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GAS CHROMATOGRAPHIC - MASS SPECTROMETRIC CHARACTERIZATION OF MONOMETHYLALKANES FROM FUEL DIESEL

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Abstract

The programmed-temperature linear retention indices of all 196 C_4–C_{30} monomethylalkanes on OV–1 stationary phase were measured with an average repeatibility of ± 0.07 i. u. The mixture of C_9–C_{30} monomethylalkanes was prepared by methylene insertion reaction to C_8–C_{29} *n*–alkanes mixture. The preliminary identification of monomethylalkanes was performed on the basis of the dependence of homomorphy factors on the number of carbon atoms of individual homologous series of monomethylalkanes. The prediction of retention of isomers with new position of methyl group beginning at higher carbon atoms number, as well as for second, third, fourth etc. member of homologous series allowed the dependence $H_P=f(C_n)$ for first, second, third etc. members of beginning homologous of monomethylalkane series. The identification was confirmed by mass spectrometry. All gas chromatographic unseparated monomethylalkane isomers with methyl- group near the middle of molecule carbon chain were resoluted by mass spectrometric deconvolution. Obtained regular dependences $H_P=f(C_n)$ allow precise retention prediction of monomethylalkanes >C_{30}. These analytical procedures were used for identification of monomethylalkanes from fuel diesel.

Keywords: monomethylated alkanes, Kovats retention indices, structure-retention correlation, identification in fuel diesel

1. Introduction

Monomethylalkanes are present in many naturally occurring and synthetic organic materials. These compounds are important constituents of petroleum crudes, bitumens, coal, and ancient geological sediments which contain numerous isoprenoids; products of shale thermolysis; product of catalytic cracking and hydrocracking of hydrocarbons; and products of Fisher-Tropsch synthesis [1]. They also were discovered in cultures of cyanobacteria as possible source of methyl–branched alkanes found in sediments and crude oils [2]. Similarly insects produce a great variety of methyl–branched alkanes with the methyl–branch located at restricted positions (2-, 3-, 7-, 9-, 11-, 13-, or 15-) of molecule carbon chain [3]. Alkanes have also been proposed as endogenous marker compounds in exhaled breath [4-7].

The principal methods used for the analysis of monomethylalkanes is capillary gas chromatography (CGC), and capillary gas chromatography–mass spectrometry (CGC–MS) by using of methylsilicones as stationary phases in temperature–programmed columns. The problem of identification of individual monomethylalkanes in broad range of carbon atoms (C>10) is related to their multicomponentity and close retention of isomers with methyl–branching near the middle of molecule carbon chain. Also, the lack of standard reference materials and the absence and/or relative poorer reproducibility of published retention data is a critical point. Often retention data are only given in graphical form. In addition, the various calculation methods of retention are not accurate enough, as well as the limitations of GC–MS hyphenated techniques mainly for gas chromatographic unseparated compounds on the other hand. Already starting with monomethylnonanes, problems of isomer separations with methyl group in the middle of carbon chain begin even with using common 25–50 m long capillary columns with apolar stationary phase.

Carlson et al. [8] studied retention behaviour of typical mono-, di-, tri- and tetra-methylalkanes comprising most of the commonly appearing series of homologous methyl–branched alkanes C_{21}–C_{53}

that are found in insect cuticular hydrocarbons, and typical insect–derived C_{34} methylalkanes with methyl on odd–numbered carbons were characterized by retention indices. To obtain more complete retention data for identification of insect alkane products (30 methylalkane congeners up to C_{30}) Katrizky et al. [3] established the quantitative structure–property relationships (QSPR) models including 178 monomethyl-, dimethyl-, trimethyl-, and tetramethylalkanes by means of topological and quantum chemical descriptors. The average standard deviation of the model was 4.6. Zarei and Atabati [9] by QSPR study of previous model, however based on the artificial neural network technique obtained lower average relative error 3.3 %. Du and Liang [10] collected retention indices on squalane of 134 different alkanes up to C_{13} into the acta set for seeking accurate quantitative relationships between molecular structure and isothermic retention indices of alkanes by projection pursuit. By a new variable class distance variable which describes the branching structure of the alkanes the fitting and prediction accuracy of the regression model was improved (standard error is about ±3 i. u.). Kenig et al. [2] by comparison of measured mass spectral and retention data with published data in the saturated hydrocarbon fractions of modern and Halocene cyanobacterial mats identified thirty C_{17}–C_{30} monomethylalkanes. The most complete GC retention behaviour of C_9–C_{36} methyl–substituted alkanes published Kissin and Feulmer [1]. The mixtures of alkanes were prepared by co–oligomerization of ethylene and different alpha alkenes to alkenic compounds which were subsequently hydrogenated with Raney nickel to the mixtures of alkyl–substituted alkanes. Identifications of compounds in the obtained mixture were performed by: expected structures and relative concentration of alkenes formed, correlations between boiling points and their peak retention, comparison with known compounds where available, and comparison of GC patterns the chromatograms from the different oligomerization products. The retention data [1] are given in graphic form like dependence of relative retention factors on the carbon atom numbers of monomethylalkanes for 127 monomethylalkanes. The missing retention data belong to the monomethylalkanes with methyl group more to the centre of molecule carbon chain which are most difficult separated from the neighbouring eluated isomers.

The aim of this work was the investigation of GC retention behaviour of all monomethylalkanes up to C_{30} on methylsilicone OV–1 as stationary phase. The monomethylalkane mixtures were prepared by methylene insertion reaction [11] from mixture of *n*–alkanes up to C_{29}. Identification of monomethylalkanes in multicomponent reaction mixture was performed using structure–retention correlations by dependence of homomorphy factors of individual homologous series of monomethylalkanes on the number of carbon atoms [12,13] and confirmed by mass spectrometry [2]. To obtain the retention indices of monomethylalkane isomers with methyl group near of the middle of carbon atom chain which were unseparated by 100 m long capillary column the means of mass spectrometric deconvolution were used. These analytical procedures were used for identification of monomethylalkanes from fuel diesel.

2. Experimental

All monomethylalkanes up to C_{30} as a model mixture were prepared from *n*–alkanes mixture C_8-C_{29} by methylene insertion reaction [11] and completed by individual C_4–C_8 methylalkanes. Recovery of this reaction was about 4 % of monomethylalkanes. For avoidance of overloading the column with present *n*–alkanes the small sample were injected and detected by electron ionization MS in SIM-mode. Obtained mixture of monomethylalkanes was separated by capillary gas chromatography in the range of 30 – 310 °C, their programmed–temperature linear retention indices were calculated, and identified by structure–retention relationships of homomorphy factors of individual monomethylalkane homologous series (2-, 3-, 4-, …15- methylalkanes) on the number of carbon atoms [12,13] and confirmed by GC–MS [2]. The C_8–C_{29} *n*–alkanes used for methylene insertion reaction were obtained from Supelco, Bellefonte, USA, and C_3–C_7 *n*–alkanes and C_4–C_8 monomethylalkanes were obtained from Sigma–Aldrich, Germany. The analyzed sample of fuel diesel was a standard commercial product of Slovnaft, a. s.

GC–MS measurements were performed on a gas chromatograph Agilent Technologies 6890 N with 5973 Network mass selective detector. The 1 µl of sample injection operated in the split injection mode with a split ratio 100:1 at the temperature 320 °C. The monomethylalkanes mixture was separated using capillary column 100 m x 0.32 mm i. d. coated with a film thickness of 0.25 µm of methylsilicone OV–1 as stationary phase (Supelco, Bellefonte, USA). The column temperature was 30 °C initially, then the temperature was increased to 310 °C at ramp rate of 5 °C.min^{-1}, temperature was held at the final temperature 310 °C for 5 min. Helium carrier gas with linear velocity 26 cm.s^{-1} was used. Mass spectral data were obtained by SIM–mode. Transfer line temperature was 330 °C. Quadrupole conditions were as follows: electron energy 70 eV, and ion source temperature 230 °C. Each GC peak was inspected for constancy of MS pattern in order to detect possible overlapping compounds and to measure their retention data. The GC–MS/SIM chromatograms were obtained for

characteristic fragment ions (Table 1). The temperature–programmed retention indices of monomethylalkanes were measured with an average repeatability of ± 0.07 index units (i. u.), from three parallel measurements.

3. Results and discussion

The obtained chromatogram of GC separation of C_9–C_{30} monomethylalkanes from methylene insertion reaction to *n*–alkanes with assigned peaks is given in Fig. 1.

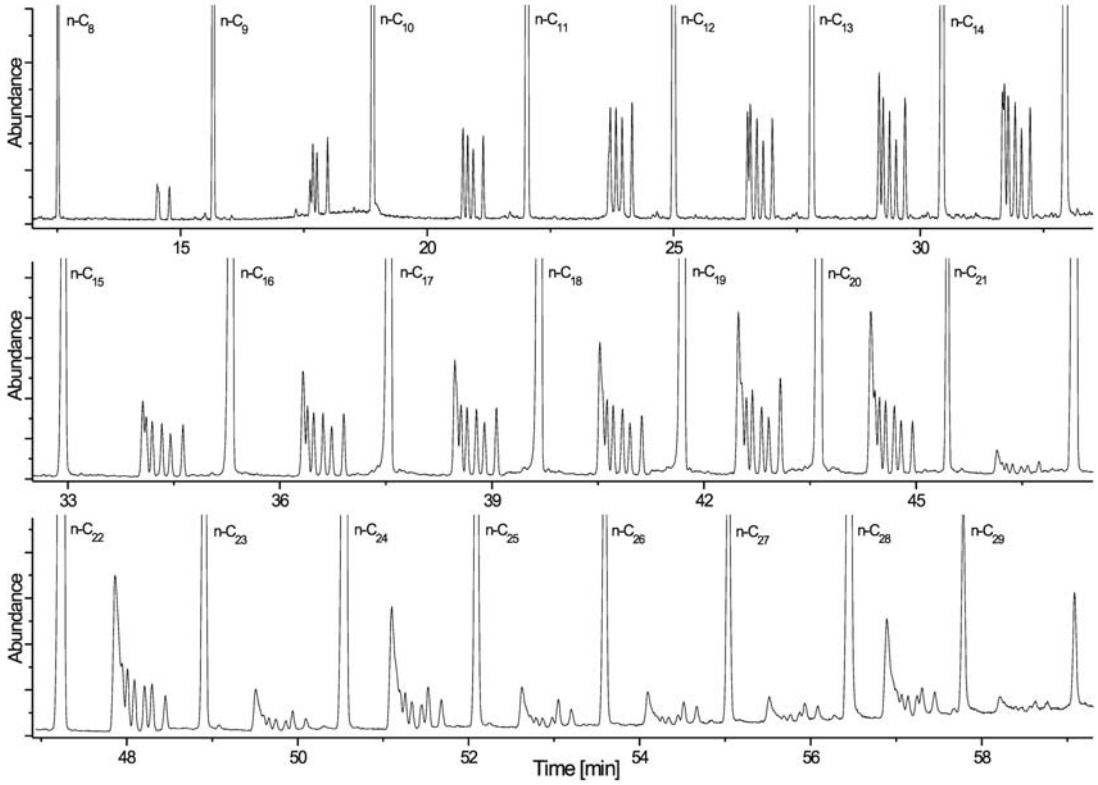

Fig. 1. Chromatogram of GC separation of C_9-C_{30} monomethylalkanes with *n*-alkanes.

It can be seen that characteristic mixtures of all isomeric monomethylalkanes were obtained. The measured programmed–temperature linear retention indices $I_P^{OV\text{-}1}$ and their standard deviation *s* from given chromatogram for monomethylalkanes up to C_{30} on methylsilicone stationary phases are given in the Table I.

Table I. Measured programmed-temperature linear retention indices I_P of C_4-C_{30} monomethylalkanes on OV-1 and their standard deviations *s*, homomorphy factors H_P, the differences of measured and extrapolated ΔH_P values, and specific and molecular MS ions m/z.

Monomethylalkane	$I_P^{OV\text{-}1}$	*s*	H_P	ΔH_P	Specific MS ions m/z
2-methylpropane	354.77	0.209	-45.23		43, 27,58
2-methylbutane	466.23	0.320	-33.77		43, 27, 72
2-methylpenatane	561.31	0.146	-38.69		43, 71, 86
3-methylpenatane	578.05	0.162	-21.95		57, 29, 86
2-methylhexane	662.48	0.101	-37.52		43, 57, 100
3-methylhexane	672.19	0.034	-27.81		43, 71, 100
2-methylheptane	764.32	0.157	-35.68	0.51	42, 70, 114
4-methylheptane	765.88	0.085	-34.12		70, 42, 114
3-methylheptane	772.17	0.119	-27.83		56, 56, 114
4-methyloctane	864.06	0.085	-35.94		70, 56, 128
2-methyloctane	865.00	0.057	-35.00	-0.05	42, 84, 128

Monomethylalkane	I_P^{OV-1}	s	H_P	ΔH_P	Specific MS ions m/z
3-methyloctane	871.89	0.120	-28.11		56, 70, 128
5-methylnonane	961.09	0.103	-38.91		84, 56, 142
4-methylnonane	962.83	0.145	-37.17		70, 70, 142
2-methylnonane	965.39	0.110	-34.61	-0.20	42, 98, 142
3-methylnonane	972.06	0.124	-27.94	0.21	56, 84, 142
5-methyldecane	1058.94	0.114	-41.06		84, 70, 156
4-methyldecane	1062.04	0.071	-37.96		70, 84, 156
2-methyldecane	1065.62	0.071	-34.38	0.13	42, 112, 156
3-methyldecane	1072.06	0.085	-27.94	0.08	56, 98, 156
6-methylundecane	1156.16	0.045	-43.84		98, 70, 170
5-methylundecane	1157.36	0.120	-42.64		84, 84,170
4-methylundecane	1161.21	0.112	-38.79	-0.21	70, 98, 170
2-methylundecane	1165.48	0.075	-34.52	-0.21	42, 126, 170
3-methylundecane	1172.15	0.067	-27.85	0.15	56, 112, 170
6-methyldodecane	1254.15	0.079	-45.85	-0.28*	98, 84, 184
5-methyldodecane	1256.18	0.087	-43.82	-0.15*	84, 98, 184
4-methyldodecane	1260.75	0.040	-39.25	-0.12	70, 112, 184
2-methyldodecane	1265.36	0.087	-34.64	-0.21	42, 140, 184
3-methyldodecane	1272.12	0.048	-27.88	-0.02	56, 126, 184
7-methyltridecane	1351.94	0.059	-48.06	0.21*	112, 84, 198
6-methyltridecane	1352.60	0.126	-47.40	-0.08*	98, 98, 198
5-methyltridecane	1355.43	0.067	-44.57	-0.14	84, 112, 198
4-methyltridecane	1360.35	0.067	-39.65	-0.17	70, 126, 198
2-methyltridecane	1365.35	0.059	-34.65	-0.11	42, 154, 198
3-methyltridecane	1372.33	0.059	-27.67	0.19	56, 140, 198
7-methyltetradecane	1450.13	0.045	-49.87	0.18*	112, 98, 212
6-methyltetradecane	1451.63	0.071	-48.37	-0.06*	98, 112, 212
5-methyltetradecane	1454.71	0.116	-45.29	-0.18	84, 126, 212
4-methyltetradecane	1460.18	0.071	-39.82	-0.05	70, 140, 212
2-methyltetradecane	1465.37	0.027	-34.63	0.01	42, 168, 212
3-methyltetradecane	1472.51	0.080	-27.49	0.15	56, 154, 212
8-methylpentadecane	1548.19	0.066	-51.81	0.25*	126, 98, 226
7-methylpentadecane	1548.85	0.028	-51.15	0.25*	112, 112, 226
6-methylpentadecane	1550.66	0.019	-49.34	-0.62	98, 126, 226
5-methylpentadecane	1554.24	0.057	-45.76	-0.23	84, 140, 226
4-methylpentadecane	1559.97	0.057	-40.03	-0.13	70, 154, 226
2-methylpentadecane	1565.24	0.066	-34.76	-0.11	42, 182, 226
3-methylpentadecane	1572.67	0.066	-27.33	0.12	56, 168, 226
8-methylhexadecane	1646.96	0.060	-53.04	0.22*	126, 112, 240
7-methylhexadecane	1647.63	0.060	-52.37	0.23*	112, 126, 240
6-methylhexadecane	1650.07	0.050	-49.93	-0.42	98, 140, 240
5-methylhexadecane	1653.97	0.040	-46.03	-0.07	84, 154, 240
4-methylhexadecane	1659.91	0.129	-40.09	0.30	70, 168, 240
2-methylhexadecane	1665.35	0.060	-34.65	0.02	42, 196, 240
3-methylhexadecane	1672.99	0.070	-27.01	0.28	56, 182, 240
9-methylheptadecane	1745.40	0.052	-54.60	0.19*	140, 112, 254
8-methylheptadecane	1745.55	0.031	-54.45	-0.12*	126, 126, 254
7-methylheptadecane	1746.93	0.052	-53.07	-0.25	112, 140, 254
6-methylheptadecane	1749.71	0.052	-50.29	-0.20	98, 154, 254
5-methylheptadecane	1753.65	0.063	-46.35	-0.19	84, 168, 254
4-methylheptadecane	1759.94	0.105	-40.06	0.03	70, 182, 254
2-methylheptadecane	1765.29	0.073	-34.71	-0.01	42, 210, 254

Monomethylalkane	I_P^{OV-1}	s	H_P	ΔH_P	Specific MS ions m/z
3-methylheptadecane	1773.21	0.021	-26.79	0.20	56, 196, 254
9-methyloctadecane	1844.03	0.055	-55.97	-0.07*	140, 126, 268
8-methyloctadecane	1844.56	0.066	-55.44	-0.04*	126, 140, 268
7-methyloctadecane	1846.51	0.077	-53.49	-0.24	112, 154, 268
6-methyloctadecane	1849.34	0.088	-50.66	-0.21	98,168, 268
5-methyloctadecane	1853.61	0.033	-46.39	0.02	84, 182, 268
4-methyloctadecane	1859.97	0.044	-40.03	0.06	70, 196, 268
2-methyloctadecane	1865.28	0.066	-34.72	-0.01	42, 224, 268
3-methyloctadecane	1873.44	0.066	-26.56	0.18	56, 210, 268
10-methylnonadecane	1942.61	0.069	-57.39	-0.25*	154, 126, 282
9-methylnonadecane	1943.01	0.046	-56.99	0.01*	140, 140, 282
8-methylnonadecane	1943.74	0.058	-56.26	-0.21	126, 154, 282
7-methylnonadecane	1945.79	0.058	-54.21	0.27	112, 168, 282
6-methylnonadecane	1948.99	0.035	-51.01	-0.20	98, 182, 282
5-methylnonadecane	1953.45	0.173	-46.55	-0.17	84, 196, 282
4-methylnonadecane	1959.94	0.058	-40.06	-0.01	70, 210, 282
2-methylnonadecane	1965.23	0.058	-34.77	-0.08	42, 238, 282
3-methylnonadecane	1973.84	0.046	-26.16	0.30	56, 224, 282
10-methyleicosane	2041.65	0.024	-58.35	-0.01*	154, 140, 296
9-methyleicosane	2042.17	0.036	-57.83	0.02*	140, 154, 296
8-methyleicosane	2043.28	0.060	-56.72	-0.29	126, 168, 296
7-methyleicosane	2045.45	0.024	-54.55	0.08	112, 182, 296
6-methyleicosane	2048.79	0.024	-51.21	-0.14	98, 196, 296
5-methyleicosane	2053.39	0.024	-46.61	-0.05	84, 210, 296
4-methyleicosane	2060.16	0.072	-39.84	0.20	70, 224, 296
2-methyleicosane	2065.34	0.024	-34.66	0.12	42, 252, 296
3-methyleicosane	2074.15	0.024	-25.85	0.30	56, 238, 296
11-methylheneicosane	2140.37	0.063	-59.63	-0.24*	168, 140, 310
10-methylheneicosane	2140.48	0.025	-59.52	-0.17*	154, 154, 310
9-methylheneicosane	2141.20	0.101	-58.80	-0.24	140, 168, 310
8-methylheneicosane	2142.57	0.063	-57.43	-0.24	126, 182, 310
7-methylheneicosane	2144.97	0.038	-55.03	-0.17	112, 196, 310
6-methylheneicosane	2148.36	0.075	-51.64	-0.20	98, 210, 310
5-methylheneicosane	2153.24	0.063	-46.76	-0.14	84, 224, 310
4-methylheneicosane	2160.05	0.101	-39.95	-0.11	70, 238, 310
2-methylheneicosane	2165.23	0.063	-34.77	-0.06	42, 266, 310
3-methylheneicosane	2174.30	0.025	-25.70	0.15	56, 252, 310
11-methyldocosane	2239.26	0.026	-60.74	-0.22*	168, 154, 324
10-methyldocosane	2239.65	0.026	-60.35	-0.12*	154, 168, 324
9-methyldocosane	2240.71	0.092	-59.29	-0.10	140, 182, 324
8-methyldocosane	2242.27	0.026	-57.73	-0.18	126, 196, 324
7-methyldocosane	2244.66	0.026	-55.34	-0.26	112, 210, 324
6-methyldocosane	2248.15	0.105	-51.85	-0.15	98, 224, 324
5-methyldocosane	2253.04	0.065	-46.96	-0.19	84, 238, 324
4-methyldocosane	2260.03	0.065	-39.97	-0.08	70, 252, 324
2-methyldocosane	2265.06	0.026	-34.94	-0.21	42, 280, 324
3-methyldocosane	2274.34	0.026	-25.66	0.05	56, 266, 324
12-methyltricosane	2338.03	0.027	-61.97	-0.20*	182, 154, 338
11-methyltricosane	2338.15	0.027	-61.85	-0.53*	168, 168, 338
10-methyltricosane	2338.69	0.027	-61.31	-0.20	154, 182, 338
9-methyltricosane	2340.01	0.027	-59.99	-0.27	140, 196, 338
8-methyltricosane	2341.69	0.041	-58.31	-0.21	126, 210, 338

Monomethylalkane	I_P^{OV-1}	s	H_P	ΔH_P	Specific MS ions m/z
7-methyltricosane	2344.25	0.027	-55.75	-0.27	112, 224, 338
6-methyltricosane	2347.92	0.055	-52.08	-0.21	98, 238, 338
5-methyltricosane	2352.88	0.069	-47.12	-0.15	84, 252, 338
4-methyltricosane	2360.07	0.082	-39.93	-0.01	70, 266, 338
2-methyltricosane	2365.04	0.069	-34.96	-0.18	42, 294, 338
3-methyltricosane	2374.70	0.055	-25.30	0.16	56, 280, 338
12-methyltetracosane	2437.35	0.028	-62.65	-0.07*	182, 168, 352
11-methyltetracosane	2437.61	0.057	-62.39	-0.14*	168, 182, 352
10-methyltetracosane	2438.25	0.028	-61.75	-0.22	154, 196, 352
9-methyltetracosane	2439.74	0.057	-60.26	-0.16	140, 210, 352
8-methyltetracosane	2441.52	0.028	-58.48	-0.08	126, 224, 352
7-methyltetracosane	2444.20	0.057	-55.80	0.21	112, 238, 352
6-methyltetracosane	2447.95	0.028	-52.05	0.04	98, 252, 352
5-methyltetracosane	2452.97	0.043	-47.03	0.09	84, 266, 352
4-methyltetracosane	2460.14	0.028	-39.86	0.11	70, 280, 352
2-methyltetracosane	2465.07	0.099	-34.93	0.01	42, 308, 352
3-methyltetracosane	2474.86	0.043	-25.14	0.13	56, 294, 352
13-methylpentacosane	2536.47	0.030	-63.53	-0.21*	196, 168, 366
12-methylpentacosane	2536.54	0.030	-63.46	-0.24*	182, 182, 366
11-methylpentacosane	2536.98	0.059	-63.02	-0.15	168, 196, 366
10-methylpentacosane	2537.74	0.030	-62.26	-0.11	154, 210, 366
9-methylpentacosane	2539.36	0.044	-60.64	-0.27	140, 224, 366
8-methylpentacosane	2541.32	0.030	-58.68	-0.18	126, 238, 366
7-methylpentacosane	2543.98	0.030	-56.02	-0.25	112, 252, 366
6-methylpentacosane	2547.85	0.074	-52.15	-0.04	98, 266, 366
5-methylpentacosane	2553.15	0.030	-46.85	0.27	84, 280, 366
4-methylpentacosane	2560.60	0.074	-39.40	0.26	70, 294, 366
2-methylpentacosane	2565.29	0.030	-34.71	0.27	42, 322, 366
3-methylpentacosane	2575.45	0.044	-24.55	0.20	56, 308, 366
13-methylhexacosane	2635.44	0.031	-64.56	-0.26*	196,182, 380
12-methylhexacosane	2635.87	0.062	-64.13	-0.16*	182, 196, 380
11-methylhexacosane	2636.31	0.046	-63.69	-0.27	168, 210, 380
10-methylhexacosane	2637.35	0.092	-62.65	-0.23	154, 224, 380
9-methylhexacosane	2639.09	0.092	-60.91	-0.26	140, 238, 380
8-methylhexacosane	2641.09	0.092	-58.91	-0.18	126, 252, 380
7-methylhexacosane	2643.84	0.031	-56.16	-0.13	112, 266, 380
6-methylhexacosane	2647.91	0.123	-52.09	0.03	98, 280, 380
5-methylhexacosane	2653.06	0.031	-46.94	0.05	84, 294, 380
4-methylhexacosane	2660.71	0.046	-39.29	0.07	70, 308, 380
2-methylhexacosane	2665.30	0.031	-34.70	0.01	42, 336, 380
3-methylhexacosane	2675.72	0.077	-24.28	0.10	56, 322, 380
14-methylheptacosane	2734.93	0.032	-65.07	-0.25*	210, 182, 394
13-methylheptacosane	2735.00	0.032	-65.00	0.02*	196, 196, 394
12-methylheptacosane	2735.45	0.063	-64.55	-0.22	182, 210, 394
11-methylheptacosane	2736.16	0.079	-63.84	0.08	168, 224, 394
10-methylheptacosane	2737.21	0.032	-62.79	-0.10	154, 238, 394
9-methylheptacosane	2739.14	0.063	-60.86	0.10	140, 252, 394
8-methylheptacosane	2741.07	0.079	-58.93	-0.01	126, 266, 394
7-methylheptacosane	2743.87	0.032	-56.13	0.05	112, 280, 394
6-methylheptacosane	2747.82	0.210	-52.18	-0.06	98, 294, 394
5-methylheptacosane	2753.22	0.079	-46.78	0.11	84, 308, 394
4-methylheptacosane	2760.86	0.063	-39.14	0.19	70, 322, 394

Monomethylalkane	I_P^{OV-1}	*s*	H_P	ΔH_P	Specific MS ions m/z
2-methylheptacosane	2765.26	0.032	-34.74	-0.01	42, 350, 394
3-methylheptacosane	2776.09	0.003	-23.91	0.19	56, 336, 394
14-methyloctacosane	2834.42	0.082	-65.58	-0.28*	210, 196, 408
13-methyloctacosane	2834.57	0.082	-65.43	0.01*	196, 210, 408
12-methyloctacosane	2835.14	0.049	-64.86	-0.16	182, 224, 408
11-methyloctacosane	2835.88	0.099	-64.12	-0.29	168, 238, 408
10-methyloctacosane	2837.14	0.099	-62.86	-0.08	154, 252, 408
9-methyloctacosane	2839.07	0.049	-60.93	0.01	140, 266, 408
8-methyloctacosane	2841.19	0.033	-58.81	0.10	126, 280, 408
7-methyloctacosane	2843.96	0.099	-56.04	0.11	112, 294, 408
6-methyloctacosane	2848.04	0.049	-51.96	0.21	98, 308, 408
5-methyloctacosane	2853.40	0.066	-46.60	0.18	84, 322, 408
4-methyloctacosane	2861.18	0.082	-38.82	0.22	70, 336, 408
2-methyloctacosane	2865.70	0.165	-34.30	0.27	42, 364, 408
3-methyloctacosane	2876.38	0.033	-23.62	0.20	56, 350, 408
15-methylnonacosane	2933.77	0.068	-66.23	-0.29*	224, 196, 422
14-methylnonacosane	2933.82	0.034	-66.18	-0.24*	210, 210, 422
13-methylnonacosane	2934.26	0.002	-65.74	-0.18	196, 224, 422
12-methylnonacosane	2934.85	0.086	-65.15	-0.20	182, 238, 422
11-methylnonacosane	2935.54	0.171	-64.46	-0.26	168, 252, 422
10-methylnonacosane	2937.00	0.034	-63.00	-0.10	154, 266, 422
9-methylnonacosane	2938.90	0.120	-61.10	-0.14	140, 280, 422
8-methylnonacosane	2941.11	0.103	-58.89	0.04	126, 294, 422
7-methylnonacosane	2943.93	0.068	-56.07	0.04	112, 308, 422
6-methylnonacosane	2948.14	0.120	-51.86	0.23	98, 322, 422
5-methylnonacosane	2953.43	0.154	-46.57	0.03	84, 336, 422
4-methylnonacosane	2961.56	0.137	-38.44	0.10	70, 350, 422
2-methylnonacosane	2965.72	0.027	-34.28	0.13	42, 378, 422
3-methylnonacosane	2976.43	0.034	-23.57	0.04	56, 364, 422
Average		0.065		0.16	

Note: With asterisks are assigned ΔH_P* values obtained on the basis of extrapolated H_P values for first, second, third, etc. members of beginning monomethylalkane homologues series.

Despite using a high resolution 100 m long capillary column, gas chromatographic separation of several monomethylalkanes were not obtained. The separation difficulties increase with the shift of the methyl group to the middle of the molecule carbon chain and with the increasing number of monomethylalkane carbon atoms. The most difficult separable isomers are those with methyl–substitution in the centre of molecule carbon chain and those isomers with new position of methyl group beginning at higher number of carbon atoms. From retention data in Table I it follows that at C_{10} the retention index difference of isomers with new methyl–position 5-methylnonane and 4-methylnonane is 1.7 i. u., at C_{12} for 6- and 5- methylundecane such difference is 1.1 i. u., at C_{14} for 7- and 6- methyltridecane is 0.8 i. u., at C_{16} for 8- and 7- methylpentadecane is 0.4 i. u., at C_{18} for 9- and 8- methylheptadecane is 0.2 i. u. Such small retention differences indicate the problem of their separation. From the chromatogram in Fig. 1 it can be seen that from C_{14} these new positional isomers are not separated from neighbouring eluted isomers at given experimental conditions. Separation problems increase with increasing carbon atom number of monomethylalkanes because of increasing number of isomers with very near physicochemical properties. E. g. for C_{20} monomethylalkanes, the isomers with methyl–position 8-, 9-, and 10- are not separated, and also isomer 7- is only very weakly separated. For C_{30} monomethylalkanes the isomers with methyl–position from 7- up to 15- are not separated.

The retention indices of gas chromatographically unseparated monomethylalkane isomers were calculated by mass spectrometric deconvolution. GC–MS deconvolution was performed by using of the characteristic fragment ions formed by cleavage of the carbon–carbon bond adjacent to the tertiary carbon atoms. Each isomer can be characterized by two even mass fragment ions [2].

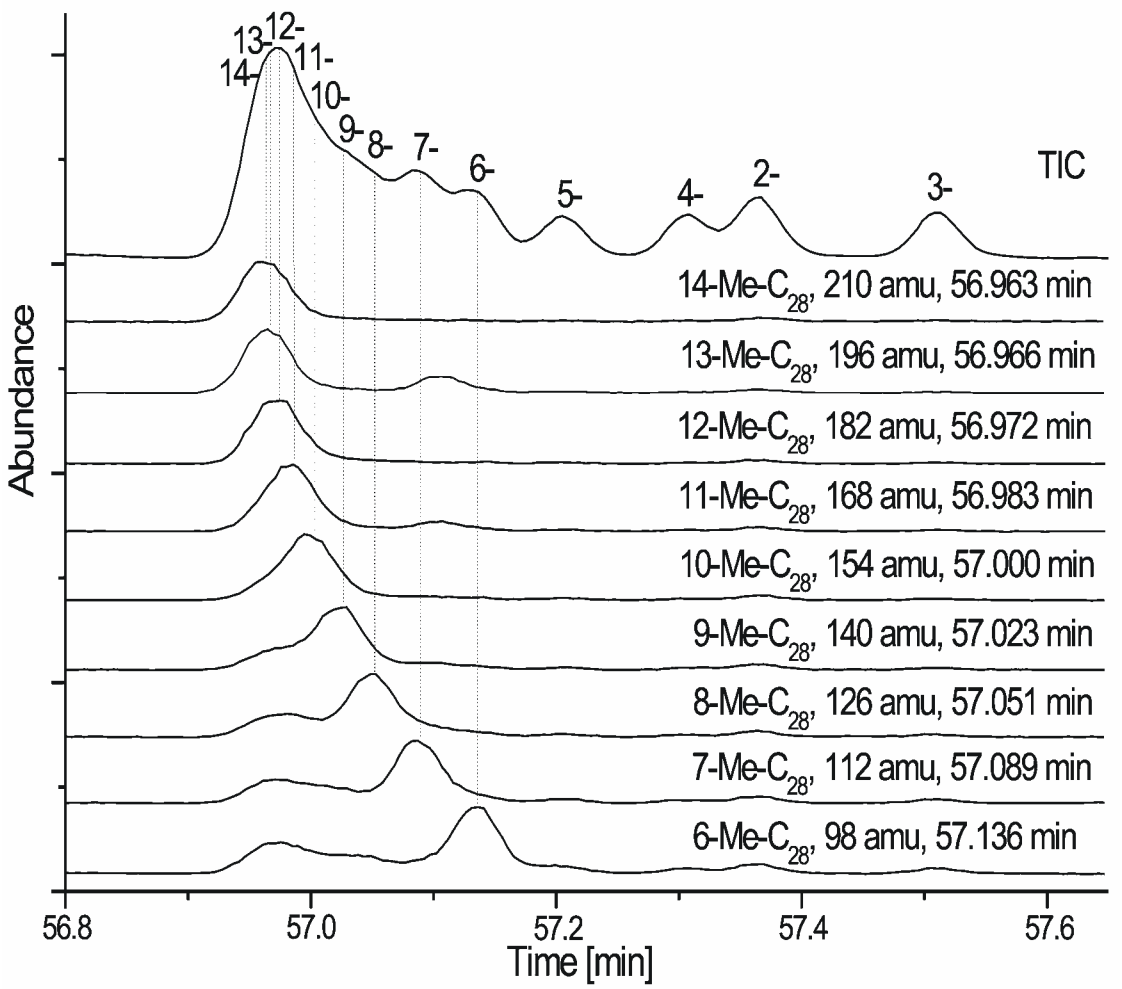

Fig. 2. Mass spectrometric deconvolution of GC unseparated isomers of monomethyloctacosanes.

As an example consider Fig. 2, which shows the result of mass spectrometric deconvolution of the GC unseparated isomers 14-, 13-, 12-, 11-, 10-, 9-, 8- monomethyloctacosanes. All these isomers were mass spectrometrically deconvoluted by detection of specific fragment ions, obtaining calculated retention times and retention indices. For the deconvoluted 14- and 13- monomethylnoctacosanes pair the retention time difference is only 0.003 min corresponding to a retention index difference 0.15 i. u.

The preliminary identification of monomethylalkanes reaction products was obtained from measured temperature-programmed linear retention indices by structure–retention relationships based on the dependence of homomorphy factors on the number of carbon atoms for individual homologous series i. e. for 2-, 3-, 4-, …and 15- methylalkanes. The homomorphy factor *H* value is defined as the difference of retention index of the given alkane homologue and *n*- alkane with the same carbon atom number. Thus the *H* value characterizes the contribution of functional group to retention index [13,14]. Under isothermic separation conditions the *H* values for hydrocarbon homologous series exhibit characteristic non–linear asymptotical decreasing dependence with increasing number of homologous carbon atoms. The decrease of *H* values is apparent up to five–six carbon atoms from the beginning of the given homologous structural trait. For linear temperature-programmed column, the measured programmed-temperature linear retention indices I_P and corresponding dependences $H_P=f(C_n)$ were used for identification homologous of C_6–C_{23} alk-1-enes, (*E*)-alk-2-enes, (*Z*)-alk-2-enes, alka-*α,ω*-dienes, and corresponding *n*–alkanes as main products of polyethylene thermal cracking [15]. In the present work similar dependence was used for preliminary identification of monomethylalkanes as products of methylene insertion reactions to *n*–alkanes. The calculated H_P values (based on the measured I_P values) are given in Table I.

The obtained dependence of $H_P=f(C_n)$ for individual homologous series of monomethylalkanes is presented in Fig. 3.

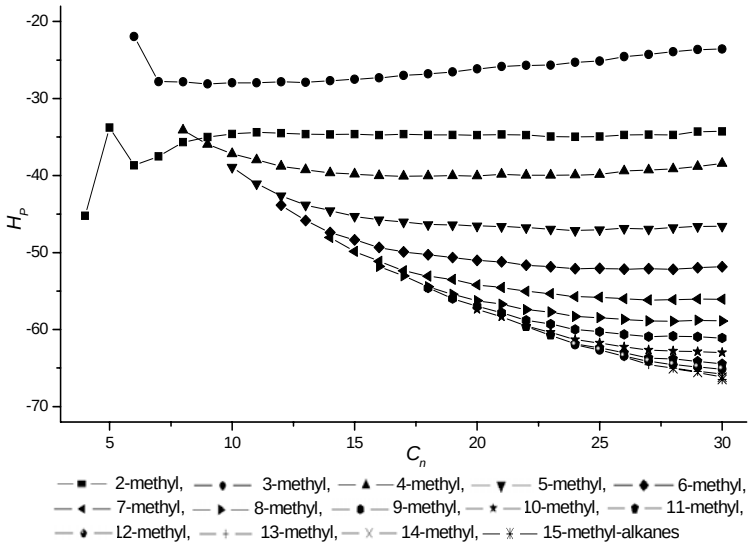

Fig. 3. Dependence of homomorphy factors on the number of carbon atoms of monomethylalkane homologues series.

As can be seen the retention of positional monomethylalkane isomers increases with the shift of methyl group from the middle to the end of molecule carbon chain, and the retention difference of neighbouring eluted isomers increase. However, all 2-methylalkanes are eluted before 3-methylalkanes, and even 2-methylheptane is eluted before 4-methylheptane. The reason of such peculiar retention behaviour of 2-methylalkanes is presence of tertiary carbon atom. Such structures exhibit higher symmetry of molecule, lower polarizability, and weaker interaction solute–solvent and correspondingly lower retention [11].

The regularity of the dependence $H_P=f(C_n)$ allows a precise extrapolation of higher homologous retention. For the calculation of extrapolated H_P values we used H_P values of the last 4 homologous by equation

$$y = a * e^{-x/b} + c$$

where x is number of carbon atoms, y is homomorphy factor, and a, b, c are coefficients. The differences of measured and extrapolated H_P values are given in Table 1, the average precision of extrapolated H_P values was ± 0.15 i. u.

However, the retention of isomers with a new position of methyl group beginning at higher number of carbon atoms with previous procedure cannot be obtained in this way. In this case, the H_P values of these isomers were obtained by extrapolation of dependence $H_p=f(C_n)$ for the first homologous members of monomethylalkanes with new position of methyl group, i.e. on the basis of H_P values for 2-methylpropane, 3-methylpentane, 4-methylheptane, 5-methylnonane, 6-methylundecane, etc., also by using the above equation. Because the retention of lower homologous monomethylalkanes is more influenced by stereochemical and conformational aspects of their structure, the more precise extrapolated H_P values were obtained on the basis of higher homologous data. Another problem is the reliable extrapolation of this dependence from data for one or two, three or four beginning homologues. In these cases, for the prediction of second, third, fourth, etc. homologue series member similar dependences $H_P=f(C_n)$ as for first members i. e. for second, third, fourth, etc. members of beginning homologues were used. In this case, the average precision of extrapolated H_P values was ± 0.17 i. u. The regularities of these dependences are evident from Fig. 4.

The dependence $H_P=f(C_n)$ for first homologous members of monomethylalkanes series with new position of methyl group is in Fig. 4 assigned as 1st series. The H_P values of second homologous members were obtained by extrapolation of dependence $H_P=f(C_n)$ for the second homologous members, i. e. 2-methylbutane, 3-methylhexane, 4-methyloctane, 5-methyldecane,14-methyloctacosane, in Fig. 4 assigned as 2nd series. Similarly for further homologous members of monomethylalkanes are assigned up to 14th series in Fig. 4.

The preliminary identification of monomethylalkanes as model analytes obtained by methylene insertion reaction to *n*–alkanes was confirmed by GC–MS [2].

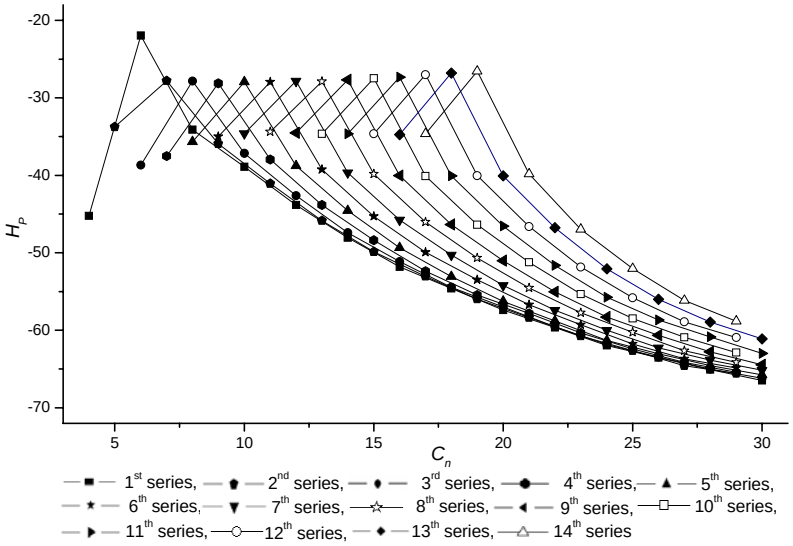

Fig. 4. Dependence of homomorphy factors on the number of carbon atoms for first, second, third, etc. member of monomethylalkane homologues series.

The measured temperature-programmed linear retention indices of monomethylalkanes up to C_{30} on apolar methylsilicone OV–1 stationary phase are in agreement on 1.7 to – 2.6 i. u. for 28 C_{10}–C_{30} monomethylalkanes of Katritzky and Chen [3] data. These differences for 30 C_{17}–C_{30} monomethylkalkanes of Kenig et al. data [2] were 2.0 to – 8.4 i.u. Comparison of our measured data with the Kissin and Feulmer data [1] for 127 of 187 possible C_9–C_{30} monomethylalkanes shows that in this work measured retention indices are in average on 2 i. u. higher. In the work of Carlson et al. [8] given retention indices of several C_{34} monomethylalkanes are on 2 i. u. lower than retention indices extrapolated from dependence in Fig. 3. These comparisons confirm the interlaboratory reliability of measured retention indices given in Table I.

3. 1 GC-MS identification of monomethylalkanes in fuel diesel

The obtained chromatogram of GC separation of fuel diesel in used separation system is given in Fig. 5.

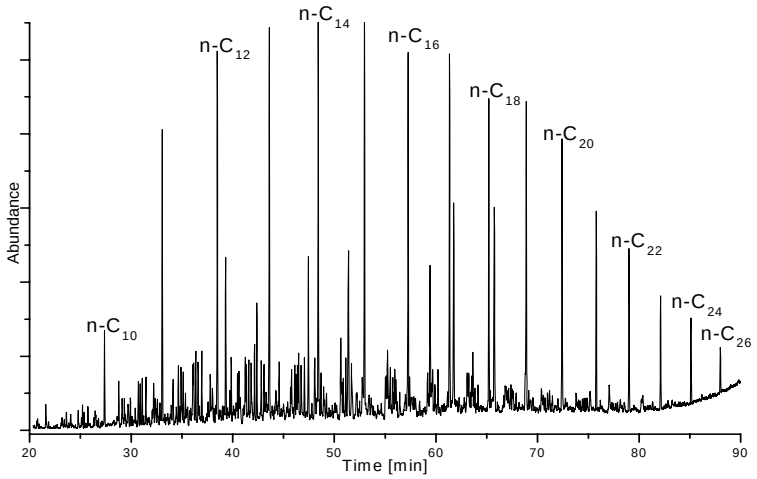

Fig. 5. GC-MS/TIC chromatogram of the separation of fuel diesel.

Fig. 6 shows the result of mass spectrometric deconvolution of the GC unseparated isomers 10-, 9-, 8-, 7-, 6- monomethylnonadecanes in fuel diesel. All these isomers were mass spectrometrically deconvoluted by detection of specific fragment ions.

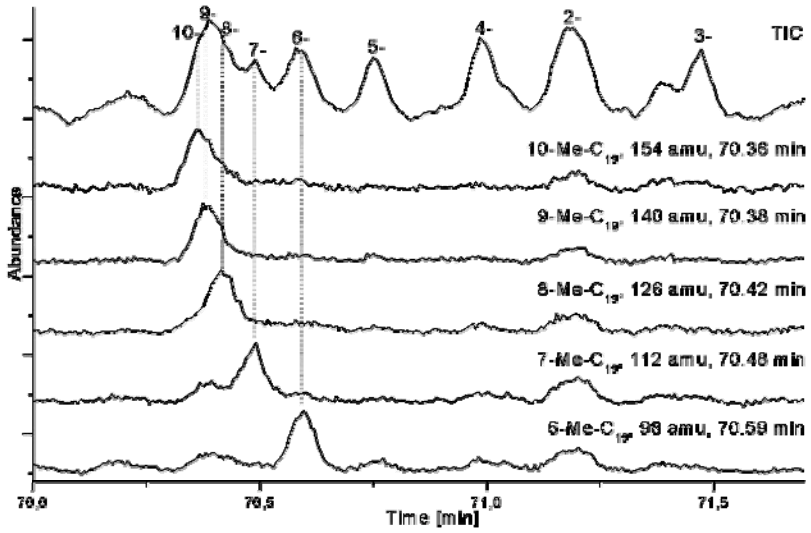

Fig. 6. Mass spectrometric deconvolution of GC unseparated isomers of monomethylnonadecanes in fuel diesel.

4. Conclusions

The mixture of methylene insertion reaction to n–alkanes up to C_{29} completed by C_3-C_8 alkanes allowed to obtain a mixture of all 196 possible monomethylalkane isomers up to C_{30}.The relative high precision of measured programmed–temperature linear retention indices of these monomethylalkanes (s = 0.07 i. u.) was obtained using high–resolution 100 m long capillary column, by avoidance of sample overloading column by injection of small samples, and by using of sensitive MS/SIM–detection. The preliminary identification was obtained from measured retention indices derived on the basis of the dependence of homomorphy factors on the number of carbon atoms of individual homologous series of monomethylalkanes. The prediction of retention of isomers with new position of methyl group beginning at higher carbon atoms number, as well as for second, third, fourth etc. member of homologous series allowed the dependence $H_P=f(C_n)$ for first, second, third etc. members of beginning homologous of monomethylalkane series. Obtained precision (s= 0.16 i. u.) of extrapolated H_P values, resp. retention indices I_P is about one order better than render the QSPR calculation methods. Preliminary identification was confirmed by mass spectrometry using the characteristic fragment ions. By gas chromatography unseparated monomethylalkane isomers were resoluted by mass spectrometric deconvolution.

The obtained retention indices can be used for identification of monomethylalkanes up to C_{30} by comparison of measured and these data, further by extrapolation of the obtained dependence $H_P=f(C_n)$ for identification of higher monomethylalkanes >C_{30}, and by using of additivity principle of H values [1,12] for retention prediction of polymethyl–substited alkanes with mutual unaffected CH_3 - groups. The obtained retention indices were used for identification of monomethylalkanes C_7 to C_{30} in diesel fuel. These results will be used also for identification of monomethylalkanes in the breath analysis as a diagnostic tool of several diseases [16].

Acknowledgements

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