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## EVALUATION OF BONDED PHASES FOR THE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN EFFLUENT WATERS

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### SUMMARY

A wide range of chemically-bonded stationary phases have been evaluated to assess their potential usefulness for the determination of polycyclic aromatic hydrocarbons in refinery effluents by high-performance liquid chromatography. Of the 30 columns tested, no more than six achieved the target value of a resolution of 1.5 for perylene-benzo[*a*]pyrene within an analysis time of 30 min using isocratic elution with aqueous acetonitrile as mobile phase. Under these conditions, a column packed with HC-ODS-Sil-X (Perkin-Elmer Corp.) was the only one to separate completely all the components of interest.

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### INTRODUCTION

The analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples has been the subject of several hundreds of papers during the last thirty years and many more will undoubtedly be published before common agreement on standard methods will be achieved. Many combinations of analytical techniques have been used usually involving various types of chromatography with molecular spectroscopy. Most procedures are time-consuming and complex, requiring expensive equipment and considerable analytical skills.

To obtain a complete analysis, a sophisticated analysis such as one based on capillary gas chromatography (GC) with mass spectrometry and UV absorption or fluorescence spectroscopy is necessary. However, for many purposes the determination of a limited number of representative PAHs is quite sufficient and provided reference samples are available, high-performance liquid chromatography (HPLC) offers a relatively simple but very powerful means of effecting this analysis.

In 1971, the World Health Organisation (WHO) set an upper limit of 200 ng/l for the total concentration of six PAHs in potable water (Table I). More recently, in 1976 the U.S. Environmental Protection Agency (EPA) drew up a list of 16 PAHs whose presence should be monitored and limited in effluent waters in the U.S.A. Reversed-phase HPLC has been examined by several workers<sup>1-15</sup> for this analysis, but with conflicting reports on the effectiveness of the separation. Others<sup>16,17</sup> have suggested the use of normal-phase chromatography using polar bonded phases. Only

TABLE I  
DESCRIPTION OF POLYCYCLIC AROMATIC HYDROCARBONS

<i>Name</i>	<i>Abbreviation</i>	<i>EPA list</i>	<i>WHO list</i>	<i>Blend concentration (µg/ml)</i>
Fluorene	Fl	+		11.2
Phenanthrene	Phen	+		11.2
Anthracene	Ant	+		8.8
Fluoranthene	Ft		+	17.6
Pyrene	Pyr	+		19.2
Benzo[ <i>a</i> ]anthracene (1,2-benzanthracene)	BaA	+		19.2
Chrysene	Chrys	+		22.4
Perylene	Per			—
Benzo[ <i>b</i> ]fluoranthene (3,4-benzofluoranthene)	BbF	+	+	16.0
Benzo[ <i>k</i> ]fluoranthene (11,12-benzofluoranthene)	BkF	+	+	20.0
Benzo[ <i>e</i> ]pyrene (1,2-benzpyrene)	BeP			—
Benzo[ <i>a</i> ]pyrene (3,4-benzpyrene)	BaP	+	+	19.2
Dibenz[ <i>a, h</i> ]anthracene (1,2,5,6-dibenzanthracene)	DiBa	+		24.0
Benzo[ <i>g, h, i</i> ]perylene (1,12-benzoperylene)	<i>ghi</i>	+	+	17.6
Indeno[1,2,3, <i>c, d</i> ]pyrene (2,3- <i>o</i> -phenylene pyrene)	123 <i>cd</i>	+	+	17.6

recently has it been recognised<sup>18</sup> that nominally similar stationary phases exhibit different selectivities towards PAHs.

During the course of our work, we have evaluated a large number of stationary phases for a wide variety of analyses, including PAH analysis. From the data reported here, we have successfully developed a chromatographic system for the analysis of PAHs, down to at least the 0.01 µg/l level, in refinery effluent water.

## EXPERIMENTAL

### *Equipment*

A Perkin-Elmer Series 2 liquid chromatograph with LC 55 UV detector was used throughout this work. Samples were injected by microsyringe via a septum injector from hetp, Macclesfield, Great Britain, excepting columns 8 and 11 for which a Rheodyne Model 7120 injection valve with 20-µl sample loop was used.

### *Reagents*

Fluorene, phenanthrene, anthracene, fluoranthene, pyrene and chrysene were purchased from BDH (Poole, Great Britain); benzo[*a*]anthracene and dibenz[*a, h*]anthracene from R. N. Emanuel Ltd. (Alperton, Great Britain); perylene from Koch-Light Labs. (Colnbrook, Great Britain); benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene and benzo[*e*]pyrene from Phase Separations (Queensferry, Great

Britain); and benzo[*g,h,i*]perylene and indeno[1,2,3,*c,d*]pyrene from Aldrich (Milwaukee, WI, U.S.A.).

Standard solutions were prepared by dissolving about 0.01 g of each solute in about 5 ml chloroform and making up to 50 ml in a volumetric flask with acetonitrile. Some solutions needed to stand 24 h before dissolution was complete. A PAH blend was made by mixing some of the above solutions. The composition of the final blend is shown in Table I.

Acetonitrile (HPLC grade) was purchased from Rathburn (Walkerburn, Great Britain); all other solvents and chemicals were obtained from BDH.

Binary test mixtures: 1% each of dimethyl (DMP) and dibutyl phthalate (DBP) in tetrahydrofuran; 0.02% each of pyrene and chrysene in acetonitrile; 0.02% each of perylene and benzo[*a*]pyrene in acetonitrile; 0.02% each of naphthalene and phenanthrene in heptane.

### Columns

The columns are described in Tables II–IV. All home-made columns were slurry-packed in either 1,1,2,2-tetrabromoethane–dioxane–carbon tetrachloride (20:15:15) or trichloroethylene–ethanol (1:1) at a pressure of 5000 p.s.i.g. Except for the commercial pre-packed columns, the same column (25 cm × 4.6 mm I.D.) and end fittings were used throughout this work.

TABLE II  
DESCRIPTION OF OCTADECYL REVERSED-PHASE COLUMNS

Column No.	Name	Particle size ( $\mu\text{m}$ )	Packing method	Source
1	LiChrosorb RP-18	5	Prepacked	Jones Chromatography Llanbradach, Glamorgan, Great Britain
2	LiChrosorb RP-18	10	Slurry	E. Merck, Darmstadt, G.F.R.
3	Spherisorb ODS	5	Prepacked	Jones Chromatography
4	Spherisorb ODS	10	Slurry	Phase Separations, Queens- ferry, Great Britain
5	Partisil ODS-1	10	Slurry	Whatman, Maidstone, Great Britain
6	Partisil ODS-2	10	Slurry	Whatman
7	Partisil-5 ODS	5	Prepacked	Whatman
8	HC-ODS-Sil-X-1	—	Prepacked	Perkin-Elmer, Norwalk, CT, U.S.A.
9	Hypersil ODS	7	Slurry	Shandon Southern Prod- ucts, Runcorn, Great Britain
10	Zorbax ODS	5	Slurry	DuPont, Wilmington, DE, U.S.A.
11	$\mu$ Bondapak C <sub>18</sub>	10	Prepacked	Waters Assoc., Milford, MA, U.S.A.
12	C <sub>18</sub> modified silica	10	Slurry	H.S.C.P., Bourne End, Great Britain

TABLE III  
DESCRIPTION OF OTHER ALKYL REVERSED-PHASE COLUMNS

Packing method: slurry.

Column No.	Name	Particle size ( $\mu\text{m}$ )	Source
13	LiChrosorb RP-2	10	E. Merck
14	Hypersil SAS	7	Shandon Southern Products
15	C <sub>5</sub> modified silica	10	H.S.C.P.
16	Spherisorb hexyl	5	Phase Separations
17	Spherisorb phenyl	5	Phase Separations
18	Zorbax C <sub>8</sub>	5	DuPont
19	LiChrosorb RP-8	10	E. Merck
20	Magnusil C <sub>22</sub> supergrade	5	HPLC Technology, Wilmslow, Great Britain
21	LiChrosorb SI 60, standard grade C <sub>22</sub>	5	HPLC Technology
22	Partisil-5-C <sub>22</sub>	5	HPLC Technology
23	Hypersil C <sub>22</sub>	7	HPLC Technology

TABLE IV  
DESCRIPTION OF POLAR BONDED-PHASE COLUMNS

Packing method: slurry.

Column No.	Description	Particle size ( $\mu\text{m}$ )	Source
24	Partisil PAC	10	Whatman
25	Nucleosil CN	10	Macherey, Nagel & Co., Düren, G.F.R.
26	Spherisorb nitrile	5	Phase Separations
27	Nucleosil NO <sub>2</sub>	5	Macherey, Nagel & Co.
28	Hypersil APS	7	Shandon Southern Products
29	LiChrosorb NH <sub>2</sub>	10	E. Merck
30	LiChrosorb DIOL	10	E. Merck

### Procedure

Reversed-phase columns were conditioned by pumping acetone, methanol, acetonitrile and acetonitrile-water mixtures for 15 min each at 3 ml/min. When operating conditions were steady, the flow-rate was set at 1.0 ml/min, and detector wavelength set to 254 nm at an appropriate sensitivity to obtain 30–80% full scale deflection. Portions of 1–5  $\mu\text{l}$  of each of the first three binary test mixtures and the PAH blend were injected and from the chromatograms, values for the retention time ( $t_R$ ), efficiency ( $N$ ), plate height ( $H$ ), and resolution ( $R_s$ ) were measured.

Normal-phase columns were conditioned by pumping ethyl acetate, dichloromethane and heptane for 15 min each. The columns were evaluated by injecting the last three binary test mixtures and the PAH blend.

### RESULTS AND DISCUSSION

Tables V and VI show the performance of the reversed-phase columns with the phthalate test mixture. Evaluations similar to this are frequently provided by commercial suppliers as a back-up to their products. Our results are in line with those generally reported in the literature. At this stage, the apparently poor performance of

TABLE V  
EVALUATION OF OCTADECYL REVERSED-PHASE COLUMNS WITH DMP AND DBP

Column No.	Mobile phase (% acetonitrile in water)	DMP			DBP			$R_s$
		$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
1	85	4.5	21140	0.012	10.4	7056	0.035	22.7
2	80	3.0	4956	0.050	6.8	4199	0.060	12.88
3	80	3.5	6790	0.037	5.4	5184	0.048	8.09
4	80	3.1	4733	0.053	6.4	3598	0.069	12.00
5	60	2.8	1866	0.13	4.3	1340	0.19	4.11
6	80	2.6	2704	0.092	6.9	2830	0.088	11.94
7	80	3.4	3844	0.057	7.9	6922	0.032	15.00
8	60	1.8	784	0.32	4.7	1414	0.18	7.87
9	80	3.7	6084	0.041	7.4	8538	0.029	14.51
10	80	3.3	4844	0.052	9.4	3944	0.063	15.44
11	80	4.9	4251	0.059	8.7	3364	0.074	8.44
12	60	5.0	3894	0.064	7.6	3697	0.068	6.34

TABLE VI  
EVALUATION OF OTHER ALKYL REVERSED-PHASE COLUMNS WITH DMP AND DBP

Column No.	Mobile phase (% acetonitrile in water)	DMP			DBP			$R_s$
		$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
13	60	3.5	3136	0.080	7.4	3505	0.071	10.40
14	60	4.5	4147	0.060	10.4	5127	0.049	13.72
15	50	3.1	1600	0.16	4.6	1936	0.13	4.11
16	80	3.4	2043	0.12	5.4	3226	0.077	5.88
17	60	3.7	4516	0.055	5.3	3091	0.081	5.33
18	80	2.5	2079	0.12	5.6	4900	0.051	11.48
19	70	2.9	2788	0.090	7.1	2500	0.10	10.59
20	80	4.6	8464	0.030	7.3	8836	0.028	10.59
21	60	4.1	3003	0.083	7.2	3181	0.079	7.65
22	80	3.3	1205	0.21	5.3	2540	0.098	5.00
23	80	4.1	6724	0.037	5.3	5013	0.050	4.80

TABLE VII  
EVALUATION OF POLAR BONDED PHASES WITH NAPHTHALENE AND PHENANTHRENE

Mobile phase, *n*-heptane.

Column No.	Naphthalene			Phenanthrene			$R_s$
	$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
24	8.6	3272	0.076	21.7	2343	0.11	10.92
25	3.2	3364	0.074	3.7	5476	0.046	2.38
26	5.2	8911	0.028	7.3	10161	0.025	8.24
27	5.2	2704	0.092	10.2	1665	0.15	7.14
28	3.7	3505	0.071	5.4	1866	0.13	4.53
29	5.0	5127	0.049	6.9	6209	0.040	6.03
30	2.9	3047	0.082	3.5	2500	0.10	2.46

column 8 is noteworthy. Table VII shows the conventional evaluation of normal-phase columns with the naphthalene-phenanthrene test mixture.

Tables VIII-XIII present the data obtained from the evaluation of all columns with the pyrene-chrysene and perylene-benzo[*a*]pyrene test mixtures. In general, the efficiencies measured on PAHs are lower than those on phthalates.

TABLE VIII

## EVALUATION OF OCTADECYL REVERSED-PHASE COLUMNS WITH PYRENE AND CHRYSENE

Column No.	Mobile phase (% acetonitrile in water)	Pyrene			Chrysene			$R_s$
		$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
1	85	13.8	3745	0.067	18.7	6922	0.036	5.44
2	85	8.2	2059	0.12	10.8	1798	0.14	3.02
3	60	14.5	5535	0.045	18.3	8391	0.030	4.81
4	70	13.2	Poor peak shapes		18.0	—	—	—
5	60	5.0	495	0.51	6.1	493	0.51	1.10
	50	9.7	1397	0.18	12.8	655	0.38	2.07
6	85	8.2	1121	0.22	10.8	1600	0.16	2.52
7	80	9.4	2500	0.088	11.0	3457	0.064	2.13
8	70	5.2	1024	0.24	11.0	1345	0.19	6.27
	80	3.5	647	0.39	6.5	1381	0.18	4.80
9	85	3.0	900	0.28	4.7	1414	0.18	3.78
	80	8.4	2304	0.11	9.7	2342	0.11	1.73
10	80	14.5	664	0.38	18.0	939	0.27	1.52
	85	10.5	784	0.32	12.4	1351	0.19	1.33
11	80	10.8	2581	0.097	12.5	2788	0.090	1.89
	70	14.4	4096	0.061	18.4	4900	0.051	4.10
12	60	10.2	1156	0.22	12.0	846	0.30	1.26

TABLE IX

## EVALUATION OF OTHER ALKYL REVERSED-PHASE COLUMNS WITH PYRENE AND CHRYSENE

Column No.	Mobile phase (% acetonitrile in water)	Pyrene			Chrysene			$R_s$
		$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
13	60	6.3	697	0.36	7.3	1183	0.21	1.11
14	60	8.8	1530	0.16	10.6	1665	0.15	1.86
15	50	6.4	—	—	6.9	—	—	<1
16	60	12.9	3272	0.076	15.4	3600	0.069	2.59
17	60	5.4	—	—	5.9	—	—	<<1
18	70	9.9	1568	0.16	11.8	1832	0.14	1.81
19	70	7.7	949	0.26	8.7	1211	0.21	1.00
	60	12.5	1276	0.20	15.3	1901	0.13	2.00
20	80	8.4	3745	0.067	9.5	3411	0.073	1.83
	70	11.9	4624	0.054	14.4	5184	0.048	3.33
21	70	6.3	1764	0.14	7.1	1515	0.17	1.20
	60	8.7	2153	0.11	10.5	1832	0.14	2.08
22	70	8.5	2343	0.11	10.4	2153	0.12	2.38
	60	13.6	1764	0.14	17.7	2540	0.098	3.03
23	70	9.7	1936	0.13	11.7	1731	0.14	1.99

TABLE X

EVALUATION OF POLAR BONDED PHASE COLUMNS WITH PYRENE AND CHRYSENE  
 Mobile phase, *n*-heptane; the mobile phase for columns 24 and 27 contained 1% ethyl acetate.

Column No.	Pyrene			Chrysene			$R_s$
	$t_R$ (min)	<i>N</i> (plates)	<i>H</i> (mm)	$t_R$ (min)	<i>N</i> (plates)	<i>H</i> (mm)	
24	9.5	2959	0.084	14.5	2788	0.090	5.56
25	3.7	3505	0.071	4.3	3272	0.076	2.18
26	6.0	900	0.28	7.3	944	0.26	1.49
27	6.4	3226	0.077	8.8	3697	0.068	4.66
28	5.2	2460	0.10	6.7	718	0.35	2.11
29	7.2	1697	0.15	9.4	1360	0.18	2.56
30	3.7	1242	0.20	4.5	662	0.38	1.43

TABLE XI

EVALUATION OF OCTADECYL REVERSED-PHASE COLUMNS WITH PERYLENE AND BENZO-  
 [a]PYRENE

Column No.	Mobile phase (% acetonitrile in water)	Perylene			Benzo[a]pyrene			$R_s$
		$t_R$ (min)	<i>N</i> (plates)	<i>H</i> (mm)	$t_R$ (min)	<i>N</i> (plates)	<i>H</i> (mm)	
1	85	23.0	3317	0.075	28.9	2153	0.12	2.88
2	85	15.3	1900	0.13	18.8	1730	0.14	2.19
3	60	24.5	6529	0.038	27.0	6922	0.038	1.99
4	70	28.0	poor peak		32.8	poor peak		—
	80	15.0	shape		17.3	shape		—
5	50	16.7	1543	0.16	18.7	1058	0.24	1.00
6	85	15.7	4356	0.057	18.3	6593	0.038	2.81
7	80	14.4	4096	0.054	15.7	5476	0.040	1.49
8	70	17.4	595	0.42	27.1	753	0.33	2.85
	80	9.3	1697	0.15	13.7	1764	0.14	4.00
	85	6.6	1600	0.16	9.4	1731	0.14	3.59
9	80	12.5	2500	0.10	13.6	1833	0.14	0.76
10	85	18.2	2343	0.11	20.1	2007	0.12	1.15
11	80	15.6	5535	0.045	16.6	4570	0.055	1.10
	70	22.7	4303	0.058	25.0	4303	0.058	1.59
12	60	15.2	—	—	15.9	—	—	≪1

If we were to set, as a criterion for a successful column for PAH analysis, an  $R_s$  value of at least 1.5 for perylene-benzo[a]pyrene achieved in an analysis time of less than half an hour, then the number of potentially useful columns falls to about six. The performance of column 8 is again noteworthy. Despite its poor efficiency, it achieved the highest  $R_s$  values for both PAH test mixtures. Although, as would be expected, the octadecyl reversed phases performed better than those with lower alkyl chains, the performances of the  $C_{22}$  bonded phases were somewhat disappointing. Of the polar bonded phases, only columns 24, 26 and 27 seemed interesting, indicating potential use in pre-separation techniques.

TABLE XII

EVALUATION OF OTHER ALKYL REVERSED-PHASE COLUMNS WITH PERYLENE AND BENZO[*a*]PYRENE

Column No.	Mobile phase (% acetonitrile in water)	Perylene			Benzo[ <i>a</i> ]pyrene			$R_s$
		$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
13	60	8.4	—	—	8.6	—	—	$\ll 1$
14	60	11.6	5595	0.045	12.5	3894	0.064	1.27
15	50	5.2	—	—	5.4	—	—	$\ll 1$
16	60	17.9	4251	0.059	19.0	3697	0.068	0.94
17	50	5.9	—	—	6.3	—	—	$\ll 1$
18	70	15.3	1901	0.13	16.3	1901	0.13	0.69
19	60	20.0	—	—	21.1	—	—	$< 1$
20	70	18.3	5069	0.049	20.0	4570	0.055	1.54
21	60	13.6	1971	0.13	14.7	1832	0.14	0.85
22	60	22.8	3697	0.068	24.9	4147	0.060	1.38
23	70	15.3	3091	0.081	16.8	3411	0.073	1.33

TABLE XIII

EVALUATION OF POLAR BONDED PHASE COLUMNS WITH PERYLENE AND BENZO[*a*]PYRENEMobile phase, *n*-heptane; mobile phase for columns 24 and 27 contained 1% ethyl acetate.

Column No.	Benzo[ <i>a</i> ]pyrene			Perylene			$R_s$
	$t_R$ (min)	$N$ (plates)	$H$ (mm)	$t_R$ (min)	$N$ (plates)	$H$ (mm)	
24	18.6	3844	0.065	21.0	4303	0.058	1.94
25	4.4	2153	0.12	4.6	1936	0.13	$\ll 1$
26	9.6	871	0.29	11.3	3648	0.069	1.66
27	11.2	3745	0.067	12.6	2830	0.088	1.67
28	7.6	924	0.27	7.6	924	0.27	0.00
29	10.4	1381	0.18	11.6	1378	0.18	1.01
30	4.9	426	0.50	5.3	449	0.56	$< 1$

Finally, Table XIV lists the retention times of all the PAHs listed in Table I obtained on the most promising columns. The PAH blend contains three groups that are difficult to separate: chrysene–benzo[*a*]anthracene; perylene–benzo[*b*]fluoranthene–benzo[*k*]fluoranthene–benzo[*e*]pyrene–benzo[*a*]pyrene; and dibenz[*a,h*]anthracene–benzo[*g,h,i*]perylene–indeno[1,2,3,*c,d*]pyrene. Column 8 was the only column to separate all components using isocratic elution with aqueous acetonitrile.

## CONCLUSIONS

Of the 30 columns we have tested, no more than six are potentially useful for PAH analysis. As a result of this work we now use a semi-preparative column packed with Partisil-PAC to effect a preliminary clean-up of a cyclohexane extract of refinery effluents, followed by a quantitative analysis using the HC-ODS-Sil-X column with variable UV wavelength detection. This allows us to see at least 0.01  $\mu\text{g/l}$  of each PAH on the WHO and EPA lists.



TABLE XIV  
RETENTION TIMES OF INDIVIDUAL POLYCYCLIC AROMATICS

Column No.	Mobile phase (% acetonitrile in water)	Fl	Phen	Ant	Flt	Pyr	BaA	Chrys	Per	Bbf	Bkf	Rep	BaP	DiBA	ghi	123dc
1	90	5.0	6.2	6.9	8.5	9.7	12.5	12.5	—	17.0	18.5	—	19.0	24.4	31.8	31.8
2	80	5.2	5.7	6.2	7.2	8.3	11.0	11.4	16.7	16.3	18.1	16.2	20.9	23.9	31.0	32.5
3	60	7.2	10.0	11.0	13.7	14.5	18.3	18.3	24.5	25.1	26.1	—	27.0	34.8	36.8	36.8
7	80	5.1	6.7	7.3	8.7	9.4	11.0	11.0	14.4	14.3	14.8	—	15.7	17.9	20.3	20.3
8	80	2.1	2.3	2.5	3.2	3.7	5.5	6.6	9.3	9.7	12.6	—	14.4	22.2	28.2	30.2
9	80	6.1	6.3	6.7	7.5	8.4	9.7	9.7	11.9	11.8	12.0	—	12.9	14.6	16.5	16.5
10	85	5.2	6.8	7.6	9.5	10.5	12.4	12.4	18.2	17.5	18.2	—	20.1	22.7	28.5	30.1
11	70	10.3	11.3	12.0	13.8	14.8	18.0	18.7	22.7	23.7	24.7	—	25.7	31.7	34.0	34.0
16	60	6.8	10.3	11.2	13.3	12.9	16.1	15.4	17.9	18.4	19.3	—	19.0	22.2	22.8	22.8
18	70	4.9	7.0	7.7	9.4	10.0	11.8	11.8	15.3	15.3	15.9	—	16.3	19.6	20.9	21.3
20	70	7.2	8.7	9.5	11.2	11.9	14.2	14.4	18.3	18.5	19.0	—	20.0	24.1	26.0	27.7
21	60	5.8	6.3	6.9	8.1	8.7	10.5	10.5	13.6	13.7	13.7	—	14.7	17.8	19.4	19.4
22	65	7.7	8.5	8.9	10.2	10.7	13.1	13.7	—	17.3	17.8	—	18.3	23.1	24.2	24.2
23	70	6.9	7.9	7.8	9.0	9.7	11.6	11.7	15.3	16.0	16.3	—	16.8	22.1	24.8	25.4
24	2% Ethyl acetate in heptane	5.4	7.0	6.8	8.5	8.5	11.9	12.4	15.5	14.8	—	—	13.9	21.3	18.4	17.7
27	1% Ethyl acetate in heptane	4.2	4.9	4.7	6.0	6.4	8.3	8.8	12.6	11.5	—	—	12.1	11.2	14.3	14.4
29	<i>n</i> -Heptane	5.7	6.9	6.3	7.3	7.3	9.4	9.0	11.6	10.6	—	—	10.6	10.4	13.2	11.7

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