\text{g}$

We have proposed to estimate the values of  $k$  and  $f$  from the slope and intercept plotting the function  $Z = (w/C_0) \ln(C_0/C - 1)$  versus solution volume,  $V$  ( $w$  volume flow rate,  $\text{cm}^3/\text{min}$ ). An experimental breakthrough curve has to be built under the conditions of interest at SPE. Only  $C_0$  can be increased up to the region detectable without preconcentration.

In paper [4] the BDSV model was applied to compare the SPE characteristics for hydroxybenzene and resorcinol on the cartridge Bakerbond SDB 1.

The aim of this work is to evaluate by the BDSV model the SPE efficiency for main representatives of oil shale originated phenols on a variety of cartridges.

## Experimental

Following the BDSV method, two chromatographic sorbents and some specific cartridges for SPE from VARIAN and BAKERBOND were evaluated. To compare affinity of the sorbents with phenolic compounds, 5-methylresorcinol, the dominating component in oil shale originated water-soluble phenols, was applied. The SPE efficiency for hydroxybenzene (Ph), resorcinol (R), 5-methylresorcinol (5-MR) and 2,5-dimethylresorcinol (2,5-DMR) was studied on Bakerbond SDB 1. The sorbent proved to be the most suitable solid phase for dihydric 5-MR in this work. The co-extraction of Ph and R were evaluated. An influence of a "salting out" agent, NaCl, on SPE characteristics was studied using 5-MR and a mixture of Ph and 5-MR.

Flow rate was held constant during an experiment by a peristaltic pump. The inner cross-section of the cartridges was  $1 \text{ cm}^2$ .

Liquefied Ph (7.5 %  $\text{H}_2\text{O}$ ) from Fisher Scientific and crystalline R, 5-MR  $\cdot \text{H}_2\text{O}$  and 2,5-DMR (assay 98-99 %), separated from oil shale originated water soluble hydroxybenzenes, were applied.

The concentration of individual compounds was estimated colorimetrically [1, 2]. For selective determination of Ph in presence of 5-MR in two-component solutions the reagent amidopyrine was used instead of 4-aminoantipyrine.

All extractions were carried out as follows. The cartridge was first conditioned by the addition of  $5 + 5 \text{ cm}^3$  of ethanol, which was allowed to set for 5 min prior to being drawn off. The cartridge was then flushed with  $5 + 5 \text{ cm}^3$  of 0.01 M HCl. The pH of samples was adjusted to 2-2.5, except when anionexchangers were used, in which case pH was adjusted to 7-9. The volume flow rate was  $2-5 \text{ cm}^3/\text{min}$ . Samples for testing were taken after every  $10-50 \text{ cm}^3$ . Finally the sorbate was eluted with  $5 + 5 \text{ cm}^3$  of ethanol. The both portions were allowed to remain in the cartridge for 5 min prior to being drawn off.

The extraction conditions used are presented in Tables 1 and 2.

Table 1. Conditions of SPE for 5-Methylresorcinol

Test number	Cartridge	Producer	Sorbent		Solution			
			Composition	$d$ , g/cm <sup>3</sup>	$G$ , g	$C_0$ , mg/dm <sup>3</sup>	pH	$w$ , cm <sup>3</sup> /min
1	Polyorb I	Waters Associates, Milford	Vinyl-divinylbenzene	0.24	0.57	0.5	2.5	2.73
2	Porapak Q	Reachim, Kharkov	Ethylvinyl-divinylbenzene	0.28	0.80	"	"	3.39
3	EnvirElite Phenol	VARIAN	Vinyl-divinylbenzene	0.57	2.84	"	"	2.68
4	PH	"	≡ Si - phenyl	0.873	0.50	1.0	"	4.29
5	SAX	"	≡ Si - (CH <sub>2</sub> ) - N(CH <sub>3</sub> ) <sub>3</sub>	"	"	"	7.0	3.98
6	NH <sub>2</sub>	"	≡ Si - (CH <sub>2</sub> ) <sub>3</sub> - NH <sub>2</sub>	"	"	"	8.9	3.96
7	Bakerbond SPE SDB 1	BAKER's Chemicals	Vinyl-divinylbenzene	0.354	0.20	"	2.5	4.07

Table 2. Conditions of SPE for Phenolic Compounds on SDB 1 ( $G = 0.2$  g)

Test number	Sorbate	$C_0$ , mg/dm <sup>3</sup>	pH	$w$ , cm <sup>3</sup> /min
7	5-MR	1.0	2.5	4.07
8	R	0.963	"	3.29
9	2,5-DMR	0.827	"	4.08
10	Ph	1.0	"	4.22
11	5-MR	"	2.5 (25 % NaCl)	3.04
12	Ph + 5-MR	"	2.5	4.05
13	Ph + 5-MR	"	2.5 (25 % NaCl)	1.36

## Results

### Breakthrough Curves

The elution percentage of retained solutes in every experiment exceeded 90 %. Therefore elution was not detailed in this study.

Breakthrough curves were developed plotting the effluent concentration versus the solution volume.

Curves for 5-MR (Fig. 1a) demonstrate that Polysorb 1 (curve 1), having been an effective sorbent both for hydroxybenzene and resorcinol series phenols at GC, is quite unsuitable at SPE. The presence of 5-MR in the first drops of the effluent indicates a very low sorbent capacity. The slope of the curve suggests also a slow sorption.

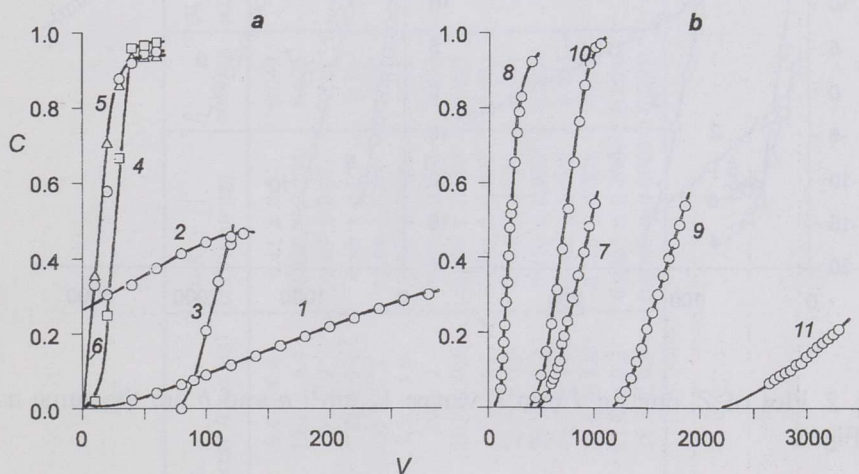


Fig. 1. Plot of  $C$ ,  $\mu\text{g cm}^{-3}$ , versus  $V$ ,  $\text{cm}^3$ : a - 5-methylresorcinol on sorbents listed in Table 1; b - sorbates listed in Table 2 on SDB 1

The other sorbent for GC, Porapac Q (curve 2), has a markable sorption capacity, but the sorption rate is even lower than on Polysorb 1.

The affinity of commercial cartridges from VARIAN containing a sorbent PH (curve 4) as well as anionion exchangers SAX (curve 5) and  $\text{NH}_2$  (curve 6) with 5-MR is fragile.

More effective is a VARIAN special SPE sorbent EnvirElute Phenol (curve 3). In this experiment the breakthrough point occurs at the effluent volume of about  $80 \text{ cm}^3$ . In particular, it must be noted that in this cartridge the sorbent mass is high, 2.89 g (Table 1). By the way, in VARIAN high-capacity cartridges, Mega Bond Elute SPE, the mass of sorbent is even 5 g.

In accordance with the published results dealing with SPE of monohydric phenols, the sorbent Bakerbond SDB 1 proves to have the largest effluent volume at breakthrough point for 5-MR,  $500 \text{ cm}^3$

(Fig. 2b, curve 7). At that, the applied commercial cartridge contains only 0.2 g of SDB 1.

The affinity of phenolic compounds with SDB 1 (Fig. 2b, curves 7-10) increases in order  $R < Ph < 5\text{-MR} < 2,5\text{-DMR}$ , according to their hydrophobicity and solubility.

25 % of NaCl (curve 11) displace the breakthrough point for 5-MR from 500 to 2300  $\text{cm}^3$ . Unfortunately, the increase of capacity occurs together with the essential decrease of sorption rate.

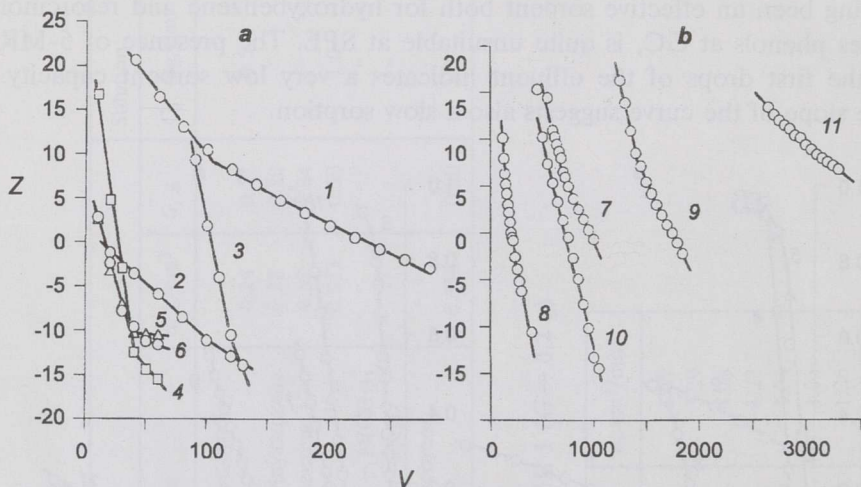


Fig. 2. Plot of  $Z$ ,  $\text{cm}^6 \mu\text{g}^{-1} \text{min}^{-1}$ , versus  $V$ ,  $\text{cm}^3$ . *a* and *b* are the same as in Fig. 1

### Function $Z$

For a quantitative evaluation of SPE efficiency, in Fig. 2 the values of the function  $Z = (w/C_0) \ln(C_0/C - 1)$  are plotted versus the corresponding volumes,  $V$ , of the effluent. The results give evidence that only when hydroxybenzene is extracted (curve 10) the relationship between  $Z$  and  $V$  is a straight line, as it has been assumed theoretically. When resorcinol series phenols are extracted, the slope, equivalent to rate constant  $K$ , does not have a constant value. The transition of the sorption characteristics during the extraction procedure gives a reference to a complicated multistage mechanism at SPE when dihydric phenols are extracted. For example, a secondary sorption of  $R$ , 5-MR and 2,5-DMR on their adsorbed layer might combine. As far as the breakthrough is of interest, the values of  $Z$  and  $V$  from the first linear part of the function  $Z$  were turned to account only. The lower limits of  $Z$  and  $V$  for the calculation were prescribed as 10 % by the precision of the analytical method applied.

Table 3. Characteristics of Cartridges

Test number	Cartridge	Sorbate	$a$ , (cm) <sup>6</sup> /(min $\mu$ g)	$b \equiv K$ , cm <sup>3</sup> /(min $\mu$ g)	$f$ , cm <sup>2</sup> /mg	$N$ , $\mu$ g/cm <sup>3</sup>	$k$ , ( $\mu$ g cm <sup>3</sup> ) <sub>s</sub> / ( $\mu$ g cm <sup>-3</sup> ) <sub>l</sub>	$A$ , cm <sup>3</sup>	$B^*1$ , $\mu$ g
1	Polyorb 1	5-MR	0.4 $\pm$ 0.4	0.11 $\pm$ 0.01	0.040	6.8	14	29	54
2	Porapac Q	"	19.2 $\pm$ 0.4	0.088 $\pm$ 0.004	0.026	38.4	77	138	85
3	EnvirElute Phenol	"	67 $\pm$ 2	0.65 $\pm$ 0.02	0.24	10.4	21	18	9.2
4	PH	"	22 $\pm$ 2	0.86 $\pm$ 0.05	0.20	45.0	45	26	11
5	SAX	"	59 $\pm$ 1.2	0.44 $\pm$ 0.04	0.11	24.5	24	14	20
6	NH <sub>2</sub>	"	5.5 $\pm$ 1.9	0.36 $\pm$ 0.06	0.09	26.3	26	15	24
7	Bakerbond SDB 1	"	39 $\pm$ 2	0.046 $\pm$ 0.002	0.011	1500	1500	2125	200
8	"	R	21.7 $\pm$ 0.5	0.109 $\pm$ 0.003	0.037	339	350	500	53
9	"	2,5-DMR	71 $\pm$ 4	0.044 $\pm$ 0.003	0.011	2488	3000	4250	200
10	"	Ph	32.5 $\pm$ 0.7	0.045 $\pm$ 0.001	0.011	1280	1280	1800	200
11	"	5-MR (25 % NaCl)	39.5 $\pm$ 0.7	0.010 $\pm$ 0.002	0.0020	6990	6990	9875	1100
12	"	Ph	42.5 $\pm$ 1.6	0.062 $\pm$ 0.002	0.015	1210	12000	1690	146
"	"	5-MR	31.6 $\pm$ 1.0	0.040 $\pm$ 0.001	0.010	1400	1400	1980	220
13	"	Ph	21.3 $\pm$ 0.2	0.0063 $\pm$ 0.0004	0.0046	5980	5980	8450	480
"	"	5-MR (25 % NaCl)	18.5 $\pm$ 0.9	0.0049 $\pm$ 0.0003	0.0031	6683	6650	9390	709

Note: \*1 Mass of the sorbents is 0.5 g.

### SPE Characteristics

In Table 3 the numerical values for the factors  $a$  and  $b$  in the relationship  $(w/C_0) \ln(C_0/C - 1) = a - bV$  and the SPE characteristics found from  $a$  and  $b$  are presented:

Capacity	$N = a d C_0 / (b G)$
Distribution factor	$k = N/C_0$
Sorption rate constant	$K \equiv b$
Rate factor	$f = b/v$ ( $v$ - linear flow rate)
$A$ and $B'$ (Equation (1)) for cartridges with $G$ 0.5 g	

The results suggest that for 5-MR the distribution factor on the Bakerbond sorbent SDB 1 overcomes nearly 100 times that on the other sorbents studied. At the same time, the kinetic characteristic on SDB 1 is lower than on the other sorbents.

It is notable that the same chemical composition of sorbents can yield quite different characteristics. So, distribution factors for 5-MR on Polysorb 1, EnvirElute Phenol and SDB 1, all of them being copolymers of vinyl- and divinylbenzene, are respectively 14, 21 and 1500. The sorption rate factors on the sorbents are, respectively, 0.041, 0.24 and 0.011. Consequently, the distribution factors and sorption rate factors do not correlate.

When 25 % of NaCl is added, the distribution factor for 5-MR on SDB 1 increases from 1500 up to 6990, while the sorption rate factor decreases from 0.011 to 0.002.

The gain in sorption capacity and the loss in sorption rate are taken into account by the factors  $A$  and  $B'$  in the Equation (1) (Table 3). The straight lines illustrate the corresponding SPE limits on the Fig. 3.

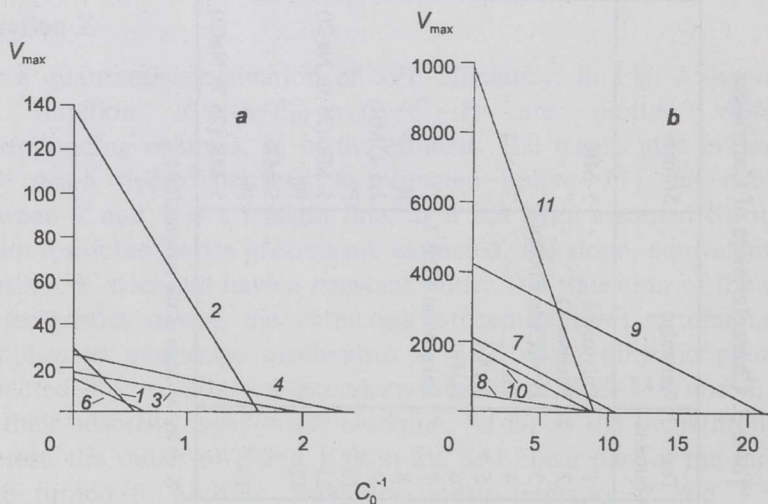


Fig. 3. Plot of  $V(\max)$ ,  $\text{cm}^3$  versus  $C_0^{-1}$ ,  $\text{cm}^3 \mu\text{g}^{-1}$ .  $a$  and  $b$  are the same as in Fig. 1



Actually, at higher values of  $C_0$  these lines must curve, due to the change of the linear isotherm into the Freundlich isotherm (4).

$$N = pC_0^{1/n} \quad (4)$$

Then

$$V(\max) = p G C_0^{1/n - 1/d} - (S/f) \ln(C_0/C - 1) \quad (5)$$

Therefore, at the region of higher  $C_0$  the real values of  $V(\max)$  must be smaller than the depicted ones. When the real values of  $V(\max)$  are needed, the factors  $p$  and  $n$  must be established building in this region some breakthrough curves under different  $C_0$ . But as a rule, for preconcentration the latter region is not of interest.

Fig. 3a demonstrates the absolute unsuitability of the cartridge Polysorb 1 (curve 1), and  $\text{NH}_2$  (curve 6) for SPE of 5-MR because the positive values of  $V(\max)$  can be obtained only under high values of  $C_0$ .

On the cartridges EnvirElut Phenol (curve 3), PH (curve 4) and Porapac Q (curve 2) the theoretical value of  $V(\max)$  at  $C_0 = 1 \text{ mg/dm}^3$  is positive, respectively 9, 15 and  $53 \text{ cm}^3$ . On these sorbents, due to the increase of sorption rate, the immediate breakthrough of 5-MR occurs under influent concentrations, respectively, 0.51, 0.42 and  $0.62 \text{ mg/dm}^3$ . Obviously such results do not satisfy needs for a preconcentration, especially for a colorimetric analysis when the detection limit without preconcentration is  $0.1 \text{ mg/dm}^3$ .

The efficiency of the Bakerbond SDB 1 (Fig. 3b) is better than that of the sorbents described above. When 0.5 g of SDB 1 is used at  $C_0 = 1 \text{ mg/dm}^3$ , the maximal solution volume of 5-MR is  $1925 \text{ cm}^3$  (curve 7). The number of hydroxyl and methyl substituents in the solute molecule has a vital influence on the SPE efficiency. So, under the latter conditions  $V(\max)$  for R is only  $450 \text{ cm}^3$  (curve 8), for Ph  $1600 \text{ cm}^3$  (curve 10) and for 2,5-DMR  $4050 \text{ cm}^3$  (curve 9). Such large values of  $V(\max)$  provide a high enrichment factor when a small volume of an elution solvent is used. Despite the large, but different values of  $V(\max)$ , the critical values of  $C_0$ , leading to the immediate breakthrough,  $C_0(\text{cr})$ , are relatively high and close together.

When 25 % of NaCl is added at  $C_0 = 1 \text{ mg/dm}^3$ ,  $V(\max)$  for 5-MR increases even up to  $8770 \text{ cm}^3$  (curve 11). But since a deep decrease of sorption rate accompanies, the concentration of the immediate breakthrough is still  $0.11 \text{ mg/dm}^3$ .

Subsequently, among the studied SPE systems not one was found being suitable for the preconcentration of oil shale originated phenols below  $0.1 \text{ mg/dm}^3$  without losses. The simplest way to lower the limit of  $C_0$  is to increase sorbent mass. For example, it is easy to calculate that for the complete retention ( $C/C_0 = 0.1$ ) of 5-MR at  $C_0 = 0.1 \text{ mg/dm}^3$  and  $V = 500 \text{ cm}^3$ , mass of SDB 1 should be 6.5 g. But larger  $G$  would bring

about a higher cost of the cartridge and the enrichment factor would diminish as well.

## Conclusions

1. The efficiency of solid phase extraction (SPE) sorbents for phenolic compounds increases in the order of: Polysorb 1 < NH<sub>2</sub> < SAX < < EnvirElute Phenol < PH < Porapac Q << Bakerbond SDB 1.
2. Affinity of phenolic compounds with the sorbent Bakerbond SDB 1 ranges as: resorcinol < hydroxybenzene, 5-methylresorcinol < < 2,5-dimethylresorcinol.
3. The solution volume being concentrated without losses decreases linearly versus reciprocal of the influent concentration. The critical concentration depends on the distribution factor and sorption rate factor.
4. Distribution factors and sorption rate factors for Ph, R, 5-MR and 2,5-DMR on SDB 1 are determined.
5. When NaCl is added to the solution preconcentrated on SDB 1, the distribution factor increases and the sorption rate factor decreases. Consequently, in the studied system NaCl can favour SPE only when the effluent concentration of 5-MR is over a critical value.
6. The best of the studied cartridges, containing 0.5 g SDB 1, enables preconcentration of 5-methylresorcinol only in cases where the effluent concentration is over 0.1 mg/dm<sup>3</sup>. To guarantee a complete retention of phenolic compounds under the lower concentrations, mass of the sorbent should be increased or the cross-section of the cartridge should be decreased.

## Acknowledgement

We acknowledge the financial support provided by the Estonian Science Foundation. Grants 1228 and 1229.

## REFERENCES

1. Standard Test Method for Phenolic Compounds in Water. ASTM D1783-96.
2. Johannes I., Mölder L., Pauku Y., Tiikma L. A colorimetric method for selective determination of non-volatile hydroxybenzenes in water // Oil Shale. 1995. Vol. 12, No. 4. P. 297-304.

3. Standard Test Method for Phenols in water by Gas-Liquid Chromatography. ASTM D 2580-94.
4. *Johannes I., Mölder L., Tiikma L.* Evaluation of solid phase extraction limits // Oil Shale. 1997. Vol. 14, No. 1. P.41-49.
5. Application Bibliography. Varian Sample Preparation Products.- Harbor City, California 1992.
6. *Blevins D. D., Burke M. F., Good Th. I. et al.* Sorbent Extraction Technology. Handbook / Ed. by N.Simpson, K.C. Horne. - Harbour City, California. 1993.
7. Separating Funnels are Old News. Today's Alternative BAKERBOND spe. Price List.- Phillipsburg, USA.1995.
8. *Chladek E., Marano R. S.* Use of bonded silica sorbents in the sampling of priority pollutants in wastewaters // J. Chromatogr. Sci. 1984. V. 22. P. 313-320.
9. *Rostad C. E., Pereira W. E., Ratcliff S. M.* Bonded-phase extraction column isolation of organic compounds in groundwater at hazardous waste site // Anal. Chem. 1984. V. 56, No. 14. P. 2856-2860.
10. *Stoup R. E., Mayer G. S.* Determination of environmental hydroxybenzenes by liquid chromatography/electrochemistry // Anal. Chem. 1982. V. 54, No. 7. P. 1164-1169.
11. Extraktion von Phenolen aus Wasser mit Bakerbond SPE C18 Polar Plus. The BAKER SPE Service. AN 377.Art. Nr. 7466-10. 1993.
12. Phenole aus Wasser mit Bakerbond SDB 1. The BAKER SPE Service. AN 393. Art. No. 7519-02. 1996.
13. Phenolic Extraction. EnvirElut Extractions. EPA method 604.-Varian Sample Preparation Products. Harbor City, California. 1991.
14. *Iokhannes I. K., Ignat A. V., Zabellevich I. V.* Sorption of 5-methylresorcinol by AV-17  $\times$  8 anion exchanger // Russian Journal of Applied Chemistry. N-Y. 1993. V. 66, No. 2. P. 1571-1574.

*Presented by J. Kann*

Received November 21, 1996