QUANTITATIVE ANALYSIS OF HYDROCARBONS IN GASOLINES BY CAPILLARY GAS–LIQUID CHROMATOGRAPHY

I. ISOTHERMAL ANALYSIS

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SUMMARY

Quantitative analysis of 238 constituents of the gasoline fraction of crude oil (paraffins, branched paraffins, aromatics and naphthenes) on squalane and structure group analysis has been performed by high-resolution capillary gas chromatography under isothermal conditions. The "area per cent technique" (area evaluated by peak height, h, times width at half-height, $w_{1/2}$, by $t_R \times h$ and by digital integration methods) and "the modified standard addition method" were used. The aromatic hydrocarbon content determined on a polar stationary phase, 1,2,3-tris(cyanoethoxy) propane, was in good agreement with the results on squalane as well as with those determined by liquid chromatography.

INTRODUCTION

High-resolution capillary gas chromatography (HRCGC) is the most generally useful method for the analysis of complex hydrocarbon mixtures in gasolines with the ultimate aim of complete component analysis. But even the best columns cannot complete resolve such mixtures comprising theoretically about 600 compounds which on squalane should be eluted before *n*-decane —paraffins, naphthenes and aromatics without olefins, as in the gasoline fraction produced by distillation of crude oil one would not expect to find an olefinic fraction.

Squalane capillary columns were among the first to be used in the analysis of gasolines[1,2]. On squalane, hydrocarbons are eluted almost in order of their boiling points. As the resolution of hydrocarbons on such columns is very high, more data

on the retention of hydrocarbons in the gasoline range have been published for squalane than for any other liquid phase[3–9]. Sanders and Maynard[3] observed 240 compounds in gasolines; up to n-C_{10} there were 207 compounds, 129 of which were paraffins, naphthenes and aromatics. Whittemore[10] reported the analysis of a gasoline sample for which a total of 378 compounds were separated, leaving only 17 unclassified. Up to n-C_{10}, 257 compounds (including olefins) were eluted, 155 being paraffins, naphthenes and aromatics.

Other liquid phases are also useful in capillary analysis, *e.g.*, silicone oils[11]. Because they have much higher temperature limits than squalane, they are especially useful in shortening analysis times by use of higher temperatures. Recently Johansen *et al.*[12] described the analysis of a gasoline sample which revealed 268 peaks; up to n-C_{10}, 172 peaks were observed, 20 of which represent olefins and 68 were unclassified.

Since gasoline is expected to contain many more compounds than has so far been identified, the aim of this work was to elucidate further the composition of the gasoline fraction of crude oil. This paper describes the use of HRCGC for the structural group analysis of hydrocarbons in gasoline by first achieving as complete a separation as possible on squalane, and then carrying out the identification on the basis of retention data and gas chromatography–mass spectrometry (GC–MS) under isothermal conditions[13]. Problems connected with generally acknowledged methods of quantitative analysis of gasolines are discussed.

EXPERIMENTAL

Measurements were performed on a Carlo Erba Model 2350 gas chromatograph equipped with a flame ionization detector, a stream splitter and on squalane in a glass capillary column (210 m × 0.3 mm I.D.)[14] with hydrogen as carrier gas at 58°C, and in a metal capillary column (50 m × 0.25 mm I.D.) with TCEP [1,2,3-tris(cyanoethoxy)propane][15] and nitrogen at 80°C.

Digital integration measurements were performed on a Hewlett-Packard 58 80 A gas chromatograph with integrator C R1 A and on squalane in a metal capillary column (100 m × 0.25 mm I.D.) under isothermal conditions as given above.

Two samples of gasolines were analysed: 1, a gasoline fraction of crude oil; 2, a gasoline fraction enriched with higher boiling hydrocarbons. The samples were injected with a 1-μl Hamilton syringe.

Peak areas were measured as:

(1) peak height, h, times the width at half-height, $w_{1/2}$, as determined with a calibrated magnifying glass having a read-out precision of ± 0.05 mm;

(2) retention time, t_R in mm, times peak height, h;

(3) degital integration response.

RESULTS AND DISCUSSION

The most common method used in the analysis of hydrocarbon mixtures using flame ionization detection (FID) has been the simplest "area per cent technique"[16]. The accuracy is higher the more similar are the hydrocarbons in the mixture and the narrower their boiling point range. A disadvantage of this method is the necessity to

elute all mixture components. Moreover, at the given limit of FID, compounds in low concentrations are not taken into consideration, so that the overall sum of the peak areas may be loaded with a large systematic error. To determine the correct contents of compounds we have introduced "the modified standard addition method". As the relative response per gram of hydrocarbons, RWR, is nearly constant for the whole series[3,17-20], both methods can be used for the calculation of weight per cent of any hydrocarbon in gasoline.

Quantitative analysis of hydrocarbons on squalane

Isothermal conditions were chosen in order to utilize published data on the characterization of the individual mixture constituents. The temperature of 58°C was selected by optimization[13] to give the best compromise between analysis time and number of peaks resolved.

"*Area per cent technique*". Two samples of gasolines were evaluated. In Table I are given the results of quantitative analysis of all constituents of sample 1 as the

TABLE I

RESULTS OF QUALITATIVE ANALYSIS OF GASOLINE DETERMINED ON SQUALANE BY "AREA PER CENT TECHNIQUE"

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
2	2-Methylbutane	0.285	0.380	0.070	0.033
3	n-Pentane	1.060	1.239	0.342	0.186
4	2,2-Dimethylbutane	0.127	0.135	0.019	–
5	Cyclopentane	0.748	0.832	0.177	0.160
6	2,3-Dimethylbutane	0.558	0.622	0.138	
7	2-Methylpentane	4.109	4.596	1.325	0.961
8	3-Methylpentane	3.234	3.728	1.017	0.706
9	n-Hexane	7.932	8.416	3.240	2.172
10	2,2-Dimethylpentane	0.114	0.129	0.022	0.012
11	Methylcyclopentane	3.259	4.168	2.044	0.704
12	2,4-Dimethylpentane	0.304	0.390	0.181	
13	Benzene	0.357	0.415	0.173	0.103
14	3,3-Dimethylpentane	0.079	0.106	0.025	–
15	Cyclohexane	1.712	1.941	1.380	1.210
16	2-Methylhexane	2.552	2.925	1.736	1.476
17	2,3-Dimethylpentane	1.062	1.239	1.701	0.588
18	1,1-Dimethylcyclopentane	0.143	0.168	0.103	0.082
19	3-Methylhexane	3.662	4.336	2.550	2.107
20	1(*cis*),3-Dimethylcyclopentane	0.776	0.942	0.789	0.685
21	3-Ethylpentane	0.349	0.428	0.208	0.173
22	1(*trans*),3-Dimethylcyclopentane	0.697	0.859	0.747	0.697
23	1(*trans*),2-Dimethylcyclopentane	1.788	1.854	1.660	1.506
24	n-Heptane	6.452	7.585	6.283	5.444
25	2,2-Dimethylhexane	0.062	0.067	0.031	–
26	1(*cis*),2-Dimethylcyclopentane	0.268	0.293	0.299	0.277
27	1,1,3-Trimethylcyclopentane	0.190	0.299	0.207	0.180

TABLE I (*continued*)

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
28	Methylcyclohexane	3.562	3.707	4.115	4.319
29	2,5-Dimethylhexane	0.371	0.419	0.389	
30	2,4-Dimethylhexane	0.510	0.545	0.428	0.424
31	Ethylcyclopentane	0.976	1.064	1.317	1.285
32	1(*trans*),2(*cis*),4-Trimethylcyclopentane	0.634	0.619	0.675	0.651
33	3,3-Dimethylhexane	0.114	0.113	0.070	—
34	Toluene	1.522	1.510	1.563	1.156
35	1(*trans*),2(*cis*),3-Trimethylcyclopentane	0.774	0.781	0.931	0.992
36	2,3,4-Trimethylpentane	0.076	0.079	0.110	0.103
37	2,3-Dimethylhexane	0.482	0.517	0.362	0.385
38	2-Methyl-3-ethylpentane	0.254	0.274	0.250	0.254
39	1,1,2-Trimethylcyclopentane +	3.419	3.142	3.243	3.485
40	2-methylheptane (1:25)				
41	4-Methylheptane	1.113	1.091	0.951	1.031
42	3,4-Dimethylhexane	0.279	0.229	0.162	0.146
43	3-Methylheptane	2.830	2.441	1.834	2.403
44	3-Methyl-3-ethylpentane	0.048	0.044	0.041	—
45	1(*cis*),2(*trans*),4-Trimethylcyclopentane	0.048	0.044	0.042	0.011
46	Naphthene	0.063	0.059	0.042	
47	1(*cis*),2(*trans*),3-Trimethylcyclopentane	0.199	0.210	0.234	0.263
48	1(*cis*),3-Dimethylcyclohexane	0.976	0.873	1.194	1.880
49	1(*trans*),4-Dimethylcyclohexane	0.488	0.438	0.732	
50	1,1-Dimethylcyclohexane	0.558	0.507	0.718	0.891
51	1-Methyl-2(*trans*)-ethylcyclopentane	0.384	0.353	0.501	2.049
52	1-Methyl-3(*cis*)-ethylcyclopentane	0.816	0.790	1.327	
53	1-Methyl-1-ethylcyclopentane	0.067	0.066	0.164	0.166
54	*n*-Octane	6.388	5.242	6.140	7.293
55	1(*cis*),2(*cis*),3-Trimethylcyclopentane +	0.733	0.650	1.055	1.335
	1(*trans*),2-dimethylcyclohexane				
56	1(*cis*),4-Dimethylcyclohexane +	0.232	0.173	0.238	0.339
	1(*trans*),3-dimethylcyclohexane				
57	Branched paraffin	0.008	0.007	0.006	
58	Branched paraffin	0.026	0.023	0.019	—
59	2,3,5-Trimethylhexane	0.119	0.106	0.098	0.028
60	Isopropylcyclopentane	0.138	0.134	0.203	0.116
61	Branched paraffin	0.005	0.005	0.014	—
62	Branched paraffin	0.010	0.009	★	—
63	2,2-Dimethylheptane	0.057	0.052	0.027	—
64	Naphthene	0.041	0.038	0.047	0.035
65	2,4-Dimethylheptane	0.287	0.282	0.330	0.393
66	1-Methyl-2(*cis*)-ethylcyclopentane	0.113	0.108	0.180	0.211
67	Branched paraffin	★	★	★	—
68	2,2,3-Trimethylhexane	0.057	0.055	0.042	—
69	Naphthene	0.075	0.071	0.064	1.784
70	2,6-Dimethylheptane	0.974	0.921	1.403	
71	Naphthene	0.030	0.026	0.014	—
72	1(*cis*),2-Dimethylcyclohexane	0.558	0.459	0.898	1.200
73	*n*-Propylcyclopentane				
74	2,5-Dimethylheptane	0.557	0.511	0.535	0.840

TABLE I (continued)

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
75	3,5-Dimethylheptane	0.172	0.159	0.164	—
76	Ethylbenzene	0.736	0.684	1.131	
77	Ethylcyclohexane	0.943	0.880	1.562	2.980
78	3,3-Dimethylheptane	0.052	0.049	0.031	—
79	Branched paraffin	0.011	0.011	0.008	—
80	Napthene	0.113	0.106	0.205	
81	Naphthene	0.975	0.921	1.317	1.832
82	1,1,3-Trimethylcyclohexane	0.184	0.164	0.304	
83	Branched paraffin	0.118	0.103	0.129	1.516
84	1(cis),3(cis),5-Trimethylcyclohexane	0.190	0.167		
85	Branched paraffin	0.157	0.139	0.293	0.526
86	Branched paraffin	0.026	0.023	0.033	—
87	Cycloalkane + p-xylene (1:1)	0.766	0.497	0.725	0.575
88	Branched paraffin	0.019	0.018	0.101	0.379
89	m-Xylene	1.103	1.045	1.321	1.293
90	Branched paraffin	0.006	0.006	0.009	—
91	Branched paraffin	0.476	0.462	0.694	0.883
92	Branched paraffin	0.010	0.010	0.005	—
93	Branched paraffin	0.250	0.221	0.213	0.078
94	Naphthene	0.193	0.171	0.303	0.048
95	1(trans),2(cis),4-Trimethylcyclohexane	0.100	0.090	0.198	0.225
96	1(trans),2(trans),4-Trimethylcyclohexane + 1(trans),3(trans),5-trimethylcyclohexane	0.207	0.188	0.310	0.325
97	4-Methyloctane	0.820	0.752	0.983	1.180
98	2-Methyloctane	0.913	0.848	1.134	1.310
99	Naphthene	0.073	0.067	0.122	
100	Naphthene	0.071	0.061	0.104	0.025
101	3-Ethylheptane	0.254	0.216	0.208	0.245
102	o-Xylene	0.642	0.558	0.905	
103	3-Methyloctane	1.427	1.244	1.702	3.355
104	Naphthene	0.087	0.077	0.194	—
105	Branched paraffin	0.016	0.014	0.020	—
106	Naphthene	0.044	0.039	0.079	0.018
107	Naphthene	0.012	0.011	0.020	
108	Naphthene	0.079	0.040	0.071	—
109	Naphthene				
110	Naphthene	0.049	0.041	0.072	—
111	1(trans),2(cis),3-Trimethylcyclohexane	0.079	0.068	0.115	0.026
112	1,1,2-Trimethylcyclohexane + 3,3-diethylpentane (5:1)	0.283	0.248	0.561	0.669
113	1(cis),2(trans),4-Trimethylcyclohexane	0.165	0.146	0.320	0.474
114	Branched paraffin	0.096	0.085	0.193	
115	1(cis),2(cis),4-Trimethylcyclohexane + 1(cis),3(cis),4-trimethylcyclohexane	0.144	0.128	0.270	0.296
116	Naphthene	0.022	0.020	0.033	—
117	Naphthene	0.095	0.080	0.156	0.253
118	Naphthene	0.067	0.056	0.112	
119	Methylethylcyclohexane	0.299	0.257	0.499	0.568

TABLE I (*continued*)

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
120	Naphthene	0.067	0.049	0.103	—
121	Naphthene	0.055	0.041	0.080	—
122	Isopropylbenzene	0.248	0.208	0.508	0.671
123	Naphthene	0.213	0.179	0.427	
124	Naphthene	—	—	0.023	—
125	Naphthene	0.053	0.043	0.119	—
126	*n*-Nonane	3.695	2.888	4.837	7.461
127	Naphthene	0.076	0.070	0.146	—
128	Naphthene	—	—	0.009	—
129	Naphthene + branched paraffin (1:1)	—	—	0.015	—
130	Naphthene	—	—	0.015	—
131	Naphthene	—	—	0.066	—
132	Naphthene	0.055	0.045	0.094	—
133	Naphthene	0.033	0.027	0.054	—
134	Branched paraffin	0.041	0.037	0.066	—
135	Branched paraffin	0.005	0.005	0.032	—
136	Naphthene	0.160	0.143	0.354	0.361
137	Naphthene	0.010	0.009	0.022	—
138	Naphthene	0.083	0.052	0.081	—
139	Naphthene			0.094	—
140	Branched paraffin	0.059	0.052	0.120	—
141	Naphthene	0.247	0.186	0.502	0.532
142	Naphthene	0.095	0.072		
143	Naphthene	0.017	0.014	0.027	—
144	Naphthene	0.046	0.025	0.010	—
145	Branched paraffin	0.104	0.073	0.162	0.037
146	Naphthene	0.030	0.025	0.003	—
147	Naphthene	0.012	0.010	0.027	—
148	Naphthene	0.030	0.025	0.076	—
149	Branched paraffin	0.036	0.030	0.076	
150	Naphthene	0.131	0.112	0.296	0.593
151	Naphthene	0.155	0.133	0.318	
152	Branched paraffin	0.151	0.103	0.233	0.048
153	*n*-Propylbenzene	0.339	0.307	0.814	0.674
154	Naphthene	0.006	0.005	0.004	—
155	Branched paraffin	0.100	0.042	0.213	—
156	Branched paraffin				—
157	Naphthene	0.013	0.011	0.011	—
158	C_9 naphthene	0.359	0.299	0.727	0.460
159	C_9 naphthene	0.271	0.202	0.555	
160	Naphthene	0.044	0.039	0.087	—
161	2,6-Dimethyloctane	0.716	0.630	1.286	1.700
162	Branched paraffin	0.019	0.017	0.004	—
163	Branched paraffin	0.033	0.028	0.093	—
164	Branched paraffin	0.065	0.045	0.124	—
165	Branched paraffin	0.039	0.034	0.063	0.015
166	2,5-Dimethyloctane	0.339	0.261	0.456	0.695
167	1-Methyl-3-ethylbenzene	0.523	0.466	0.762	0.895
168	1-Methyl-4-ethylbenzene	0.232	0.207	0.324	
169	Naphthene	0.081	0.071	0.147	0.675

TABLE I (*continued*)

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
170	Naphthene	0.047	0.042	0.084	
171	C_{10} branched paraffin	0.032	0.030	0.058	—
172	Branched paraffin	0.038	0.036	0.041	—
173	Branched paraffin	0.015	0.012	0.004	—
174	C_{10} branched paraffin	0.045	0.037	0.071	0.020
175	Naphthene	0.038	0.031	0.046	—
176	Branched paraffin	0.030	0.025	0.051	0.013
177	Branched paraffin	0.012	0.010	0.021	—
178	Branched paraffin	—	—	0.013	—
179	Naphthene	—	—	0.009	—
180	Naphthene	0.029	0.026	0.070	0.021
181	Naphthene				
182	Branched paraffin	0.056	0.045	0.150	0.143
183	Branched paraffin	—	—	0.004	—
184	Branched paraffin	—	—	0.003	—
185	1-Methyl-2-ethylbenzene	0.391	0.308	0.713	1.443
186	Branched paraffin	0.103	0.086	0.167	—
187	Branched paraffin	—	—	0.023	—
188	Branched paraffin	0.008	0.007	0.014	—
189	Naphthene	0.024	0.020	0.083	0.070
190	Naphthene				
191	1,3,5-Trimethylbenzene	0.169	0.158	0.192	0.517
192	Branched paraffin	—	—	0.005	
193	Branched paraffin	0.086	0.083	0.199	
194	Branched paraffin	*	*	*	—
195	Naphthene	0.190	0.169	0.298	1.451
196	4-Methylnonane	0.357	0.312	0.756	
197	*tert.*-Butylbenzene	0.008	0.007	0.029	—
198	Naphthene	0.041	0.036	0.097	0.057
199	Naphthene	0.017	0.015	0.030	—
200	2-Methylnonane	0.330	0.271	0.670	1.086
201	Naphthene	0.052	0.044	0.130	—
202	C_{10} naphthene	0.035	0.030	0.076	—
203	Naphthene	0.009	0.007	0.010	—
204	Naphthene				
205	Naphthene	0.018	0.011	0.062	—
206	Naphthene	—	—	0.005	—
207	3-Methylnonane	0.244	0.215	0.539	0.683
208	Naphthene	0.027	0.023	0.074	—
209	Naphthene	0.035	0.031	0.090	—
210	1,2,4-Trimethylbenzene	0.659	0.580	0.807	0.754
211	Branched paraffin	—	—	0.038	—
212	Naphthene	0.018	0.016	0.049	—
213	Branched paraffin	0.019	0.016	0.049	—
214	*sec.*-Butylbenzene	0.103	0.065	0.143	0.156
215	Branched paraffin	—	—	0.017	—
216	Naphthene	0.078	0.058	0.185	0.505
217	Naphthene	0.111	0.083	0.247	

TABLE I (continued)

Peak No.	Component	Sample 1 (%)		Sample 2 (%)	
		$h \times w_{1/2}$	$t_R \times h$	$t_R \times h$	Digital integr.
218	Naphthene	0.067	0.050	0.137	0.189
219	Branched paraffin	—	—	0.017	—
220	Naphthene	0.048	0.034	0.104	0.016
221	Branched paraffin	★	★	★	—
222	2-Naphthenes	0.177	0.104	0.223	0.383
223	Branched paraffin	—	—	0.024	—
224	Naphthene	0.044	0.036	0.061	—
225	Naphthene	0.022	0.018	0.049	—
226	Branched paraffin	0.033	0.027	0.043	—
227	Branched paraffin	0.033	0.027	0.025	—
228	Naphthene	0.033	0.027	0.106	—
229	Naphthene	0.055	0.046	0.132	0.058
230	Naphthene	0.044	0.037	0.127	
231	Branched paraffin	—	—	0.051	—
232	Branched paraffin	—	—	0.045	—
233	Naphthene	—	—	★	—
234	1,2,3-Trimethylbenzene	0.218	0.211	0.358	
235	Branched paraffin	0.060	0.058	0.033	
236	1-Methyl-4-isopropylbenzene	0.048	0.039	0.119	
237	Branched paraffin	—	—	0.027	
238	n-Decane	1.110	0.943	2.175	3.398

★ Less than 0.001%.

contents of hydrocarbons estimated by the $h \times w_{1/2}$ and $t_R \times h$ methods of peak area evaluation. Comparing the weight per cents of individual constituents determined by both methods it is seen that the per cent of low boiling compounds determined by the $h \times w_{1/2}$ method is lower and that of high boiling compounds higher than those determined by the $t_R \times h$ method. This is probably connected with the precision of measurement of the peak widths. The results of the group analysis of hydrocarbons of gasoline sample 1 calculated as the sum of the contents of individual hydrocarbons in corresponding structural groups determined by the above methods are listed in Table II. The differences between the two methods are in the range of 0.33–1.92% for each hydrocarbon group.

To avoid errors in peak width measurements, the contents of compounds in gasoline sample 2 enriched in aromatics and naphthenes were evaluated by the $t_R \times h$ and digital integration methods. As an example of the separation power of the squalane column used, a chromatogram of the separation of the hydrocarbon constituents of gasoline sample 2 is given in Fig. 1. The results of the quantitative analysis by the $t_R \times h$ method on a high-resolution glass capillary column [210 m; over 500,000 theoretical plates (TPs)] and by digital integration after separation on a metal capillary column (100 m; 200,000 TPs) are given in Table I. From these results and the preceding group analysis it is evident that for sufficient component separation it is necessary to use a capillary column having as high resolution as possible. With columns of lower efficiency it is often the case that several peaks overlap, which

TABLE II

GROUP ANALYSIS OF GASOLINE SAMPLE 1 DETERMINED BY $h \times w_{1/2}$ AND $t_R \times h$ METHODS

Compounds	Weight per cent (%)	
	$h \times w_{1/2}$	$t_R \times h$
n-Paraffins	26.64	26.31
Branched paraffins	35.87	37.79
Aromatics	7.68	7.02
Naphthenes	29.79	28.84

complicates qualitative as well as quantitative analysis. From the results in Table I it is also seen that many constituents present in very low weight per cents could not be evaluated by the integrator and because of this the contents of other components increased, significantly influencing the group analysis (Table III). The differences between the two methods lay in the range of 2.93–4.73% for each hydrocarbon group,
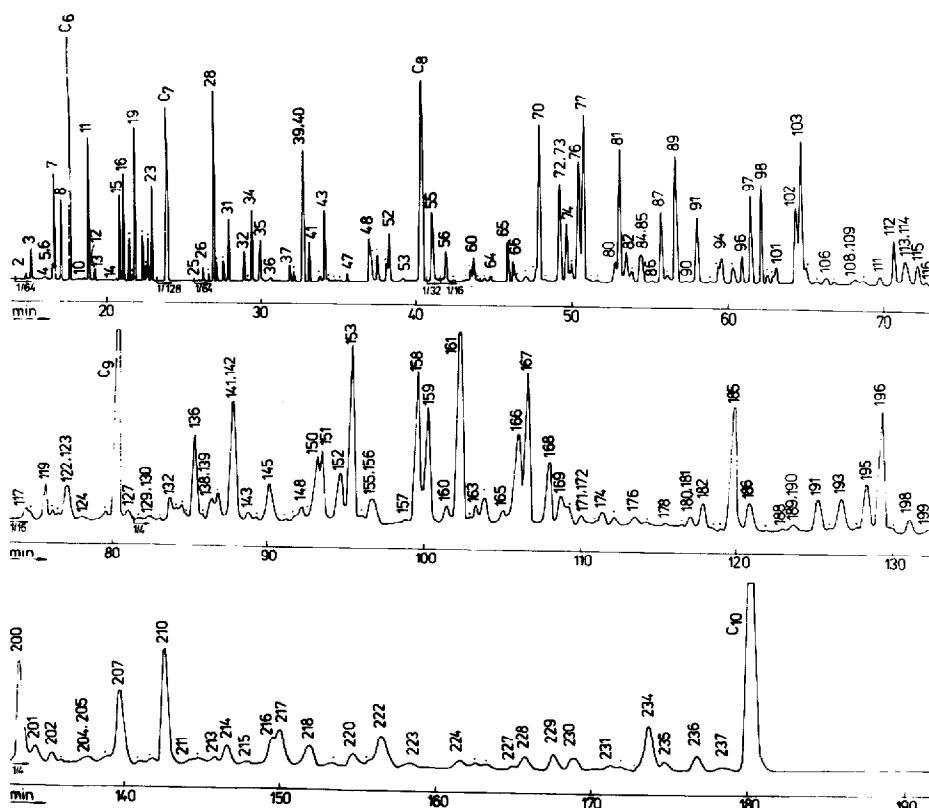
Fig. 1. Chromatogram of the separation of hydrocarbon constituents of gasoline sample 2 on a high-resolution squalane glass capillary column at 58°C at a hydrogen pressure of 2.48 atm and different instrument attenuations. Splitting ratio: 1:120.

TABLE III

GROUP ANALYSIS OF GASOLINE SAMPLE 2 DETERMINED BY $t_R \times h$ AND DIGITAL IN-TEGRATION METHODS

Compounds	Weight per cent (%)		Weight per cent $\times f$ (%) $(t_R \times h)$
	$t_R \times h$	Digital integr.	
n-Paraffins	23.02	25.95	21.78
Branched paraffins	30.01	26.58	28.39
Aromatics	10.23	14.95	9.67
Naphthenes	36.74	32.01	34.76

the greatest difference being in the analysis of naphthenes and aromatic hydrocarbons. (Factor *f* is explained in the next section).

"The modified standard addition method". Unlike "the area per cent technique" where the relative proportions of hydrocarbons calculated from the peak areas correspond directly to their weight per cents, this method allows the determination of components which at the given limit of FID are not measurable or under the given conditions are not eluted from the column. The standard addition method requires precise and reproducible sample injection. In order to circumvent this problem we have modified the standard addition method.

Ethylbenzene was chosen as the standard for addition. Three control analyses were performed (three weights of gasoline sample 2 with the content of the standard added in the range of 0.6–1.1%). The weight per cent of ethylbenzene in gasoline, X', was calculated according to

$$X' = \frac{A_e A_i' \cdot \%_{st.add.}}{A_i A_e' - A_e A_i'} \qquad (1)$$

where A_e is ethylbenzene peak area in the gasoline sample, A_i = area of neighbouring peak in gasoline sample, A_e' = ethylbenzene peak area upon standard addition, A_i' = area of neighbouring peak in gasoline sample upon standard addition and $\%_{st.add.}$ = weight per cent of standard added.

The results obtained with the modified standard addition technique are given in Table IV. Factor *f* (Table IV), which designates the proportions of the content

TABLE IV

RESULTS FOR GASOLINE SAMPLE 2 OBTAINED BY THE STANDARD ADDITION TECHNIQUE WITH ETHYLBENZENE AS STANDARD

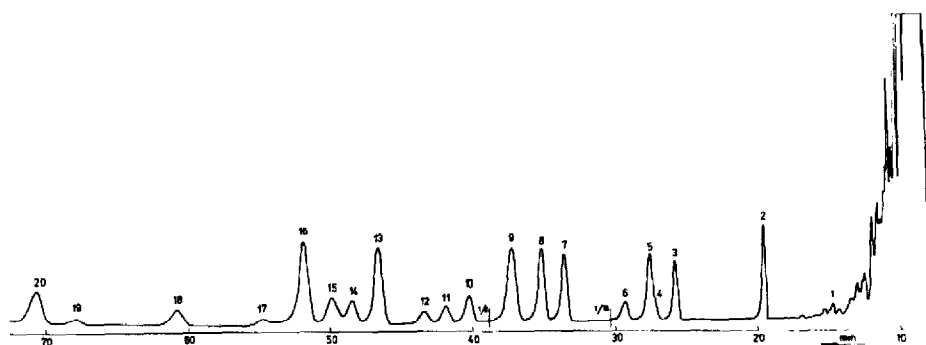| Gasoline sample (g)	Ethylbenzene added		X' of ethylbenzene (%)	f
	g	%		
0.75325	0.00537	0.71	1.07	0.9461
0.75218	0.00452	0.60	1.10	0.9726
0.75014	0.00810	1.08	1.04	0.9200

Fig. 2. Chromatogram of the separation of aromatics in gasoline sample 2 on TCEP in a metal capillary column at 80°C and a nitrogen pressure of 0.7 atm. Beginning of separation at the instrument attenuation of 1/32. Splitting ratio: 1:400.

TABLE V

RESULTS OF QUANTITATIVE ANALYSIS OF AROMATICS IN GASOLINE SAMPLES 1, 2 DETERMINED ON TCEP BY MODIFIED STANDARD ADDITION METHOD AND BY FIA METHOD

Peak No.	Compound	Weight %	
		Sample 1	Sample 2
1	Benzene	0.264	0.124
2	Toluene	1.206	1.266
3	Ethylbenzene	0.625	1.029
4	*p*-Xylene	0.526	0.407
5	*m*-Xylene	1.281	1.238
6	Isopropylbenzene	0.176	0.380
7	*n*-Propylbenzene	0.327	0.772
8	*o*-Xylene + *sec.*-butylbenzene	0.569	0.874
9	1,3- + 1,4-Methylethylbenzene + *tert.*-butylbenzene	0.752	0.933
10	1,3,5-Trimethylbenzene	0.173	0.192
11	Unidentified	0.043	0.125
12	1-Methyl-4-isopropylbenzene	0.031	0.098
13	1-Methyl-2-ethylbenzene	0.286	0.620
14	Unidentified	0.108	0.219
15	Unidentified	0.124	0.250
16	1,2,4-Trimethylbenzene	0.609	0.762
17	Unidentified	0.039	0.076
18	Unidentified	0.053	0.191
19	Unidentified	0.027	0.085
20	1,2,3-Trimethylbenzene	0.206	0.417
	Σ Aromatics	7.32	10.05
	FIA method	6.72	10.00

determined by the modified method of standard addition and the peak area technique, was calculated according to

$$f = X'/X \tag{2}$$

where X represents the weight per cent of ethylbenzene as estimated by the area per cent technique. The sum of the components determined by the area per cent technique multiplied by the mean value of factor f from Table IV is equal to 94.61%, the remaining 5.39% represents the compounds which were not considered in the peak area technique, therefore the content of other compounds was found higher using this technique, *cf.*, results in Table III.

Quantitative analysis of aromatic hydrocarbons on TCEP

The aromatic hydrocarbon content was determined also on the polar stationary phase TCEP where normal, branched paraffins and naphthenes are eluted rapidly. Both gasoline samples were analysed. A chromatogram of the separation of aromatics in sample 2 on TCEP in a metal capillary column at 80°C and with a nitrogen pressure of 0.7 atm is shown in Fig. 2. The component numbering is as in Table V. Comparing Fig. 2 with Fig. 1 for squalane, it is seen that the sum of aromatic hydrocarbons on squalane does not include aromatics eluted after *n*-decane.

TABLE VI

RESULTS OF QUANTITATIVE ANALYSIS OF AROMATICS IN GASOLINE SAMPLE 2 ON SQUALANE AND TCEP

Compound	Squalane ($t_R \times h$)		TCEP (%)	Squalane (digital integr.) (%)
	%	% · f		
Benzene	0.173	0.164	0.124	0.103
Toluene	1.563	1.479	1.266	1.156
Ethylbenzene	1.131	1.070	1.029	2.980
p-Xylene	0.363	0.343	0.407	0.575
m-Xylene	1.321	1.250	1.238	1.293
o-Xylene	0.905	0.856	0.874	3.355
Isopropylbenzene	0.508	0.481	0.380	0.671
n-Propylbenzene	0.814	0.770	0.772	0.674
1-Methyl-3-ethylbenzene	0.762	0.721	0.933	0.895
1-Methyl-4-ethylbenzene	0.324	0.307		0.675
1-Methyl-2-ethylbenzene	0.713	0.675	0.620	1.143
1,3,5-Trimethylbenzene	0.192	0.182	0.192	0.517
tert.-Butylbenzene	0.029	0.027	*	—
1,2,4-Trimethylbenzene	0.807	0.764	0.762	0.754
sec.-Butylbenzene	0.143	0.135	**	0.156
1,2,3-Trimethylbenzene	0.358	0.339	0.417	—
1-Methyl-4-isopropylbenzene	0.119	0.113	0.098	—
Σ Aromatics	10.225	9.674	9.112	14.947

* Eluted with 1,3- and 1,4-methylethylbenzene.

** Eluted with *o*-xylene.

The content of aromatics on TCEP was calculated using the modified standard addition method with ethylbenzene as the standard. For both gasoline samples the weight per cent of ethylbenzene was determined using eqn. 1 as described for squalane. The weight per cent of other aromatic components was calculated according to

$$X_i = \frac{A_i}{A_e} \cdot X'' \tag{3}$$

where X_i is the weight per cent of component i in the gasoline sample, A_i = peak area of component i in gasoline, A_e = peak area of ethylbenzene in gasoline and X'' = weight per cent of ethylbenzene in gasoline determined according to eqn. 1. The results of quantitative analysis of individual aromatic hydrocarbons in gasoline samples determined by the modified standard addition method and their total sum analysed also by the FIA method[21] are in good agreement (Table V).

In Table VI are summarized the results of quantitative analysis of aromatics in sample 2 eluted on squalane up to n-decane and on TCEP. There is not only good agreement in the content of aromatics on both stationary phases but it can also be concluded that the resolution of aromatics on the squalane capillary column is sufficient and can be used for their analysis.

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