AUTOMATIC SYSTEM FOR THE HIGH-RESOLUTION GAS CHROMATOGRAPHIC ANALYSIS OF GASOLINE-RANGE HYDROCARBON MIXTURES

E. R. ADLARD, A. W. BOWEN and D. G. SALMON

Shell Research Ltd., Thronton Research Centre, P.O. Box 1, Chester CH1 3SH (Great Britain)

SUMMARY

Equipment has been developed for the high-resolution gas chromatographic analysis of complex hydrocarbon mixtures in the gasoline boiling range. The equipment can operate continuously; the data generated are automatically presented as a printed list and are also stored on magnetic cassette tape for further processing.

INTRODUCTION

In the late 1960s it was shown that low-resolution gas chromatography (GC) was an excellent tool for the prediction of the volatility characteristics of gasolines in terms of the standard parameters of Reid Vapour Pressure and ASTM distillation[1]. A logical extension of this work was to predict other gasoline properties, in particular octane rating, by high-resolution GC.

High-resolution GC of gasolines was pioneered by Sanders and Maynard[2] but, with the crude methods of sub-ambient temperature control available at the time, it was difficult to achieve good retention data precision; this, in turn, made automatic data handling a difficult task. Gradually, from the early 1970s onward, the manufacturers of GC equipment introduced reliable sub-ambient temperature control of GC columns and automatic devices for sample introduction; at the same time, considerable advances were made in data handling. The conjunction of these three developments has made possible the continuous operation of GC apparatus. The ability to do this is an essential pre-requisite for the technique to have any chance of wide application, since the turn-round time, *i.e.* the time between the injections of successive samples, is approximately two hours. This means that in an ordinary working day a maximum of only four runs is possible and, in practice, it is difficult to achieve more than three runs per day.

This paper describes an automated system and its application to the analysis of hydrocarbon mixtures in the gasoline boiling range, *i.e.* —42° to about 220°.

EXPERIMENTAL

GC apparatus and automatic sampler

The apparatus used was a standard Perkin-Elmer Model F30 gas chromato-

graph equipped with a Model AS41 auto-sampler[3] and an oven capable of operating below ambient temperature by means of a controlled supply of liquid nitrogen. A sample size of 0.5 μl of the mixture to be analysed is injected manually from a small syringe into an aluminium capsule, which is then sealed by crimping the open end. Ten of these capsules can be placed in a magazine and up to ten magazines can be loaded into the sampler. Injection into the gas chromatograph takes place when a capsule is withdrawn from its magazine, is passed through two pairs of O-ring seals and is pierced by a hollow spike in a hot part of the injection zone, which is also swept by the carrier gas. At the end of the cycle the empty capsule is withdrawn from the apparatus. Once the magazines containing the loaded capsules are placed in the equipment, the cycle of operations is completely automatic. In addition, the sampler gives a two-digit signal to identify each capsule; the electrical signal from the second of these digits is used to actuate the other automatic cycles —temperature programming, pressure programming, data capture, etc.

The procedure for filling and sealing the capsules is a relatively time-consuming operation compared with that of auto-samplers operating on an automated syringe system. However, once the sample is sealed in the capsule it can be safely left for a period of months without loss of low-boiling components and, if the analysis time is two hours, then two or three minutes to fill and seal a capsule is of little consequence. Great care must be taken to maintain the integrity of the sample by avoiding loss of volatile components whilst filling the capsules, especially if only 1–2 ml of sample is available. The sample containers are cooled in dry ice and opened and are then allowed to warm up to 0° in an ice–water bath. About 10 μl are removed in a syringe previously cooled in dry ice and 0.5 μl is placed in the capsule, which is also cooled in dry ice. The capsule is then sealed in the special crimping device.

Apart from difficulties in sealing capsules at one stage, owing to incorrect alignment of the jaws on the crimping tool, the sampler has worked extremely well provided that routine maintenance is carried out on critical parts at regular intervals.

Analytical conditions

A pair of 70 m × 0.25 mm I.D. stainless-steel columns coated with squalane have been used throughout this work and show no obvious signs of deterioration after five years of constant operation. The columns are temperature programmed from 0° to 95° at 2°/min. They are also pressure programmed with helium carrier gas from 16 to 65 p.s.i. at 0.5 p.s.i./min (115–454 kPa at 3.5 kPa/min), to give a flow-rate varying from 0.5 to 2.0 ml/min. A sample size of 0.5 μl is used with a split ratio of 1:60. Under these conditions, the efficiency of the column is 140,000 theoretical plates for *n*-heptane. As can be seen from the chromatogram in Fig. 1, the major part of the gasoline has left the column after 60 min, but it needs nearly as long again to elute the remaining part. The reason for this is that the upper temperature limit for squalane for prolonged use is about 100°. If it were possible to increase the final temperature to 150°, the overall analysis time could be halved. Unfortunately, none of the likely candidate stationary liquids we have tried to date (mainly methyl silicones) gives as good a separation as squalane so that we have retained it in spite of its drawbacks. A secondary reason for retaining squalane is that we have been able to utilize the peak identities established by gas chromatography–mass spectrometry (GC–MS) with a similar squalane column[2].

Data handling

It is obvious that with chromatograms of more than 200 peaks, sophisticated data handling techniques must be used. Electronic integrators giving lists of retention times and percentage peak areas represent a step in the right direction but still leave a large amount of data to process. The course eventually adopted made use of an Instem Datachrom-2 system employing a Digital Equipment Co PDP/11 computer. The system measures peak heights, records retention times, calculates and normalizes peak areas and, from calibration data stored in the memory, assigns chemical identities to peaks. In the normal mode of operation, manual operation is necessary to synchronize the start of data collection with the injection of sample into the gas chromatograph, to "accept" the calculated results and to re-set. In general, no channel (out of the twelve available) is permanently associated with any particular gas chromatograph, but an exception was made in the case of the F'0/AS41 combination. Software modifications supplied by Instem Ltd., and applicable to one specific channel, permitted the automatic acceptance of results, re-setting, and the storage of data on magnetic tape cassettes (Racal-Thermionic Ltd. "Digistore") as a dedicated peripheral with a writing speed of 350 characters per second. Additional standard output to a 10 characters per second teletype was retained as a programmable option. The capacity of the cassettes (approximately 50,000 characters) is sufficient to store the results from up to 14 analyses, and cassettes have to be changed only once a day.
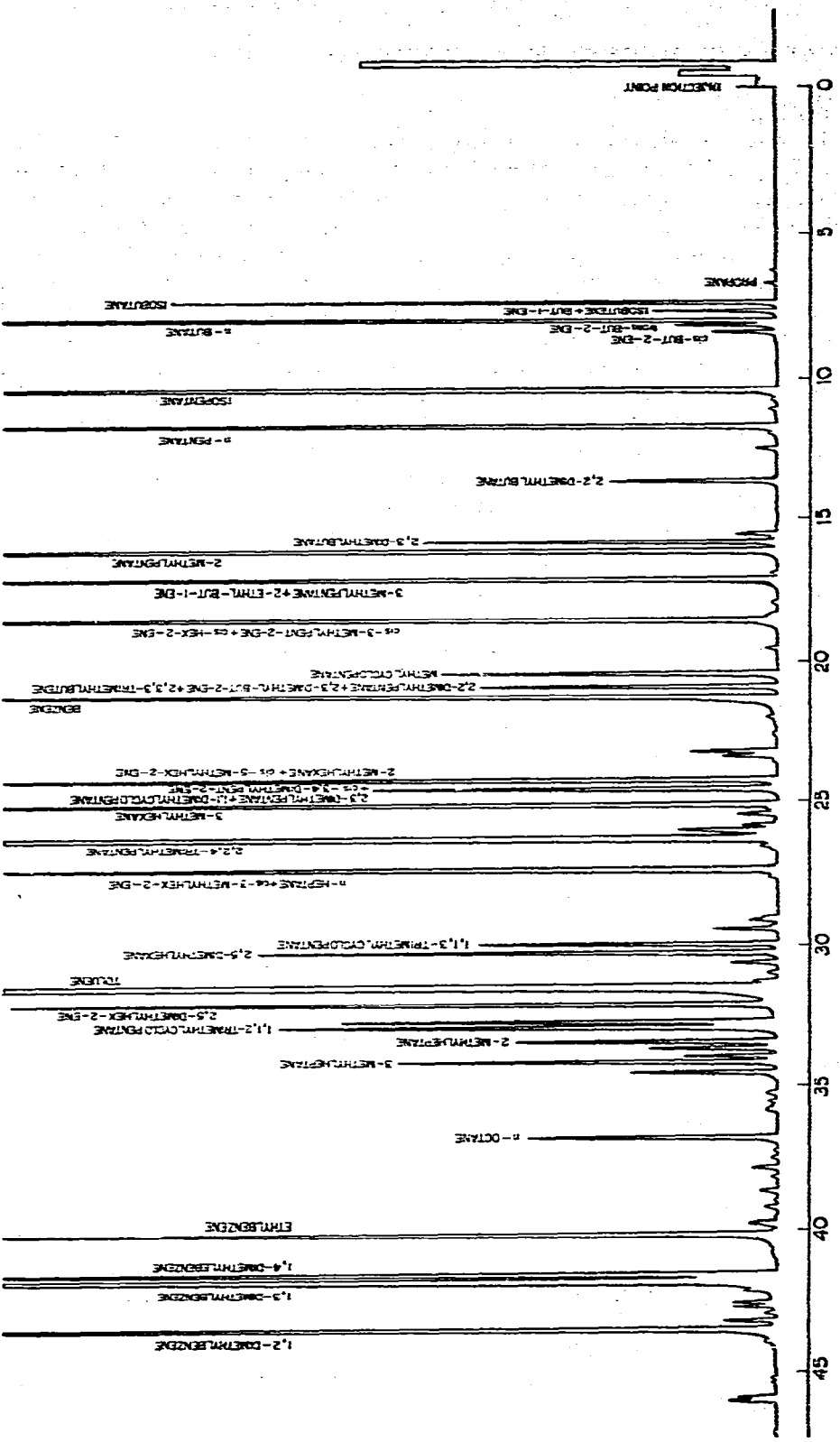
Overall system control

The Datachrom-2 system at Thornton possessed a number of limitations, in particular a relatively small capacity (16K core, 64K disk) and insufficient information from the manufacturers to permit program modifications. Each channel will supply one external command but only within the time, pre-set by the operator, in which that channel searches for data. The GC equipment, however, needs several signals in the "dead" time between the end of one analysis and the start of the next, *e.g.* to vent and re-set the pressure programmer requires three signals.

The problem was solved by using a Hewlett-Packard 9820 programmable calculator to supply the necessary signals; the general layout and timing diagram are shown in Figs. 2 and 3.

Recently, this rather clumsy hybrid system has been replaced by a Hewlett-Packard 3352 computer, and the Perkin-Elmer gas chromatograph is now linked to this via a standard Hewlett-Packard event control module.

RESULTS AND DISCUSSION

Table I and Fig. 4 show the precision data obtained on the Datachrom II system for the quantitative output for some of the components of a gasoline. From Fig. 4 it can be seen that the percentage standard deviation tends to plateau-out at about 1.5% for components in concentrations greater than 2%. Quantitative figures obtained from the Hewlett-Packard computer and from an Infotronics 304 microprocessor differ marginally from the Datachrom values owing to the different logic built into the three systems, but the precision of the data from all three is essentially the same. Table II shows a comparison between experimentally determined percentage peak areas and the known composition of a synthetically prepared mixture. Relatively

Chromatogram (retention time axis 0–45)

- INJECTION POINT
- PROPANE
- ISOBUTANE
- ISOBUTENE + BUT-1-ENE
- n-BUTANE
- trans-BUT-2-ENE
- cis-BUT-2-ENE
- ISOPENTANE
- n-PENTANE
- 2,2-DIMETHYL BUTANE
- 2,3-DIMETHYLBUTANE
- 2-METHYLPENTANE
- 3-METHYLPENTANE + 2-ETHYL-BUT-1-ENE
- cis-3-METHYLPENT-2-ENE + cis-HEX-2-ENE
- METHYL CYCLOPENTANE
- 2,2-DIMETHYLPENTANE + 2,3-DIMETHYL-BUT-2-ENE + 2,3,3-TRIMETHYLBUTANE
- BENZENE
- 2-METHYLHEXANE + cis-5-METHYLHEX-2-ENE
- cis-3,4-DIMETHYL PENT-2-ENE
- 2,3-DIMETHYLPENTANE + 1,1-DIMETHYLCYCLOPENTANE
- 3-METHYLHEXANE
- 2,2,4-TRIMETHYLPENTANE
- n-HEPTANE + c4-1-METHYLHEX-2-ENE
- 1,1,3-TRIMETHYL CYCLOPENTANE
- 2,5-DIMETHYLHEXANE
- TOLUENE
- 2,5-DIMETHYL-HEX-2-ENE
- 1,1,2-TRIMETHYLCYCLO PENTANE
- 2-METHYLHEPTANE
- 3-METHYLHEPTANE
- n-OCTANE
- ETHYLBENZENE
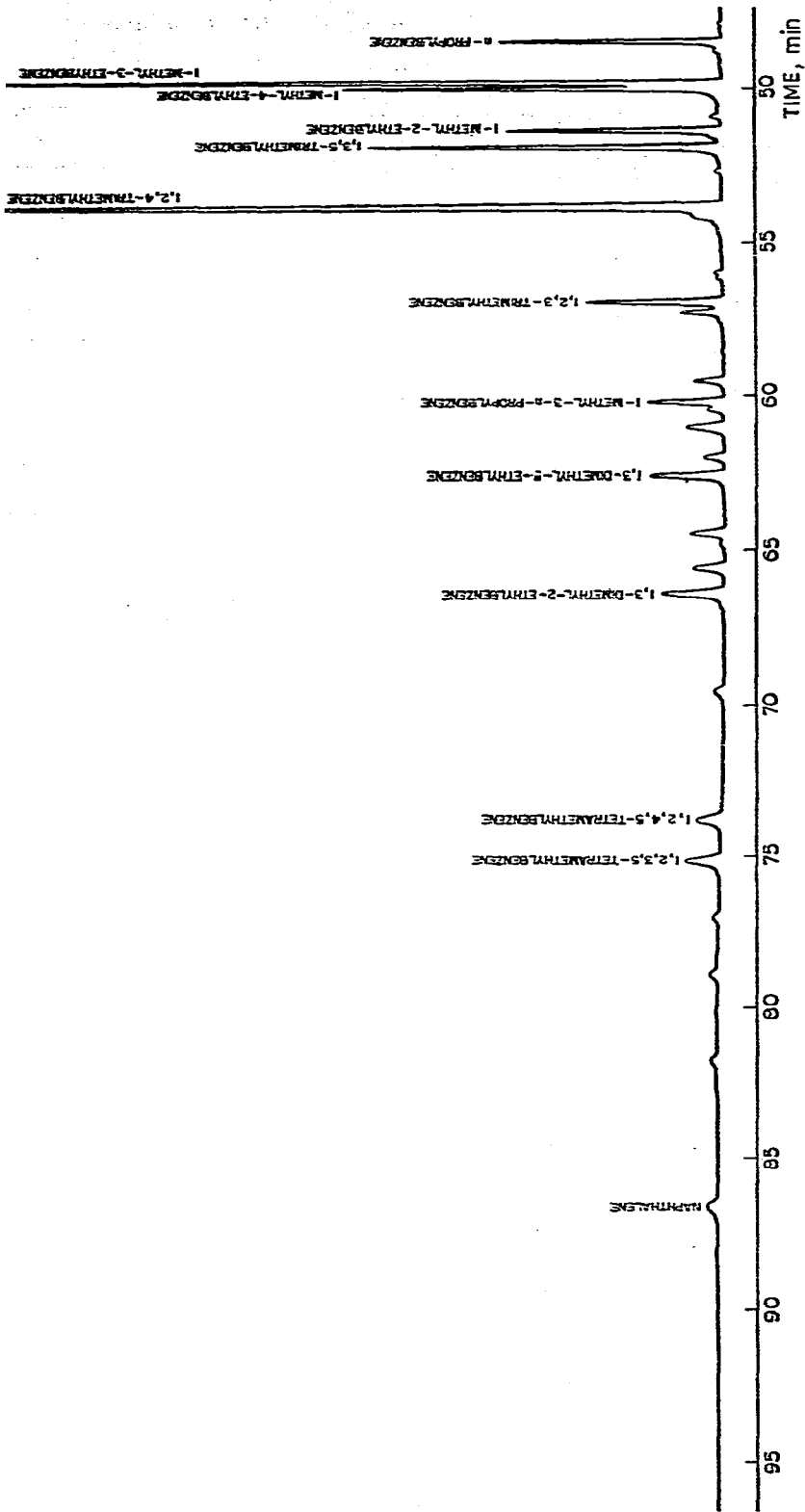- 1,4-DIMETHYLBENZENE
- 1,3-DIMETHYLBENZENE
- 1,2-DIMETHYLBENZENE

Fig. 1. Chromatogram of a full-range gasoline. For experimental details, see text.
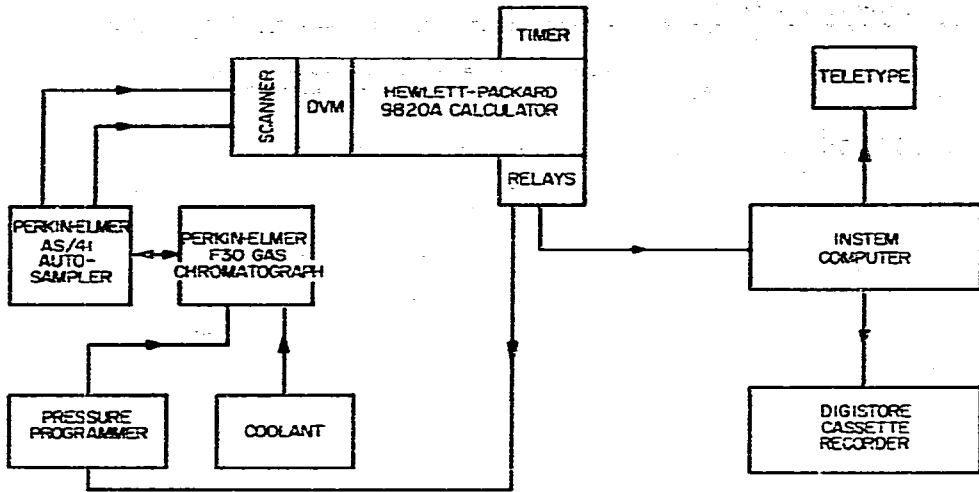
Fig. 2. Schematic diagram of control signals for GC system.

END OF HEWLETT-PACKARD CALCULATOR PROGRAM, VENT PRESSURE
PROGRAMMER, CONTINUE TO HOLD 5V d.c. SIGNAL ON RELAY ON
COMPUTER LINE

START OF COOL-DOWN CYCLE OF GC OVEN

END OF COMPUTER DATA COLLECTION – OUTPUT NORMALIZED
RESULTS ON EITHER CASSETTE RECORDER OR TELETYPE

TIME

INJECTION POINT SIGNAL

SAMPLE
SERIAL No.   CAPSULE NUMBER
SIGNALS   2nd VENT OF PRESSURE PROGRAMMER

MAGAZINE NUMBER

VOLTS

THE INJECTION SIGNAL FROM THE GC:

(a) STARTS TEMPERATURE PROGRAMMING OF THE OVEN

(b) STARTS GC COMPUTER PROGRAM

(c) STARTS PRESSURE PROGRAMMING OF GC CARRIER GAS

(d) HOLDS 5V d.c. SIGNAL ON RELAY ON COMPUTER LINE

Fig. 3. Cycling operation of automated GC system.

TABLE I

PRECISION DATA FOR PEAK AREA MEASUREMENTS FOR SOME OF THE COMPONENTS IN A TYPICAL FULL-RANGE GASOLINE (ANALYSED 42 TIMES)

Peak identification	Mean % peak area, $\bar{x}$	Standard deviation, σ	% Standard deviation, V^*
Isobutane	1.56	0.110	7.05
Isobutene + but-1-ene	0.555	0.028	5.12
Isopentane	1.889	0.046	2.44
2,2-Dimethylbutane	0.382	0.010	2.62
3-Methylpentane + ethylbut-1-ene	2.89	0.042	1.42
cis-3-Methylpent-2-ene + cis-2-hexene	4.84	0.080	1.65
Methylcyclopentane	2.63	0.091	3.46
Benzene	7.90	0.100	1.27
3-Methylhexane	3.29	0.035	1.07
cis-1,2-Dimethylcyclopentane	0.223	0.006	2.65
2,5-Dimethylhexane	0.812	0.020	2.36
Toluene	10.72	0.170	1.58
2,2-Dimethyl-3-ethylpentane + 2-methyl-4-ethylhexane	0.149	0.010	6.37
1,3,5-Trimethylbenzene	0.296	0.011	3.83
n-Propylbenzene	0.410	0.020	4.87
1,2,3-Trimethylbenzene	0.771	0.024	3.15
1,3-Dimethyl-5-ethylbenzene	0.330	0.018	5.44
1,4-Dimethyl-2-ethylbenzene	0.160	0.007	4.37
sec.-Butylbenzene	0.116	0.005	4.38

$$* \; V = \frac{100\sigma}{\bar{x}}$$

poor agreement is shown between the two sets of values for toluene and ethylbenzene, but this is not surprising in view of the well known deviation in response of flame ionization detectors for the lower aromatics, for which no correction factor was
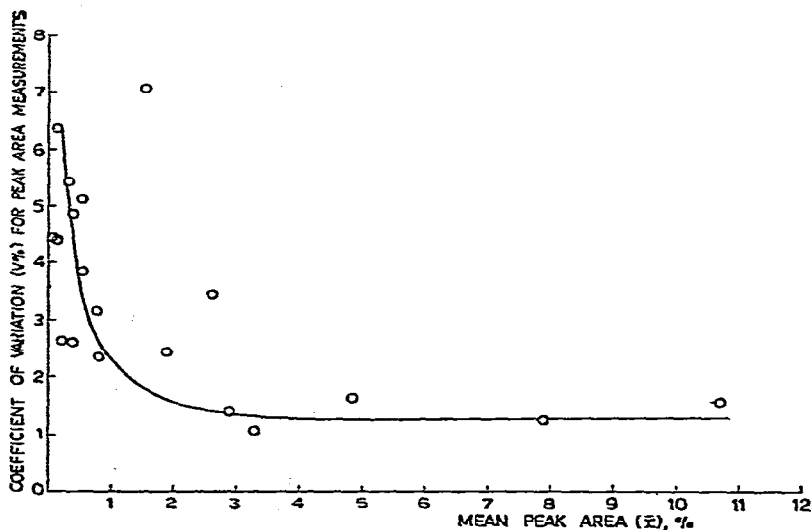

Fig. 4. Precision data for peak area measurements.

TABLE II

COMPARISON OF EXPERIMENTAL AND KNOWN COMPOSITION FOR A SYNTHETIC MIXTURE

No.	Hydrocarbon	Time, sec	% Area	% Weight
1	2-Methylbutane	656	10.59	10.41
2	Pent-1-ene	676	0.64	0.71
3	n-Pentane	739	1.23	0.92
4	trans-Pent-2-ene	744	0.63	0.99
5	cis-Pent-2-ene	756	0.42	0.16
6	3,3-Dimethylbut-1-ene			
7	2-Methylbut-2-ene	790	0.05	0.03
8	2,2-Dimethylbutane	867	3.06	3.05
9	4-Methylpent-1-ene	926	0.17	0.20
10	Cyclopentane	984	1.01	1.09
11	2,3-Dimethylbutane	1005	3.94	3.77
12	2-Methylpentane	1028	7.15	6.38
13	2-Methylpent-1-ene	1076	0.31	0.42
14	Hex-1-ene	1087	1.12	1.10
15	2-Ethylbut-1-ene	1139	0.46	0.53
16	trans-Hex-2-ene	1165	0.14	0.98 c/t
17	2-Methylpent-2-ene	1171	0.26	0.37
18	n-Hexane	1181	1.25	1.26
19	4,4-Dimethylpent-1-ene			0.17
20	cis-3-Methylpent-2-ene	1195	0.58	0.38 c/t
21	cis-Hex-2-ene			
22	trans-3-Methylpent-2-ene	1246	0.10	—
23	Methylcyclopentane	1305	0.38	0.22
24	2,3-Dimethylbut-2-ene	1309		0.25
25	2,4-Dimethylpentane	1335	0.52	0.60
26	Benzene	1358	1.35	1.42
27	2,2,3-Trimethylbutane	1374	1.10	0.49
28	2,4-Dimethylpent-1-ene			0.58
29	2,4-Dimethylpent-2-ene	1404	0.11	0.11
30	3-Methylhex-1-ene	1412	0.48	0.51
31	trans-2-Methylhex-3-ene	1437	0.13	0.18
32	5-Methylhex-1-ene	1446	0.38	0.43
33	4-Methylhex-1-ene	1494	1.43	0.13
34	Cyclohexane			1.33
35	2,3-Dimethylpentane	1563	0.44	0.27
36	1,1-Dimethylcyclopentane			0.45
37	3-Methylhexane	1597	0.31	0.37
38	2-Methylhex-1-ene	1609	0.15	0.16
39	cis-1,3-Dimethylcyclopentane	1617	0.16	0.42 c/t
40	Hept-1-ene	1632	0.38	0.45
41	trans-1,3-Dimethylcyclopentane	1645	0.39	0.18
42	cis-2,5-Dimethylhex-3-ene			
43	3-Ethylpentane	1649		0.13
44	trans-1,2-Dimethylcyclopentane	1657	0.38	0.43 c/t
45	trans-Hept-3-ene	1665	0.34	0.06
46	2,2,4-Trimethylpentane			0.06
47	cis-Hept-3-ene	1679	0.21	0.37 c/t
48	2-Methylhex-2-ene	1686		0.11
49	trans-2,5-Dimethylhex-3-ene	1712	0.17	0.20

TABLE II *(continued)*

No.	Hydrocarbon	Time, sec	% Area	% Weight
50	*trans*-Hept-2-ene	1730	}1.91	0.03
51	*n*-Heptane	1739		1.78
52	*cis*-Hept-2-ene	1753	0.28	0.96 c/t
53	*cis*-1,2-Dimethylcyclopentane	1840	0.02	—
54	Methylcyclohexane	1867	0.78	0.83
55	2,5-Dimethylhexane	1899	0.29	0.41
56	2,4-Dimethylhexane	}1920	0.44	0.06
57	Ethylcyclopentane			0.42
58	2,3-Dimethylhex-1-ene	1960	0.23	0.30
59	*trans*-2-Methylhept-3-ene	1976	0.10	0.11
60	Toluene	1993	5.77	4.90
61	2,5-Dimethylhex-2-ene	2025	0.17	0.20
62	2,3,4-Trimethylpentane	2030	0.15	0.14
63	2,3-Dimethylhexane	2081	0.16	0.19
64	2-Methylheptane	2110	0.26	0.32
65	4-Methylheptane	2123	0.12	0.13
66	3,4-Dimethylhexane	2141	0.20	0.24
67	3-Methylheptane	}2153	0.21	0.18
68	3-Ethylhexane			0.06
69	2-Methylhept-1-ene	}2176	0.26	0.06
70	2,2,5-Trimethylhexane			0.25
71	Oct-1-ene	2205	0.30	0.38
72	*trans*-1,4-Dimethylcyclohexene	}2228		0.41
73	*cis*-1,3-Dimethylcyclohexene		}1.04	0.61 c/t
74	1,1-Dimethylcyclohexane	2236		0.37
75	2-Methylhept-2-ene	2256	0.10	0.10
76	*trans*-Oct-2-ene	2301	0.13	0.64 c/t
77	*n*-Octane	}2308		3.77
78	*trans*-1,2-Dimethylcyclohexene		}4.82	0.42
79	*cis*-Oct-2-ene	2325		—
80	*trans*-1,3-Dimethylcyclohexene	}2344	0.56	—
81	*cis*-1-4-Dimethylcyclohexene			0.43
82	2,4-Dimethylheptane	2430	1.04	1.02
83	2,6-Dimethylheptane	2465	0.44	0.63
84	*cis*-1,2-Dimethylcyclohexene	2486	}0.74	0.70
85	2,5-Dimethylheptane	2497		0.16
86	Ethylbenzene	2526	7.52	6.53
87	1,4-Dimethylbenzene	2608	2.15	2.11
88	1,3-Dimethylbenzene	}2622	3.49	2.43
89	2,3-Dimethylheptane			0.70
90	3,4-Dimethylheptane	2641	0.25	0.25
91	4-Methyloctane	2668	}0.93	0.13
92	2-Methyloctane	2678		0.81
93	3-Methyloctane	2710	0.19	0.19
94	1,2-Dimethylbenzene	2733	3.64	3.21
95	Non-1-ene	2773	0.55	0.62
96	Isopropylbenzene	}2877	4.47	0.65
97	*n*-Nonane			3.48
98	*n*-Propylbenzene	3046	2.56	2.52
99	3-Ethyltoluene	3133	0.10	0.08
100	4-Ethyltoluene	3147	0.16	0.14

TABLE II *(continued)*

No.	Hydrocarbon	Time, sec	% Area	% Weight
101	2-Ethyltoluene	}3240	0.21	0.15
102	5-Methylnonane			0.07
103	4-Methylnonane	3251	0.15	0.13
104	2-Methylnonane	}3275	1.21	0.49
105	1,3,5-Trimethylbenzene			0.94
106	*tert.*-Butylbenzene	3305	0.29	0.31
107	3-Methylnonane	3323	0.22	0.19
108	1,2,4-Trimethylbenzene	3410	2.52	1.78
109	Dec-1-ene			0.25
110	Isobutylbenzene	}3461	0.41	0.22
111	*sec.*-Butylbenzene			0.23
112	*n*-Decane	3567	1.32	1.39
113	1,2,3-Trimethylbenzene	}3625	1.21	1.23
114	4-Isopropyltoluene			0.11
115	Indan	3647	0.49	0.52
116	1,3-Diethylbenzene	3801	0.29	0.28
117	*n*-Butylbenzene	3868	0.59	0.65
118	4-*n*-Propyltoluene	3906	0.27	0.21
119	4-Methyldecane	4178	0.16	0.14
120	2-Methyldecane	4233	0.27	0.25
121	3-Methyldecane	4303	0.05	0.07
122	*n*-Undecane	4729	0.76	0.91
123	1,2,4,5-Tetramethylbenzene	4780	0.51	0.51
124	1,2,3,5-Tetramethylbenzene	4869	0.26	0.24
125	1,2,3,4-Tetramethylbenzene	5284	0.08	0.08
126	Naphthalene	5578	0.09	0.10

applied. With the exception of these lower aromatics, components at 1% or greater concentration can be determined with an accuracy of about $\pm 10\%$, the error rising to $\pm 20\%$ at concentrations below 0.5%. This accuracy was considered to be adequate for the project utilizing the data.

Table III and Fig. 5 show the precision data for the retention times of the compounds listed in Table I and obtained from the same set of 42 analyses. The variation in retention time reaches a minimum around the middle of the chromatogram and is larger at the beginning and the end. Overall, however, the retention time data show a remarkably high repeatability, especially considering that the analyses are both temperature and pressure programmed.

The main drawback of the technique is the rather long analysis time which, as indicated earlier, is partly due to the volatility of squalane. Apart from replacing this stationary liquid, the only other likely possibility is to improve the efficiency of the column. It is feasible that a column with a higher efficiency per unit length could effect a significant reduction in the analysis time, and a further reduction could be achieved by using hydrogen instead of helium as carrier gas to give a turn-round time of about 70–90 min. Another possible way of reducing analysis time would be by the use of so-called two-dimensional GC. This would involve the separation of of the saturates and olefins from the aromatics on a polar column, followed by complete separation on two relatively short, non-polar capillary columns connected in parallel.

TABLE III

PRECISION DATA FOR PEAK RETENTION TIMES FOR SOME OF THE COMPONENTS IN A TYPICAL FULL-RANGE GASOLINE (ANALYSED 42 TIMES)

Peak identification	Mean retention time, sec*	Standard deviation, σ	% Standard deviation, V
Isobutane	462.5	3.47	0.75
Isobutene + but-1-ene	485.2	3.45	0.71
Isopentane	673.9	4.96	0.74
2,2-Dimethylbutane	899.4	5.11	0.57
3-Methylpentane + ethylbut-1-ene	1140.1	5.92	0.52
cis-3-Methylpent-2-ene + cis-2-hexene	1236.9	5.43	0.43
Methylcyclopentane	1370.3	5.75	0.42
Benzene	1429.6	6.08	0.43
3-Methylhexane	1685.2	5.82	0.35
cis-1,2-Dimethylcyclopentane	1948.1	5.66	0.29
2,5-Dimethylhexane	2032.6	8.58	0.42
Toluene	2115.7	6.48	0.30
2,2-Dimethyl-3-ethylpentane + 2-methyl-4-ethylhexane	2487.7	6.20	0.25
1,3,5-Trimethylbenzene	2612.4	6.88	0.26
n-Propylbenzene	3261.0	11.04	0.33
1,2,3-Trimethylbenzene	3533.6	10.56	0.30
1,3-Dimethyl-5-ethylbenzene	3952.5	12.85	0.33
1,4-Dimethyl-2-ethylbenzene	4431.4	16.44	0.37
sec.-Butylbenzene	5470.4	23.64	0.43

* The flow conditions used here differed from those used to obtain the chromatogram in Fig. 1; hence, the retention times in the table and the figure do not correspond.
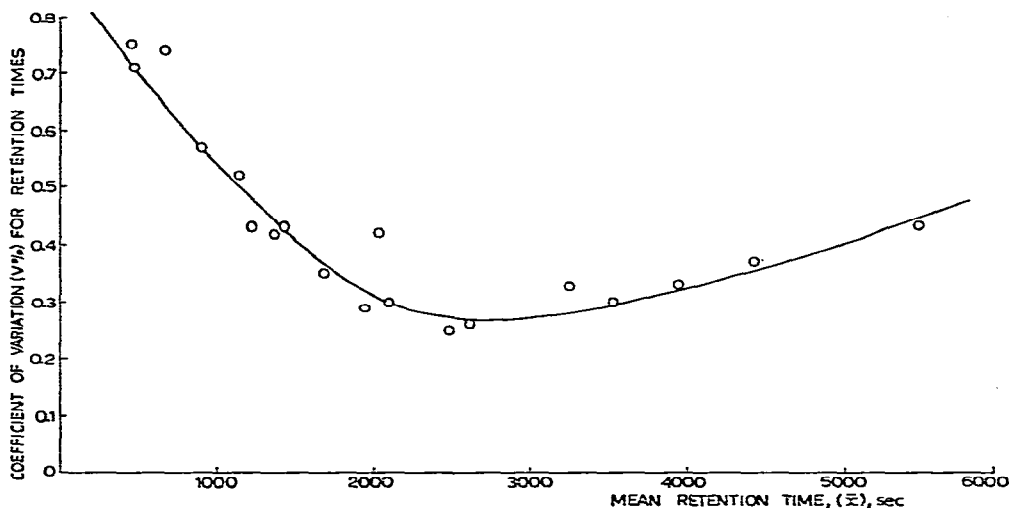

Fig. 5. Precision data of retention times.

CONCLUSIONS

An apparatus has been assembled for the automatic GC analysis of complex hydrocarbon mixtures in the boiling range —42° to 220°. The information obtained

can be presented as a conventional chromatogram, as a print-out of retention times and percent areas and on magnetic tape for further processing. The quantitative accuracy of the normalization method is not as high as can be achieved by other GC methods, such as internal standardization, but is thought to be adequate for most applications. The precision of the retention data is sufficient to enable automatic computer identification of many key peaks.

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