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AUTOMATIC GAS CHROMATOGRAPHIC DETERMINATION OF GASOLINE COMPONENTS

APPLICATION TO OCTANE NUMBER DETERMINATION

J. P. DURAND*, Y. BOSCHER and N. PETROFF
Institut Français du Pétrole, BP 311, 92506 Rueil Malmaison (France)

and

M. BERTHELIN
Cedil Solaize, BP 3, 69360 Vernaison (France)

SUMMARY

An automatic method has been developed for the determination of gasoline components by gas chromatography. Separation has been achieved on squalane and cross-linked OV-1 capillary columns. Analytical conditions were optimized and all peaks were identified. Programmed temperature indices, I_{PT} , were used for automatic identifications. These indices appear to be reproducible on different capillary columns having the same commercial specifications with identical analytical conditions. Application of this method to the automatic determination of the Research Octane Number (RON) is demonstrated for samples from reformers and calculated value are compared to values measured by the ASTM standardized engine method (D2699).

INTRODUCTION

Detailed analysis of gasoline is required for refining process control (*e.g.*, straight run distillation of crude oil, reforming, cracking, hydrotreating). It enables some gasoline properties to be predicted (*e.g.*, Reid vapour pressure, flash point, octane number). Numerous methods based on GC capillary columns, have been described^{1–11} during the last 20 years. Much development work has been done with squalane as the liquid phase. Several years ago, squalane was replaced by polydimethyl siloxanes (such as OV-1 or OV-101) which are cross-linked on the fused-silica tubing and can be used to 300°C. The most complete studies on identifying the compounds have been published by Whittemore⁷ for squalane and Johansen *et al.*⁸ for OV-101.

With the recent advance of GC data systems, the automatic identification of compounds has become feasible. However, there are three difficulties:

- (1) The chromatogram is complex (more than 200 peaks);
- (2) the retention time (t_R) difference between two peaks is small (down to 5 s);

(3) with programmed temperature, reproducible retention times are not easily achieved on different columns of the same specifications.

Generally, identification was made from the relative retention time of the peak (RRT) with an identification window. The repeatability is excellent⁸ and gives automatic identification, but the repeatability decreases with time when the column is used on a routine basis. This phenomenon requires a readjustment to be made. Moreover, the comparison of RRT values obtained by different laboratories often reveals great variations, which hampers the exchange of data and methods.

Calculation of the research octane number (RON) from gas chromatographic data has been described in many papers¹¹⁻¹⁴. The most important have been published by Jenkins¹², especially for samples from reformers, and by Walsh *et al.*¹³ for various gasolines.

This paper describes an automated method for the determination of gasoline compounds by achieving as complete a separation and identification as possible and by developing an automatic data handling system usable in the laboratory or for process control. The system is applied for the determination of the RON value.

EXPERIMENTAL

The GC analyses were performed on a Hewlett-Packard (Palo Alto, CA U.S.A.) 5880 or 5890 gas chromatograph, equipped with a flame ionization detector and a split-injector. An automatic Hewlett-Packard 7673A injector was used for sample injection.

In the first method, a metal capillary column (100 m × 0.25 mm I.D.) with a 0.3- μ m film of squalane (Perkin Elmer, Norwalk, CT, U.S.A.) was employed. The column oven temperature was programmed from 40°C to 98°C at 1.1°C/min. The helium carrier gas flow-rate was set at 1.7 ml/min.

In the second method, the column was a fused-silica capillary (50 m × 0.2 mm I.D.) cross-linked with a 0.52- μ m film of methyl silicone OV-1 (Hewlett-Packard). The column oven temperature was programmed from 35°C to 150°C at 1.1°C/min with an initial isothermal period of 10 min at 35°C. The helium carrier gas flow rate was set at 1.2 ml/min.

In both methods, the detector and injector temperatures were held at 250°C, the split ratio was 1/100 and the sample size 1.0 μ l.

Data handling was carried out using a Hewlett-Packard Model 3350C which provided raw data integration. Weight percents were obtained from area percents without any response factor correction. Component identification and octane number determination were performed after completely the run using a Fortran program developed in our company.

RESULTS AND DISCUSSION

The work was carried out with the two major liquid phases used for petroleum hydrocarbon separation. Separation on squalane is better than on OV-1 (or OV-101), especially for C₈-C₁₁ hydrocarbons. But the maximum operating temperature of squalane is low (100°C). Consequently, methyl silicone was selected when the samples had a final boiling point higher than 220°C and for process control, which requires greater column stability.

The variation of the retention indices with temperature is different for every group of hydrocarbons, and is particularly significant for aromatics, naphthenes and highly branched alkanes. This effect can be used to optimise the separation by column temperature adjustments. The temperature program selected yields the minimum number of simultaneously eluted compounds in different hydrocarbon groups and achieves separation of major compounds which are not easily resolved, especially aromatics from methyl alkanes.

Identification was made on the basis of retention data and by the use of GC-MS. All alkanes, naphthenes and aromatics with a boiling point $< 200^{\circ}\text{C}$ and olefins with a boiling point $< 100^{\circ}\text{C}$ were identified. For olefins with a boiling point $> 100^{\circ}\text{C}$, the resolution of capillary columns is not sufficient to give complete separation from other compounds. The samples containing olefins (such as catalytic cracking gasoline) cannot be completely separated with capillary columns.

Programmed temperature index

Under isothermal temperature conditions, Kováts' retention indices are the most convenient means for peak identification. They can be calculated in programmed temperature analysis, but their use requires caution, because they depend on other parameters than in isothermal analysis, *i.e.* on the temperature programme, gas flow-rate and film thickness of the stationary phase.

Under programmed temperature conditions, the retention temperature (column temperature at the top of the peak) of n -alkanes increases linearly with the number of carbon atoms. An index can be derived from the one proposed by Van den Dool and Kratz¹⁵ by using the retention time instead of the retention temperature.

$$I_{\text{PT},i} = \frac{t_{\text{R},i} - t_{\text{R},n}}{t_{\text{R},n+1} - t_{\text{R},n}} + n \quad (1)$$

where t_{R} is the retention time of compound i , eluted between the n -alkanes with n and $n+1$ carbon atoms. This index is reproducible if the retention temperature of each compound can be kept constant. In fact, it is sufficient that this condition is met only for the n -alkanes. Consequently, the retention times of the n -alkanes have to be adjusted, by adjusting the column flow-rate, until the values are equal to those used for setting up of the reference index table. Our experience over a period of three years shows that the repeatability of indices on the same column and their reproducibility on several identical commercial columns are sufficient to allow the use of the same reference index file for the automatic identification of peaks.

Reference index and window determination

The reference indices were determined from analysis of ten different gasolines, as the arithmetic average of the values found for each peak. The extreme values were used to establish the window (W) of the index, *i.e.* the identification zone. There is no overlapping of contiguous zones, allowing the use of the indices for automatic application. For routine analysis, the indices are calculated from eqn. 1, and values are compared with the reference indices. The automatic identification will be correct

TABLE I
 VARIATION OF RETENTION TIMES, RELATIVE RETENTION TIMES, AND PROGRAMMED TEMPERATURE RETENTION INDICES OF SE-
 LECTED COMPOUNDS WITH COLUMN AGE

OV-1 capillary column with gasoline condition. (1) New column. (2) Same column after three years of routine analyses under the same conditions. (3) Differences of t_R , RRT and I_{PT} between the new and the old column. W_R : reference window for each peak.

Compound	t_R (min)			RRT (1.00 for <i>o</i> -Xylene)						I_{PT}		
	1	2	3	W_R	1	2	3	W_R	1	2	3	W_R
3-Methylpentane	9.61	7.91	1.70	0.30	0.212	0.200	0.012	0.006	5.758	5.754	0.004	0.050
Benzene	14.32	11.67	2.65	0.25	0.316	0.296	0.020	0.005	6.405	6.410	0.005	0.025
Methylcyclohexane	21.96	17.97	3.99	0.20	0.485	0.455	0.030	0.004	7.161	7.163	0.002	0.012
Toluene	26.37	21.88	4.49	0.24	0.583	0.554	0.029	0.005	7.487	7.483	0.004	0.018
<i>o</i> -Xylene	45.26	39.47	5.79	0.15	1.00	1.00	—	—	8.756	8.749	0.007	0.010
1-Methyl-3-ethyl-benzene	56.52	50.39	6.13	0.15	1.249	1.277	0.028	0.003	9.464	9.459	0.005	0.010
2-Methylhexane	59.48	53.34	6.14	0.13	1.314	1.351	0.037	0.003	9.650	9.648	0.002	0.009
1,3-Dimethyl-5-ethylben- zene	71.81	65.35	6.46	0.12	1.587	1.656	0.069	0.003	10.441	10.435	0.006	0.008
3-Methylhexane	75.94	69.47	6.47	0.08	1.678	1.760	0.082	0.002	10.712	10.710	0.002	0.005

for each peak, if the difference Δ between the reference and calculated index is lower than or equal to the defined window.

Repeatability of I_{PT}

In routine analysis, the retention capacity varies with the age of the column, e.g. due to a film thickness decreasing. Table I shows the variations (Δ) of t_R , RRT, and I_{PT} on a new column and on the same column after three years of routine analyses. With a great reduction of t_R , only the variation of I_{PT} is narrower than the reference window of each peak. During these three years it was not necessary to modify the reference I_{PT} file.

Reproducibility of I_{PT}

The reproducibility was determined on three commercial OV-1 capillary columns (characteristics and conditions listed in experimental part). Table II shows the maximum variation Δ , of t_R , RRT, and I_{PT} , obtained with the three columns for the same compounds as in Table I. The I_{PT} values show less variations than the t_R or RRT values and, moreover, the variations are within the index window defined above (see Table I).

It is easy to reproduce the method on another gas chromatograph provided with a new column. With the conditions given in the Experimental section, the indices I_{PT} are calculated. If the differences between the measured indices and the reference indices is greater than the identification window, the carrier gas flow-rate has to be modified to adjust the t_R values of the *n*-alkanes to the reference method values, with a tolerance of about 3% for *n*-undecane.

Data handling

Fig. 1 shows the flow-chart of the data handling. A reference table for the t_R values of the *n*-alkanes is created for each new column with the raw data handling method. This method adjusts the reference table to match with the t_R values of the analysis if all *n*-alkanes are identified. The I_{PT} values are calculated from the integrated data and compared with the reference index file. For each compound this file contains the index under the analytical conditions listed in the Experimental section, together with an identification window. The report contains the weight percent and the name of the compound, according to hydrocarbon group (alkanes, naphthenes, aromatics, olefins). An analysis of the individual members of each group of hydrocarbons is also provided.

Analysis of gasoline

In our laboratory, this method has been used for three years for the routine analysis of different types of gasolines: straight-run, reforming, hydrocracking, and hydrovisbreaking. The results of quantitative analysis of various nonolefinic gasolines has been compared with the results obtained by alkanes-naphthenes-aromatics determination¹⁶ with a multicolumn chromatograph (Hewlett-Packard 5880) modified by Analytical Controls (Delft, The Netherlands). This method separates the gasoline in hydrocarbon groups by the number of carbon atoms. In all cases, the difference between the methods was less than 10%, and for most of the analysis, less than 5%. A comparison of the results for the heavy C₈ to C₁₁ hydrocarbons, which are the

TABLE II
 REPRODUCIBILITY OF RETENTION TIMES, RELATIVE RETENTION TIMES AND PROGRAMMED TEMPERATURE RETENTION INDICES
 OF SELECTED COMPOUNDS WITH THREE COMMERCIAL OV-1 CAPILLARY COLUMN UNDER THE SAME ANALYTICAL CONDITIONS

Δ = Maximum difference between the three columns.

Compound	t_R (min)			RRT (1.000 for <i>o</i> -Xylene)						I_{PT}		
	OV1-1	OV1-2	OV1-3	Δ	OV1-1	OV1-2	OV1-3	Δ	OV1-1	OV1-2	OV1-3	Δ
3-Methylpentane	9.61	8.51	9.01	1.10	0.212	0.198	0.206	0.014	5.757	5.758	5.758	0.001
Benzene	14.32	13.60	13.58	0.74	0.316	0.317	0.310	0.007	6.495	6.410	6.411	0.006
Methylcyclohexane	21.96	19.94	20.99	2.02	0.485	0.465	0.479	0.020	7.161	7.167	7.166	0.006
Toluene	26.37	24.22	25.29	2.05	0.583	0.564	0.577	0.019	7.487	7.488	7.487	0.001
<i>o</i> -Xylene	45.26	42.88	43.82	2.38	1.000	1.000	1.000	—	8.756	8.754	8.758	0.004
1-Methyl-3-ethylbenzene	56.52	54.08	54.86	2.44	1.249	1.261	1.252	0.012	9.464	9.466	9.461	0.005
2-Methylnonane	59.48	57.07	57.82	2.41	1.314	1.320	1.319	0.011	9.651	9.652	9.657	0.002
1,3-Dimethyl-5-ethylbenzene	71.61	69.33	69.83	2.28	1.582	1.617	1.594	0.035	10.441	10.444	10.438	0.006
3-Methyldecane	75.94	73.44	73.94	2.50	1.678	1.713	1.687	0.035	10.712	10.713	10.412	0.001

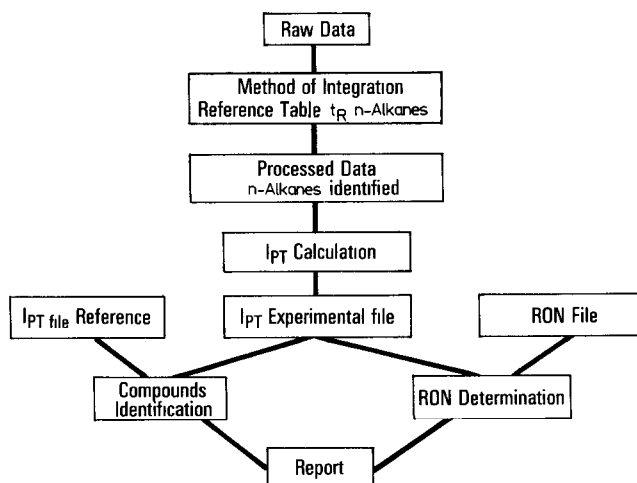


Fig. 1. Flow-chart of the data handling.

most difficult compounds to separate on capillary columns, is excellent. This is illustrated in Table III for a heavy gasoline from a hydrocracker.

For olefinic gasoline, the results have been compared with a PONA method¹⁷ on a Packard (Delft, The Netherlands) A412 multicolumn chromatograph, for hydrocarbons up to C₇. Table IV shows the comparison for light catalytic cracking gasoline. The variations are the same as for the non-olefinic gasolines.

TABLE III

RESULTS OF QUANTITATIVE ANALYSIS OF HEAVY GASOLINE BY CAPILLARY-COLUMN GC AND ALKANES-NAPHTHENES-AROMATICS METHOD (% , w/w)

(1) alkanes-naphtenes-aromatics method, (2) squalane capillary column (conditions in the Experimental section).

Carbon number	Paraffins		Naphthenes		Aromatics		Compounds of boiling point > 200°C	
	1	2	1	2	1	2	1	2
3	0.05	0.05						
4	0.47	0.47						
5	2.01	1.95	0.20	0.19				
6	4.54	4.36	1.95	1.85	0.11	0.11		
7	7.56	7.64	3.62	3.78	0.96	0.94		
8	9.39	9.31	4.11	3.82	3.00	3.40		
9	9.50	9.54	4.88	4.90	5.95	6.50		
10	10.61	11.08	4.31	3.87	8.01	7.25		
11	8.32	7.84	3.42	3.26				
Total	52.45	52.24	22.49	21.67	18.03	18.20	7.03	7.89

TABLE IV

RESULTS OF QUANTITATIVE ANALYSIS OF HIGH-OLEFINIC GASOLINE BY CAPILLARY COLUMN GC AND PONA METHOD (WEIGHT %)

(1) PONA method, (2) squalane capillary column (conditions in the Experimental section).

Carbon number	Paraffins		Naphthenes		Aromatics		Olefins		Compounds of B.P. > 100°C	
	1	2	1	2	1	2	1	2	1	2
4	1.54	1.33					3.49	3.67		
5	9.98	10.23	0.26	0.19			10.98	10.50		
6	8.60	8.99	2.33	2.29	0.68	0.68	10.16	9.92		
7	6.01	6.43	3.65	3.60	3.57	3.86	8.72	7.95		
Total	26.13	26.98	6.24	6.08	4.25	4.54	33.35	32.04	30.03	30.36

Octane number determination for reforming samples

Experimental conditions. Detailed analysis and determination of the RON values are needed for process control of high-RON reforming plants. To achieve this, we modified the chromatographic gasoline analysis conditions given in the Experimental section, to take into account restraints related to on-line process analyses:

(1) A stable stationary phase is used far below its maximum operating temperature; (2) An initial temperature of the column higher than room temperature is selected to avoid the use of a cooling system; (3) The analysis of the heaviest significant compounds (*i.e.* methylnaphthalenes) is achieved in the shortest possible time, while maintaining good resolution of the lightest hydrocarbons.

It was possible to shorten the analysis time, because the number of hydrocarbons present in a reformat is less than in a gasoline.

The equipment used was the same as that used for gasoline analysis. The OV-1 column was selected and the oven temperature setting was modified: the column temperature is increased from 40 to 200°C at a rate of 2°C/min with a final isothermal time of 20 min. A typical chromatogram is shown in Fig. 2.

Calculation method. The automatic identification program described in Fig. 1 was extended to include the calculation of RON values by a method classifying compounds into 31 groups (Table V), as defined by Walsh¹³. The individual or border compounds are identified by the automatic identification program. Table V gives the indices and applied coefficients for the calculation of the RON value based on eqn. 2.

$$\text{RON} = \sum k_i C_i \quad (2)$$

where C_i is the concentration in weight percent of the group i and k_i is the corresponding contribution factor. Obviously, the reference index (I_{PT}) file is not the same as that for the gasoline analysis. Fig. 3 reproduces the shortened computer report for the analysis and calculation of the RON value for a sample from a reformer.

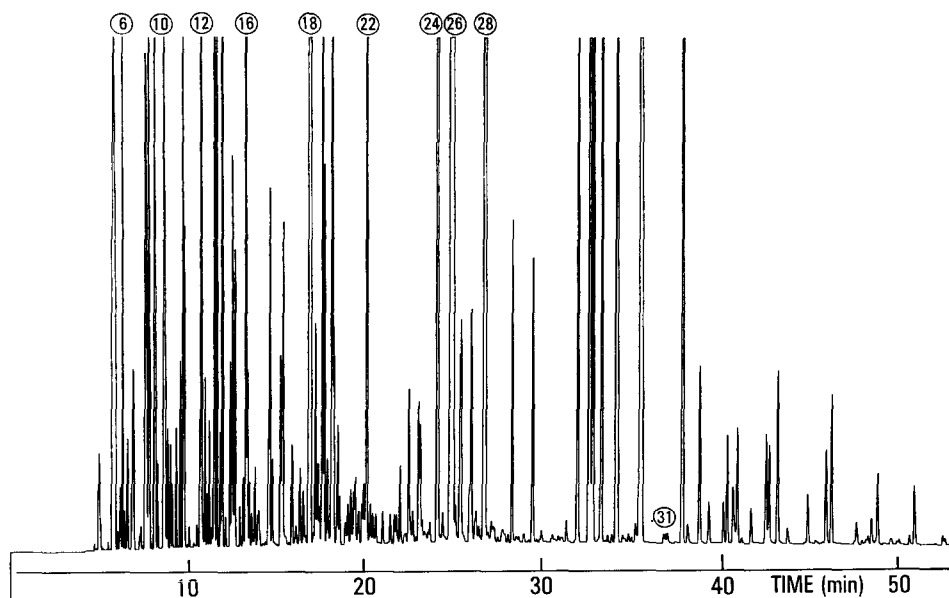


Fig. 2. Chromatogram of reformate. Conditions for RON determinations. The numbers identifying the individual peaks correspond to Table V.

Repeatability and reproducibility of RON values calculated from GC analysis. The performance of GC were evaluated for gasoline analysis above and showw the same level of reliability for reformate analysis. Therefore, we only show the results for the calculation of RON values.

The repeatability was evaluated for six months with two samples with different RON values on the basis of 16 analyses, using the same apparatus and the same column. The first sample showed a mean RON value of 89.38 with a standard deviation of 0.090 and confidence interval at 95% probably between 89.33 and 89.43. For the second sample the mean RON value was 102.61, the standard deviation 0.102 and the 95% confidence interval between 102.56 and 102.66.

The reproducibility was evaluated by the simultaneous analysis on two different columns having the same characteristics and fitted to two different gas chromatographs (HP5880, HP5890). About 40 samples were tested and the difference of the two calculated RON values was less than 0.3 RON units.

Comparison of RON values calculated from GC analysis and measured with an engine. The chromatographic method yields very good reliability, but the results must be compared with the octane numbers determined with an engine, according to ASTM procedure D2699. All the RON measurements were performed in the pilot-plant center (CEDI) of our company, and all the reformer samples analysed were obtained in this plant with various feeds and under different operating conditions. A comparison between measured RON values and calculated RON values from GC analysis was made for about 60 samples, and the results are shown in Fig. 4. The agreement of the two RON values is very good for RON values between 95 and 100.

TABLE V

COEFFICIENTS FOR CALCULATION OF RON VALUES ACCORDING TO EQN. 2 WITH LIMITING RETENTION INDICES FOR EACH GROUP

Group No.	Components	I_{PT}		Coefficient
1	Components eluted before <i>n</i> -butane	0	3.999	1.039
2	<i>n</i> -Butane		4.0000	0.881
3	Components eluted between <i>n</i> -butane and isopentane	4.0001	4.6589	1.443
4	Isopentane	4.6590	4.6650	0.840
5	Components eluted between isopentane and <i>n</i> -pentane	4.6651	4.9999	1.982
6	<i>n</i> -Pentane		5.0000	0.679
7	Components eluted between <i>n</i> -pentane and 2-methylpentane	5.0001	5.6059	0.952
8	2- and 3-methylpentane and components eluting between 2 and 3-methylpentane	5.6060	5.7920	0.866
9	Components eluted between 3-methylpentane and <i>n</i> -hexane	5.7921	5.9999	0.959
10	<i>n</i> -Hexane		6.0000	0.209
11	Components eluted between <i>n</i> -hexane and benzene	6.00001	6.4419	0.949
12	Benzene	6.4420	6.4620	1.052
13	Components eluted between benzene and 2-methylhexane	6.4621	6.6029	1.136
14	2- and 3-methylhexane and components eluting between 2- and 3-methylhexane	6.6030	6.7160	0.800
15	Components eluted between 3-methylhexane and <i>n</i> -heptane	6.7161	6.9999	0.978
16	<i>n</i> -Heptane		7.0000	-0.478
17	Components eluted between <i>n</i> -heptane and toluene	7.0001	7.5299	0.623
18	Toluene	7.53	7.5600	1.139
19	Components eluted between toluene and 2-methylheptane	7.5601	7.6219	1.151
20	2- and 3-methylheptane and components eluting between 2- and 3-methylheptane	7.6220	7.7150	0.817
21	Components eluted between 3-methylheptane and <i>n</i> -octane	7.5151	7.9999	1.097
22	<i>n</i> -Octane		8.0000	0.105
23	Components eluted between <i>n</i> -octane and ethylbenzene	8.00001	8.4769	0.961
24	Ethylbenzene	8.4770	8.4970	1.226
25	Components eluted between ethylbenzene and <i>p</i> -xylene	8.4971	8.5759	0.454
26	<i>p</i> -Xylene plus <i>m</i> -xylene	8.5760	8.6115	1.020
27	Components eluted between <i>m</i> -xylene and <i>o</i> -xylene	8.6116	8.8069	0.733
28	<i>o</i> -Xylene	8.8070	8.8270	1.236
29	Components eluted after <i>o</i> -xylene up to and including <i>n</i> -nonane	8.8271	9.0000	0.350
30	Components eluted between <i>n</i> -nonane and <i>n</i> -decane	9.0001	9.9999	1.120
31	<i>n</i> -Decane and components eluted after <i>n</i> -decane	10.000	20.0000	0.856

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:          :  C4  C4  C5  C6  C7  C8  C9  C10  C11  >C11  TOTAL
:  ****
: n-ALKANES :  0.00  .03  .75  1.30  .55  .11  .02  .00  0.00  .00  2.76
:
: ISOALKANES :  0.00  0.00  .80  3.02  2.09  .49  .07  0.00  0.00  0.00  6.47
:
: NAPHTENES  :  0.00  0.00  0.00  .32  .23  .11  .00  0.00  0.00  0.00  .66
:
: AROMATICS  :  0.00  0.00  0.00  8.88  29.47  33.18  14.25  1.58  .12  .19  87.66
:
: OLEFINS    :  0.00  .00  .17  .42  .30  .10  .05  0.00  0.00  0.00  1.05
:
: UNKNOWN    :  .00  0.00  0.00  0.00  .00  0.00  .00  .19  .02  .56  .78
:  ****
: OCTANE NUMBER              105.80
:
    
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Fig. 3. Simplified report of reformat sample for RON determinations.

Dispersion of the data points increases for RON values around 105. Since the RON calculation from GC analysis has the same repeatability in the 90–105 RON range, the dispersion of the points is probably caused by the RON engine measurements. Indeed the ASTM method gives a reproducibility of about 0.7 RON unit for the

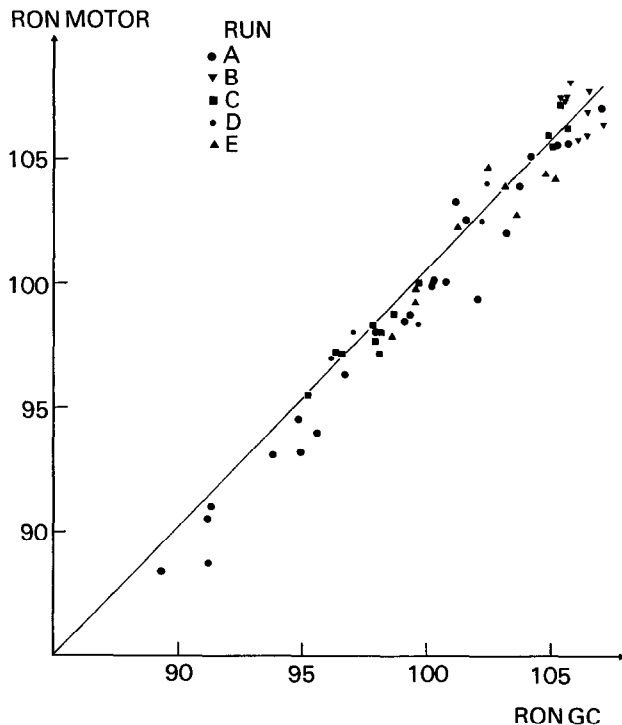


Fig. 4. Graphic representation of the correlation measured RON values versus calculated RON values.

90–100 range. This value increases to about 2 RON units for the 105–110 range. Under these conditions, rigorous mathematical linearization is quite difficult because the reproducibility of the two compared methods is too different. However, simple linearization by the least squares method led to corrections of calculated RON values which are less than or equal to 1 RON unit. Consequently, for reformer samples the RON value calculated from GC analysis is considered to give the RON value measured by the engine, without any correction. Compared to the engine procedure which is time-consuming and requires expensive and bulky apparatus and large sample volume (250 ml), the GC measurement of RON values appears to be a rapid, flexible, and inexpensive and the method is easy to use with complete automation. Moreover, it gives a detailed analysis of the product.

CONCLUSION

With a reproducible-identification method based on programmed temperature indices obtained on commercial columns having the same characteristics, the identification of gasoline compounds can be automated the data handling system can be used in the laboratory or for process control. The method can be used in routine analysis for all different types of gasoline without any operator intervention.

Because of the reliability of this automatic identification method, it has been optimized for the analysis of reformer samples and extended to the automatic determination of research octane-numbers. The repeatability is about 0.1–0.2 RON units. The reproducibility is about 0.3 RON unit in the whole range of RON values (90–110). Comparisons with the engine ASTM method were made for about 60 samples. The difference in RON values, calculated from GC analysis and measured by the engine method, turns out to be less than 1 RON unit in most cases. Reforming process control may be improved by the use of this method with on-line automated gas chromatography.

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