SOLID-PHASE DISK EXTRACTION
OF RESORCINOL SERIES PHENOLS
BY BAKERBOND *Speedisk*™ DVB

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Solid-phase disk extraction of resorcinol-series phenols, the main compo-nents of oil-shale-originated phenolic pollution, is described by bed depth-service volume model. The effect of concentration ($C_0 = 0.025$–1.5 mg dm^{-3}) and flow rate ($w = 3.3$–97 cm^3 min^{-1}) on the dynamic capacity and the extraction rate constant γ for disk extraction of resorcinol (R), 5-methyl-resorcinol (5-MR) and 2,5-dimethylresorcinol (2,5-DMR) on the disk BAKERBOND Speedisk™ SDB is studied.

The linear isotherm is revealed with distribution factors for R – 55; 5-MR – 265, and 2,5-DMR – 553 (mg dm^{-3})$_S$/(mg dm^{-3})$_L$. The proportional increase of γ with increase in w and in C_0^{-1} is proved.

Introduction

Alkylderivatives of 1,3-dihydroxybenzene, alkylresorcinols, are the main components of phenolic pollution coming from Estonian oil shale thermal destruction products. The enacted maximum admissible concentration of pollution by total dihydric phenols in ground and bottom water is 0.1 mg dm^{-3}. The conditions are regarded to be good when the total content is 0.001 mg dm^{-3} [1].

A preconcentration step is necessary for testing concentrations below 0.1 mg dm^{-3} using gas-chromatographic or spectrophotometric methods [2]. Nowadays, solid-phase extraction (SPE) is the common technique for sample enrichment. A typical SPE cartridge consists of a small column containing 100–500 mg of a chemically bound silica sorbent or polymeric resin. The small cross-section area of cartridges results in slow sample processing rates. Channelling reduces the capacity of the cartridge to retain analytes. The recently developed particle-loaded membranes, SPE disks, enhance the process. Due to the larger cross-sectional area and decreased pressure drop the disks provide shorter processing time and reduced channelling compared

with SPE cartridges. However, the loading recoveries for disks are found to be lower than for cartridges under the same conditions [3].

The loading recovery is controlled by capacity and kinetic parameters. In our previous paper [4] these parameters were evaluated for preconcentration of (Ph), resorcinol (R), 5-methylresorcinol (5-MR) and 2,5-dimethylresorcinol (2,5-DMR) on a variety of commercial SPE cartridges. The mathematical model applied in this work was based on another starting point than the usual experiment-based chromatographic one. Namely, the bed depth-service time model, common in the field of chemical engineering [5], was modified and expressed as the bed depth-service volume (BDSV) model:

$$\ln(C_0C^{-1} - 1) = \ln[\exp(\gamma A W w^{-1}) - 1] - \gamma C_0 w^{-1} V \qquad (1)$$

where C_0 is solute influent concentration, mg dm^{-3};

$\quad C$ is solute effluent concentration, mg dm^{-3};

$\quad \gamma$ is rate constant, dm^3 mg^{-1} min^{-1};

$\quad A$ is sorbent dynamic capacity, mg dm^{-3} = µg cm^{-3};

$\quad W$ is sorbent bed volume, cm^3;

$\quad w$ is volume flow rate, cm^3 min^{-1};

$\quad V$ is solution volume passed the cartridge, cm^3.

When all the parameters above, except C and V, are constant, Equation (1) must represent a linear relationship

$$Q = a - bV \qquad (2)$$

where

$$Q = \ln(C_0C^{-1} - 1) \qquad (3)$$

$$a = \ln[\exp(\gamma A W w^{-1}) - 1] \qquad (4)$$

$$b = \gamma C_0 w^{-1} \qquad (5)$$

Therefore, γ and A can be easily evaluated from the slope and intercept of the experimentally established plot of Q versus V as follows:

$$\gamma = bw C_0^{-1} \qquad (6)$$

and

$$A = C_0(bW)^{-1} \ln(1 + \exp a) \qquad (7)$$

For the best cartridge found, BAKERBOND^{TM} SDB 1, when C_0 was 1 mg dm^{-3}, the following characteristics were estimated:

A, mg dm^{-3}: R – 364
5-MR – 1490
2,5 – DMR – 2990

γ, dm^3 mg^{-1} min^{-1}: R – 102   ($w = 3.29$ cm^3 min^{-1})
5-MR – 47   ($w = 4.07$ cm^3 min^{-1})
2,5 DMR – 45   ($w = 4.08$ cm^3 min^{-1}).

The data in the work [4] were found assuming that the sorption isotherm is linear and the sorption rate is proportional to the linear flow rate. Presumption of the linear isotherm was applied in the former models [6, 7] as well, where the breakthrough volume at SPE was predicted by equations containing distribution factor, or by a polynomial solvation parameter model without any concentration contribution. The kinetic parameter was found to be insignificant for columns with high plate numbers ($n \geq 25$) [8].

Poole et al. [7] have shown a linear decrease of breakthrough volume for SPE cartridge devices in the flow-rate region 10–50 $cm^3 min^{-1}$. However, for disks the breakthrough volume was found not being strongly affected by flow rate in the range 10–30 $cm^3 min^{-1}$. At both higher and lower flow rates a decrease in the breakthrough volume was expected. The highest plate number for disks, nine, was found at the flow rate 13 $cm^3 min^{-1}$ [9].

The aim of this paper is to characterise the effects of concentration and flow rate on the disk extraction of resorcinol-series phenols, R, 5-MR and 2,5-DMR, using BDSV model.

Experimental

The sorbent BAKERBOND *Speedisk*™ DVB was chosen as a patented extraction disk for use in preparing for analysis aqueous samples containing moderately polar compounds such as phenols [10]. The disk is suggested as ideal for preparation of large volume of samples. The bed dimensions are 50 mm by diameter and 0.5 mm by height ($W = 0.981 \ cm^3$). The sorbent divinyl benzene polymer has spherical 10 μ microparticles and is supported on a fritted glass filter.

All extractions were carried out as follows. The disk was first conditioned by the addition of 5 + 5 cm^3 of ethyl alcohol, which was allowed to set for 5 min before being drawn off. The disk was flushed with 5 + 5 cm^3 of 0.01M HCl and then 1 dm^3 of the solution adjusted with HCl to pH 2–2.5 was passed through the disk. Samples for breakthrough curves were taken after every 20–30 cm^3. The exact amount of the samples V_i was estimated by weight. The effluent concentration C_i was estimated in an appropriate aliquot of the sample. Finally the sorbate was eluted with 5 + 5 cm^3 of ethyl alcohol. Both portions were allowed to remain in the cartridge for 5 min before being drawn off. The disk was rinsed with distilled water. The solutions obtained were collected in a 25-cm^3 volumetric flask and, if necessary, diluted before analysis.

The concentration of resorcinols was estimated by a spectrophotometer *SPEKOL 10* at 420 nm as that of a yellow compound with *p*-nitroaniline [11].

The influent concentration of the alkylresorcinols was varied in the ranges 0.025–1.5 mg dm^{-3}. Naturally, it was impossible to obtain break-through curves experimentally for the concentration region, which could not

be tested without preconcentration. Therefore, only the eluted amount of the analyte was estimated for concentrations being below the sensitivity of the test method.

The flow rate was varied in the ranges 3–97 cm³ min⁻¹ and held constant during an experiment (± 0.1 cm³ min⁻¹) by a peristaltic pump.

Results and Discussion

Effect of Concentration on A and γ

The effect of concentration was studied applying the device flow rate, 9.3 cm³ min⁻¹. The breakthrough curves obtained (Fig. 1) demonstrate a considerable difference between disk extraction efficiency of R (Fig. 1,*a*), 5-MR (Fig. 1,*b*) and 2,5-DMR (Fig. 1,*c*). An increase in the breakthrough volume in the row R<5-MR<2,5-DMR proves that the DVB sorbent declared for moderately polar compounds prefers the more hydrophobic sorbates among the alkylresorcinols studied.
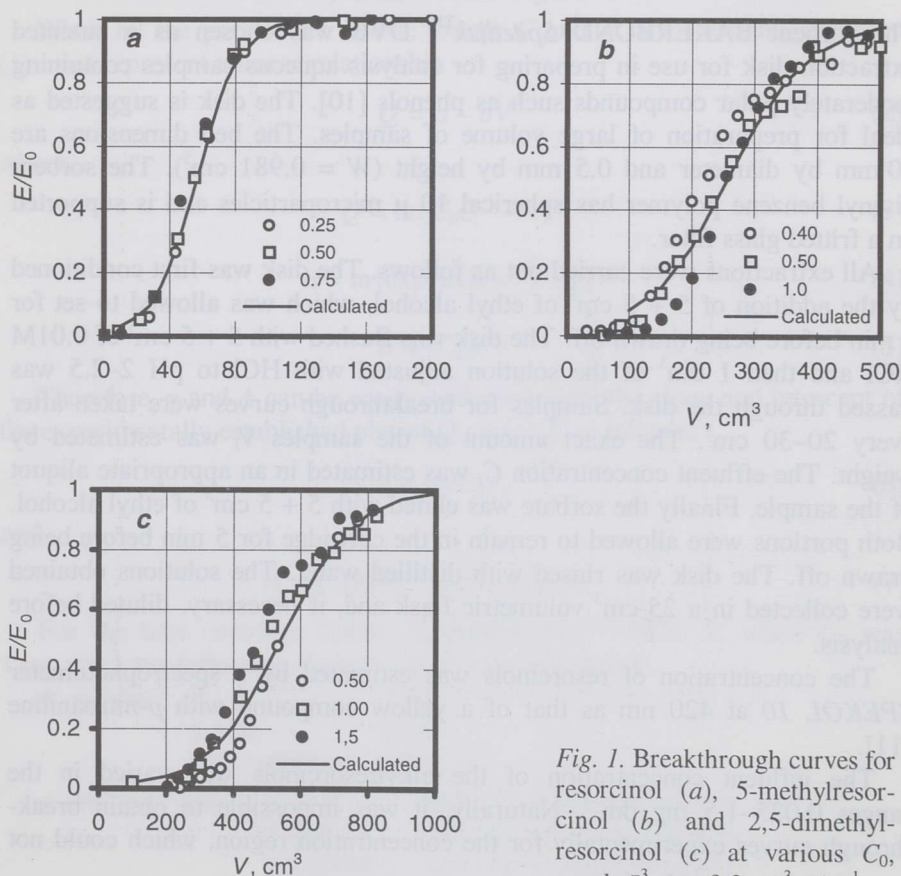

Fig. 1. Breakthrough curves for resorcinol (*a*), 5-methylresorcinol (*b*) and 2,5-dimethylresorcinol (*c*) at various C_0, mg dm⁻³. w = 9.3 cm³ min⁻¹

Noteworthy is that the plots of E/E_0 versus V obtained at various C_0 are quite close. The reduction of the concentration effect suggests that a linear isotherm

$$A = kC_0 \tag{8}$$

where k is distribution factor is in force for the disk devices studied.

To estimate BDSV model and disk extraction characteristics the function

$$Q = \ln(C_0 C^{-1} - 1) = \ln(E_0 E^{-1} - 1) \tag{9}$$

was plotted versus V using the values of EE_0^{-1} in Fig. 1 between 5–80 % giving the most reliable values for Q.

Figure 2 demonstrates that the plots can be approximated to linear tradelines, as it has been assumed theoretically. The linear plot of Q versus V evidence that the values of A and γ are practically constant during a disk extraction process.

The close values of b for various effluent concentrations evidence that the so-called rate constant γ and C_0 are actually inversely proportional:

$$\gamma_w = \chi_w C_0^{-1} \tag{10}$$

where χ_w is rate factor (min^{-1}) valid at the flow rate w.

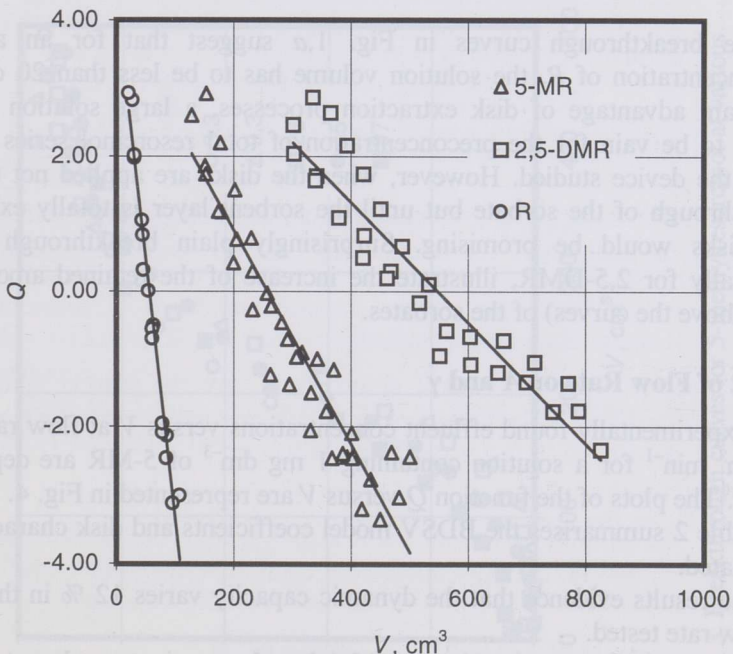Effect of w on the factor will be discussed later.

Fig. 2. Plot of function Q values versus solution volume for experimental data in Fig. 1

Table 1. **The BDSV-Model Coefficients
and Disk Characteristics; $w = 9.3$ cm^3 min^{-1}**

Coefficients and characteristics	R	5-MR	2,5-DMR
	Concentration region, mg dm^{-3}		
	0.25–0.75	0,5–1.0	0.5–1.5
a	4.35	4.08	5.03
$-b$, cm^{-3}	0.0768	0.0158	0.0093
r_Q	0.984	0.944	0.953
k, (mg dm^{-3})$_S$/(mg dm^{-3})$_L$	58	265	553
χ_w, min^{-1}	0.71	0.15	0.086

Table 1 summarises the BDSV model coefficients found for Equation (2), and the disk extraction factors for Equations (8) and (10).

The accordance of the experimental points and breakthrough curves predicted by the relationship

$$EE_0^{-1} = [1 + \exp(a - bV)]^{-1} \tag{11}$$

and presented in Figure 1 proves suitability of BDSV model for disk extraction.

The results obtained evidence that the dynamic capacity of the disk tested for alkylresorcinols is 6–7 times lower than that of the best cartridge in paper [4].

The breakthrough curves in Fig. 1,*a* suggest that for an adequate preconcentration of *R*, the solution volume has to be less than 20 cm^3. So, the main advantage of disk extraction processes, a large solution volume, seems to be vain for the preconcentration of total resorcinol series phenols using the device studied. However, when the disks are applied not until the breakthrough of the sorbate but until the sorbent layer is totally exhausted, the disks would be promising. Surprisingly plain breakthrough curves, especially for 2,5-DMR, illustrate the increase of the retained amount (the area above the curves) of the sorbates.

Effect of Flow Rate on *A* and γ

The experimentally found effluent concentrations versus *V* at flow rates 3.3–97 cm^3 min^{-1} for a solution containing 1 mg dm^{-3} of 5-MR are depicted in Fig. 3. The plots of the function *Q* versus *V* are represented in Fig. 4.

Table 2 summarises the BDSV model coefficients and disk characteristics calculated.

The results evidence that the dynamic capacity varies 12 % in the ranges of flow rate tested.

Figure 5 illustrates that the plot of *A* has the maximum value at the flow rate 13 cm^3 min^{-1}. Just the same flow rate was calculated to correspond to the minimum plate height by Fernando *et al.* [9].

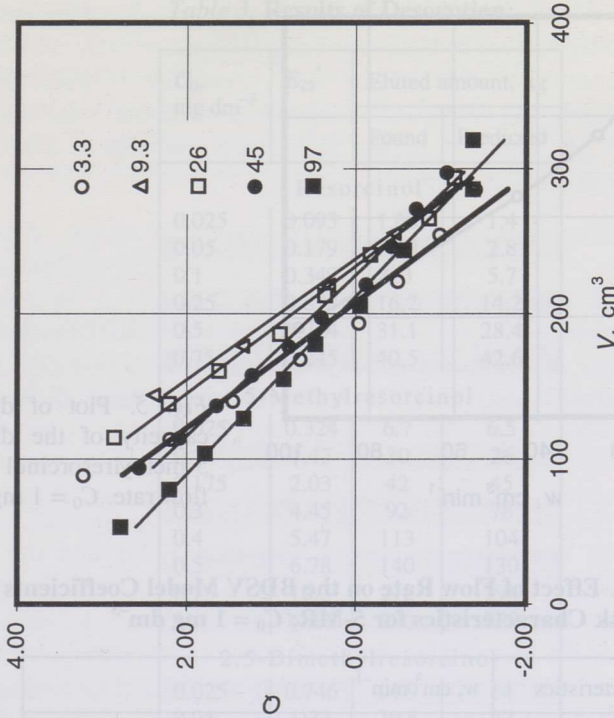*Fig. 4.* Plot of function Q values versus solution volume at various flow rates, cm³ min⁻¹, for experimental data in Fig. 3
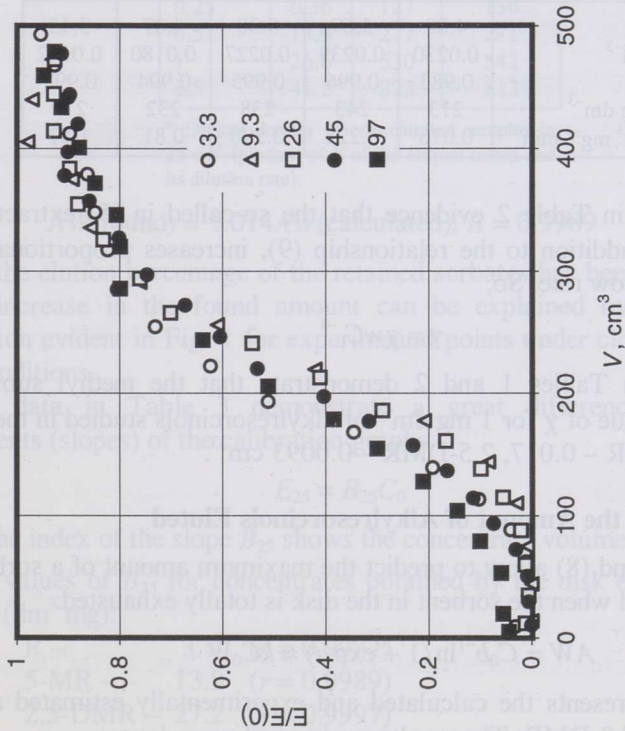

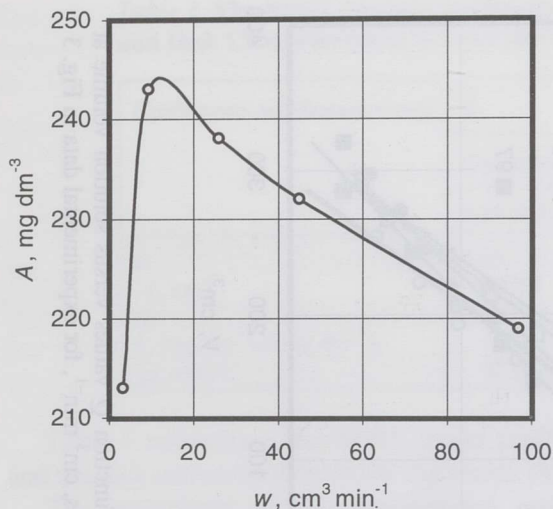*Fig. 3.* Breakthrough curves for 5-methylresorcinol at various flow rates, cm³ min⁻¹. $C_0 = 1$ mg dm⁻³

Fig. 5. Plot of dynamic capacity of the disk for 5-methylresorcinol versus flow rate. $C_0 = 1$ mg dm^{-3}

Table 2. **Effect of Flow Rate on the BDSV Model Coefficients and Disk Characteristics for 5-MR; $C_0 = 1$ mg dm^{-3}**

Characteristics	w, cm^3 min^{-1}				
	3.3	9.3	26	45	97
a	4,80	5.69	5.30	4.07	3.45
B, cm^{-3}	0.0230	0.0239	0.0227	0.0180	0.0162
r_Q	0.983	0.996	0.995	0.994	0.993
A, mg dm^{-3}	213	243	238	232	219
γ, dm^3 mg^{-1} min^{-1}	0.076	0.222	0.590	0.81	1.57

The results in Table 2 evidence that the so-called in [5] extraction-rate constant γ, in addition to the relationship (9), increases proportionally with an increase in flow rate. So,

$$\gamma = \chi w C_0^{-1} \tag{12}$$

The data in Tables 1 and 2 demonstrate that the methyl substituents decrease the value of χ for 1 mg dm^{-3} of alkylresorcinols studied in the row: R – 0.077, 5-MR – 0.017, 2,5-DMR – 0.0093 cm^{-3}.

Effect of C_0 on the Amount of Alkylresorcinols Eluted

Equations (7) and (8) allow to predict the maximum amount of a sorbate that can be extracted when the sorbent in the disk is totally exhausted:

$$AW = C_0 b^{-1} \ln(1 + \exp a) \approx k C_0 W \tag{13}$$

Table 3 represents the calculated and experimentally estimated amounts of R, 5-MR and 2-DMR. The results are in good accordance:

Table 3. **Results of Desorption**

C_0, mg dm^{-3}	E_{25}*	Eluted amount, µg	
		Found	Predicted
Resorcinol			
0.025	0.093	1.68	1.4
0.05	0.179	3.23	2.8
0.1	0.349	6.3	5.7
0.25	0.898	16.2	14.2
0.5	1.724	31.1	28.4
0.75	2.245	40.5	42.6
5-Methylresorcinol			
0.025	0.324	6.7	6.5
0.1	1.43	30	26
0.175	2.03	42	45
0.3	4.45	92	78
0.4	5.47	113	104
0.5	6.78	140	130
0.75	10.3	212	194
1	14.05	290	259
2,5-Dimethylresorcinol			
0.025	0.746	14.9	14
0.05	1.33	26.5	27
0.1	2.6	52	54
0.25	6.36	127	136
0.5	13.9	277	271
1	26.6	530	542
1.5	41.2	823	813

* Optical density of concentrated samples in 25 cm^3 (product of E of the aliquot tested and its dilution rate).

$$AW(\text{found}) = 1.014 AW(\text{calculated}), \ R = 0.9989 \qquad (14)$$

So, the elution percentage of the retained sorbates has been complete. The trivial increase in the found amount can be explained by the secondary absorption evident in Fig. 1 for experimental points under close to the steady state conditions.

The data in Table 3 demonstrate a great difference between the coefficients (slopes) of the calibration graphs

$$E_{25} = B_{25}C_0 \qquad (15)$$

where the index of the slope B_{25} shows the concentrate volume, cm^3.

The values of B_{25} for concentrates obtained by the disk extraction are as follows (dm^3 mg):

R –   3.17 ($r = 0.9937$)
5-MR –   13.9 ($r = 0.9989$)
2,5-DMR –   27.2 ($r = 0.9997$)

One can understand that the coefficient can be increased by decreasing volume of the eluting solvent or by evaporating the concentrate.

It must be considered that in the disk extraction concentrate of an environmental sample the component composition of the total alkylresorcinols cannot be the same as in the initial solution due to the different dynamic capacity of alkylresorcinols.

Conclusions

1. When alkylresorcinols are extracted using BAKERBOD *Speedisk*™ DVB the linear dependencies of A on C_0, and γ on w and C_0^{-1} allow to express the BDSV-model coefficients for disk extraction as follows

$$a = \ln[\exp(\chi kW) - 1] \qquad (16)$$

$$b = \chi \qquad (17)$$

Therefore, the breakthrough curves (Equation (11)) and the sorbate amount retained (Equation (13)) divided to C_0 are practically independent of C_0 and w under the conditions studied.

2. The values of the distribution factor k for alkylresorcinols on the disk studied are comparatively low. To obtain the highest preconcentration rate, the total dynamic capacity of the sorbent layer should be applied. For that, at least 1 dm^3 of the environmental water sample should be passed through the disk.

3. The photometric estimation using disk extraction can result in serious arte-facts for the total contamination due to the great difference between the distribution ability of various alkylresorcinols. For the chromatographic estimation, the whole SPE procedure has to be followed for every component.

Acknowledgements

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