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THE RETENTION BEHAVIOUR OF KETONES AND OTHER ORGANIC COMPOUNDS ON SEPARON SGX C18 COLUMN BY USING METHANOL-WATER ELUENTS

(Presented by Ü. Lille)

More than 30 compounds, mostly ketones, were subjected to investigation to identify oxygen-containing compounds in shale oil and other mixtures.

A Laboratorni Přistroje (Prague, Czechoslovakia) HPLC System with a high-pressure pump HPP 4001, a UV-VIS detector LCD 2563 (with fixed wavelengths), a linear recorder TZ 4601, an integrator IT2 and a 10 μl sample loading loop AD-1 (Special Designing Bureau, Estonian Academy of Sciences) were used. The spectrophotometric detector was used at 254 and 290 nm. The SEPARON SGX C18 (particle diameter 7 μm) glass column (Laboratorni Přistroje) was thermostated at 35±0.1 °C using a water jacket and eluated with methanol-water (40—100% of methanol) at a flow rate of 0.5 cm^3/min. The column pressure varied from 4.2 to 16 MPa depending on the mobile phase composition.

Samples were supplied by the following companies: methyl ethyl ketone by Reanal (Hungary), ethyl hepthyl ketone by Schuchart (München, FRG), acetophenone, camphor, limonene by VEB Laborchemie (Apolda, GDR), and other compounds by Reakhim (USSR). 2,5-Dimethylresorcinol was separated from the oil shale alkyl resorcinol fraction and purified in the Institute of Chemistry, Tallinn. The samples were dissolved in the mobile phase or in pure methanol, aliphatic ketones up to 0.1—1 and aromatic compounds up to 0.001—0.1 wt. %. Methanol was purified and dried by rectification. Bidistilled water was used. The mobile phase was mixed with separately measured component volumes.

The retention time (t_R) was measured using an integrator (sec). The t_R value for unretained sample molecules (t_0) was determined as the elution time of $Co(NO_3)_2$ (measured at 436 nm). The column void volume was calculated as 0.76 cm^3.

The retention behaviour of ketones and other organic compounds was examined by using the capacity factor k'. In order to investigate the effect of eluent contents on k', some empirical relationships were examined

$$lnk' = a + b\varphi, \quad (1)$$
$$lnk' = a + bM, \quad (2)$$
$$lnk' = a + b\varphi + c\varphi^2, \quad (3)$$

where φ — the volume fraction, and M — the molarity of methanol in the mobile phase.

According to [1] c in (3) must be proportional to the molecular volume (V_m) of substances. It is difficult to find or calculate the values of V_m for solid compounds, because the critical volumes were used ($V_c \approx qV_m$) and in case of need calculated according to Lydersen [2]. Formula 3 can be modified as follows:

$$lnk' - c\varphi^2 = lnk' - zV_c\varphi^2 = a + b\varphi. \quad (4)$$

Table 1

lnk' mobile phase composition relationship

Solute	Methanol vol., %	Formula 1			Formula 2			Formula 4			
		a	$-b$	S_k	a	$-b$	S_k	a	$-b$	c	S_k
1	2	3	4	5	6	7	8	9	10	11	12
2-propanone	40—90	0.24	1.90	0.027	2.20	1.17	0.020	0.82	3.85	1.53	0.020
2-butanone	40—90	1.20	2.81	0.053	4.40	1.83	0.025	2.06	5.45	1.95	0.026
2-hexanone	40—90	3.71	5.28	0.164	9.62	3.40	0.156	4.89	8.97	2.74	0.042*
4-methyl-2-pentanone	40—90	3.21	4.76	0.184	8.44	3.03	0.065	4.36	8.37	2.71	0.031*
2-heptanone	40—100	4.85	6.22	0.710	11.88	4.06	0.309	6.24	10.51	3.07	0.037*
4-heptanone	40—90	4.98	6.56	0.175	11.59	3.99	0.297	6.15	10.52	3.07	0.204
2-octanone	40—90	6.54	7.94	0.527	14.40	4.77	0.502	7.85	12.43	3.54	0.218*
2-nonanone	75—90	6.92	8.09	0.115	20.43	6.70	0.092	9.61	14.62	3.94	0.098
5-nonanone	60—90	6.64	7.89	0.221	17.95	5.92	0.209	8.88	13.88	3.94	0.190
3-decanone	60—90	8.73	9.91	0.270	22.97	7.44	0.543	11.21	16.52	4.34	0.287
2-undecanone	70—90	9.77	10.67	0.225	26.61	8.52	0.394	12.82	18.30	4.75	0.348
6-undecanone	75—90	9.54	10.65	0.330	27.23	8.79	0.270	12.76	18.47	4.75	0.290
7-tridecanone	75—90	11.85	12.65	0.743	32.93	10.47	0.604	15.63	21.84	5.55	0.650
2-hexadecanone	80—100	15.32	15.23	2.211	43.74	13.60	2.048	20.69	27.32	6.72	2.081
cyclopentanone	40—90	1.51	3.05	0.058	4.77	1.91	0.019	2.30	5.62	1.96	0.024
cyclohexanone	40—90	2.39	3.88	0.134	6.58	2.45	0.054	3.33	6.89	2.28	0.073
4-methylcyclohexanone	40—90	2.48	3.90	0.116	6.66	2.46	0.044	3.57	7.47	2.69	0.045
champhor	40—90	5.67	6.93	0.882	13.08	4.35	0.748	7.16	11.73	3.63	0.217*
acetophenone	40—90	3.60	5.14	0.180	8.98	3.19	0.079	4.58	8.37	2.47	0.040*
propiophenone	40—90	4.97	6.52	0.457	11.70	4.01	0.298	6.09	10.25	2.88	0.057*
butyrophenone	40—90	6.14	7.57	0.453	13.66	4.56	0.527	7.36	11.74	3.28	0.229*
valerophenone	60—90	6.93	8.17	0.128	18.40	6.05	0.174	8.96	13.70	3.68	0.104
benzophenone	40—90	6.96	8.38	2.155	15.85	5.24	1.478	8.56	13.58	3.96	0.137*
4-hydroxybenzophenone	40—90	5.42	7.54	0.835	13.19	4.62	0.205	6.95	12.63	3.97	0.282
4-methoxybenzophenone	40—90	7.36	8.89	2.518	16.58	5.49	0.837	9.14	14.75	4.50	0.166*
1,3-diphenyl-2-propanone	70—90	1.53	3.23	0.032	6.70	2.60	0.029	4.57	10.88	4.76	0.026
methyl-1-naphtylketone	40—90	6.06	7.43	0.884	13.88	4.62	0.728	7.59	12.42	3.81	0.270*
9-fluorenone	40—90	7.09	8.23	3.112	15.70	5.11	0.838	8.61	13.28	3.87	1.029
2-isobutylanthraquinone	60—90	10.71	11.13	0.744	26.75	8.37	1.867	14.04	19.98	5.80	1.243
benzylbiphenylketone	70—90	9.92	11.07	0.159	27.30	8.80	0.270	13.72	20.63	5.96	0.256
9-xanthenone	60—90	6.18	7.02	0.249	15.97	5.18	0.072	8.32	12.87	3.93	0.102
dibutylphthalate	60—90	10.11	11.47	0.223*	26.44	8.56	0.998	13.67	20.99	6.28	0.817

Table 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
dioctylphthalate	75—90	19.14	19.75	2.738	51.71	16.22	3.609	25.56	35.39	9.49	3.399
2,5-dimethylresorcinol	40—90	2.54	5.68	0.038*	8.47	3.52	0.093	3.67	9.31	2.73	0.080
benzene	40—90	4.59	5.76	0.049*	10.52	3.53	0.615	5.85	8.23	1.90	0.292
toluene	40—90	5.94	6.97	0.088*	13.29	4.34	1.737	6.89	10.02	2.31	0.777
anthracene	75—90	9.19	9.76	0.337	25.50	8.09	0.267	11.96	16.46	4.04	0.293
phenanthrene	75—90	9.04	9.65	0.267	25.07	7.97	0.209	11.78	16.33	4.04	0.229
limonene	70—90	10.95	11.40	0.249	29.22	9.19	0.646	13.26	17.13	3.53	0.443

* The best regression at a confidence level of 95% or more.

Table 2

Comparison of experimental and published k' values

φ	k'_{exp}	k'_{ref}
	2-propanone	
0.3	0.82*	0.53[a]; 0.36[b]; 0.33[c]; 0.38[d] [3]
0.4	0.63±0.02	0.50[a] [3]; 0.36[e] [4]
0.6	0.36±0.03	0.26[a] [3]; 0.23[e] [4]
	2-butanone	
0.3	1.82*	1.19[a]; 0.71[b]; 0.57[c]; 0.61[d] [3]
0.4	1.23±0.09	0.96[a] [3]
0.6	0.59±0.02	0.51[a] [3]; 0.39[e] [4]
0.7	0.46±0.02	0.32[e] [4]
0.8	0.35±0.03	0.22[e] [4]
	2-hexanone	
0.3	11.5*	8.78[a]; 3.57[b]; 2.13[c]; 1.73[d] [3]
0.4	5.60±0.19	5.53[a] [3]; 4.2[e] [4]
0.6	1.63±0.04	1.60[e] [4]; 1.47[a] [3]
0.7	1.00±0.05	0.77[a] [3]; 0.77[e] [4]
0.8	0.59±0.01	0.39[e] [4]
	2-octanone	
0.3	84.7*	11.47[c]; 4.88[d] [3]
0.4	30.5±3.2	24[e] [4]
0.6	5.29*	5.0[e] [4]; 5.73[a] [3]
0.7	2.39±0.13	2.11[a] [3]; 2.1[e] [4]
0.8	1.22±0.02	1.16[a] [3]; 0.81[e] [4]
	2-undecanone	
0.7	9.50±0.13	9.2[e] [4]; 10.3[a] [3]
0.8	3.59±0.12	3.84[a] [3]; 2.4[e] [4]
	acetophenone	
0.1	43.3*	78.24[r] [5]
0.15	29.4*	22.44[f] [6]
0.2	20.2*	31.28[r] [5]
0.3	9.89*	9.96[a]; 4.40[b]; 2.92[c]; 2.96[d] [3]; 9.60[f] [7]; 7.53[g] [8]; 14.61[r] [5]
0.4	5.16±0.09	5.54[a] [3]; 4.40[f] [7]; 4.41[h]; 3.86[f]; 3.46[i]; 3.56[j]; 9.26[k]; 1.94[l] [9]; 3.94[g] [8]; 6.827[r] [5]; 7.72[m]; 8.19[m] [10]; 4.05[g]; 4.09[g] [11]
0.45	3.72*	2.95[g] [8]; 2.85[f] [7]
0.5	2.75*	2.07[g] [8]; 2.03[f] [7]; 2.00[a] [3]; 1.54[n] [12]; 2.03[g] [11]; 5.206[r] [5]
0.6	1.53±0.01	1.35[a] [3]; 2.45[m]; 2.33[m] [10]; 2.44[o] [13]; 1.08[g] [8]; 0.79[n] [12]; 0.62[p] [14]; 0.93[g] [11]; 1.05[f] [15]; 1.836[r] [5]
0.7	0.92±0.04	0.72[a] [3]; 1.38[m]; 1.39[m] [10]; 0.57[g] [8]; 0.40[n] [12]; 0.32[p] [14]; 0.51[g] [11]; 1.061[r] [5]
0.75	0.73±0.04	1.04[m]; 1.11[m] [10]; 1.35[o] [13]; 0.41[g] [8]; 0.39[g]; 0.35[g] [11]
0.8	0.62±0.02	0.45[a] [3]; 0.78[m]; 0.90[m] [10]; 0.684[r] [5]; 0.30[g] [8]; 0.18[p] [14]; 0.29[g] [11]
0.85	0.44±0.01	0.58[m]; 0.74[m] [10]; 0.20[g]; 0.21[g] [11]; 0.21[g] [8]
0.9	0.39±0.01	0.44[m]; 0.62[m] [10]; 0.16[g] [8]; 0.10[p] [14]; 0.486[r] [5]
1.0	0.267*	0.351[r] [5]
	propiophenone	
0.15	101*	66.7[f] [6]
0.3	26.4*	25.9[a]; 9.24[b]; 5.43[c]; 4.76[d] [3]; 25.8[f] [7]
0.4	11.7±0.3	10.63[f] [7]; 13.1[a] [3]; 10.57[h]; 9.18[f]; 7.62[i]; 6.99[j]; 20.53[k]; 3.21[l] [9]; 9.01[g]; 9.02[g] [11]
0.45	7.87*	6.45[f] [7]
0.5	5.39*	4.37[f] [7]; 4.04[a] [3]; 4.08[g] [11]
0.6	2.65±0.06	2.58[a] [3]; 4.01[o] [13]; 1.69[g]; 1.70[g] [11]
0.7	1.37±0.04	1.07[a] [3]; 0.86[g] [11]
0.8	0.71±0.03	0.61[a] [3]; 0.45[g]; 0.46[g] [11]

φ	k'_{exp}	k'_{ref}
	butyrophenone	
0.15	291*	201.1*f* [6]
0.3	62.4*	67.9*a*; 20.6*b*; 10.3*c*; 8.00*d* [3]; 67.7*f* [7]
0.4	23.7±1.9	31.3*a* [3]; 24.7*f* [7]
0.5	10.1*	8.00*a* [3]; 8.94*f* [7]
0.6	4.47*	4.59*a* [3]; 6.58*o* [13]
0.7	2.11±0.07	1.74*a* [3]
0.75	1.49±0.01	2.32*o* [13]
0.8	1.14±0.05	0.93*a* [3]
	valerophenone	
0.3	178*	193.5*f* [7]; 22.2*c*; 14.4*d* [3]
0.4	58.5*	62.3*f* [7]
0.5	20.7*	17.3*a* [3]; 19.51*f* [7]
0.6	7.78±0.11	8.79*a* [3]; 10.8*o* [13]
0.7	3.27±0.26	2.88*a* [3]
0.75	2.20±0.06	3.08*o* [13]
0.8	1.47±0.01	1.42*a* [3]
	benzophenone	
0.3	126.8*	219.5*r* [5]
0.4	43.2±0.9	45.4*m*; 107.8*m* [10]; 64.656*r* [5]
0.5	15.8*	20.610*r* [5]
0.6	6.21±0.14	7.460*r* [5]; 9.43*m*; 10.6*m* [10]; 1.83*p* [14]
0.7	2.60±0.01	3.024*r* [5]; 4.30*m*; 4.16*m* [10]; 0.76*p* [14]
0.75	1.84±0.01	2.90*m*; 2.75*m* [10]
0.8	1.30±0.03	1.372*r* [5]; 1.96*m*; 1.89*m* [10]; 0.34*p* [14]
0.85	0.82±0.03	1.32*m*; 1.34*m* [10]
0.9	0.63±0.02	0.747*r* [5]; 0.89*m*; 0.99*m* [10]; 0.15*p* [14]
1.0	0.346*	0.436*r* [5]

* Calculated according to Formula 4.
Column key: *a* — Hypersil ODS, *b* — Hypersil SAS, *c* — Magnusil C22, *d* — Spherisorb phenyl, *e* — Bondapak ODS, *f* — 5 μm Hypersil ODS, *g* — ODS, *h* — 3 μm Hypersil ODS, *i* — 5 μm Techsil ODS, *j* — 5 μm Spherisorb ODS, *k* — 5 μm Zorbax ODS, *l* — 10 μm Partisil ODS, *m* — Merck RP-18, *n* — Fast LC-8™ (Technicon), *o* — 5 μm Rainin Microsorb C8, *p* — 7.5 μm Silasorb C8 and *r* — Whatman ODS-3.

The best set of regression coefficients was calculated using the least-squares technique. All experimental data points were taken into account. The value of z was found minimizing the sum of a residual dispersion of k' (S_k) for all the ketones under study (solutes 1—31).

From the results in Table 1 it follows that the best fit for $\ln k'$ of ketones is obtained using Formula 4, while for the other compounds Formula 1 gives a maximum fit. The k' values in reversed-phase LC depend strongly on the solid phase quality. A comparison of experimental and published data on k' shows that the retention behaviour of ketones on SEPARON SGX C18 is similar to that on Hypersil ODS column (Table 2). Agreement is good even for the data extrapolated according to Formula 4.

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KETOONIDE JA TEISTE ORGAANILISTE ÜHENDITE RETENTSIOONI ISEÄRASUSED KOLONNIS SEPARON SGX C18 METANOOLI VESILAHUSEGA ELUEERIMISEL

On määratud 39 orgaanilise ühendi, sh. 31 alifaatse ja aromaatse ketooni, mahtuvuskoefitsiendid kolonnis SEPARON SGX C18 metanooli vesilahusega elueerimisel temperatuuril 35±0,1 °C. Ketoonide puhul on mahtuvuskoefitsiendi logaritm kirjeldatav teist järku ja muude ühendite puhul esimest järku lineaarsõltuvusena metanooli mahuosast (40—100%) eluendis. Trükis avaldatud andmete alusel on näidatud, et ketoonide retentsioon kasutatud kolonnis on võrreldav retentsiooniga kolonnis HYPERSIL ODS.

Яак АРРО, Велло ТАЛВЕС

ОСОБЕННОСТИ УДЕРЖИВАНИЯ КЕТОНОВ И ДРУГИХ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ В КОЛОНКЕ SEPARON SGX C18 ПРИ ЭЛЮИРОВАНИИ ВОДНЫМИ РАСТВОРАМИ МЕТАНОЛА

Определены коэффициенты емкости 39 органических соединений, в том числе 31 алифатического и ароматического кетона, в колонке SEPARON SGX C18 при элюировании водными растворами метанола (от 40 до 100 % об.) при температуре 35±0,1 °C. Зависимость логарифма коэффициента емкости от доли метанола в элюенте хорошо описывается линейным регрессионным уравнением, для кетонов — уравнением второго порядка, для других — первого порядка. Сравнение с литературными данными показывает, что по характеру удерживания кетонов использованная колонка сходна с колонкой HYPERSIL ODS.