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ON-LINE GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBON EFFLUENTS

CALIBRATION FACTORS AND THEIR CORRELATION

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SUMMARY

A flexible gas chromatographic hydrocarbon analysis train has been calibrated for off-line analysis of petroleum fractions and for on-line analysis of a thermal cracking effluent. Special attention was paid to the calibration factors of hydrocarbons on flame ionization detectors. Correlations for these calibration factors that have been presented in the literature, together with those introduced in this paper, are tested against the experimental data for their adequacy and parameter significance.

INTRODUCTION

For the study of the thermal cracking of hydrocarbons ranging from ethane up to gas oil, the Laboratorium voor Petrochemische Techniek designed and built a flexible and highly automated pilot plant[1]. It is equipped with an analysis train that permits on-line analysis of the reactor effluent, ranging from hydrogen to C_{30} hydrocarbons[2]. Off-line analysis of petroleum fractions is also possible. The on-line analysis is entirely based on the internal standard technique. Nitrogen is injected into the reactor effluent and serves as an internal standard. A special hot-gas sampling device allows for the analysis of the complete reactor effluent without any previous condensation[2,3].

Calibration for C_4^- components has been current practice[2]. For most C_5^+ components, mass response factors on flame ionization detectors do not differ much, and it has been suggested that calibration is superfluous[4–7]. This approximation is no longer justified: to obtain the required precision in the characterization of the reactor effluent or feed, it was found necessary to perform a complete calibration of the gas chromatographs. In the present paper, calibration for C_5^+ components is discussed in detail. In particular, an experimental method for linking the C_5^+ calibration to the internal standard is presented.

Refining and petrochemical process feedstocks and effluents are often very

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complex hydrocarbon mixtures, containing a few hundreds of components. It is impossible to determine calibration factors for all of them. Therefore, it is important to devise correlations for the flame ionization detection (FID) calibration factors. A number of correlations that have been presented in literature are tested and a new type of correlation is introduced.

GAS CHROMATOGRAPHIC ANALYSIS

Sampling system

Fig. 1 shows a schematic view of the reactor outlet and of the sampling system. The reactor outlet pressure is controlled by means of a restriction valve (1). The nitrogen that is used as internal standard is injected into the effluent gas stream at the reactor outlet (2) to ensure efficient mixing. It also contributes to cooling and diluting the effluent. The nitrogen flow-rate is controlled by means of a thermal mass flow meter-controller with an accuracy exceeding 0.5%. A hot gas sample[2,3] of the full effluent is taken at 350–400°C, depending on flow-rates and reactor outlet temperature. The hot sampling device consists of two high temperature injection valves (3), kept at 300°C in an oven (4). Each sampling valve is preceded by a shut-off valve (5), kept at 350°C in a separate section of the oven. The temperature upstream of the shut-off valves is kept high to prevent condensation of high-molecular-weight products. The valves (5) are opened for only a short time just before injection to reduce fouling of the sampling valves (3). Between injections, the sampling valves can be

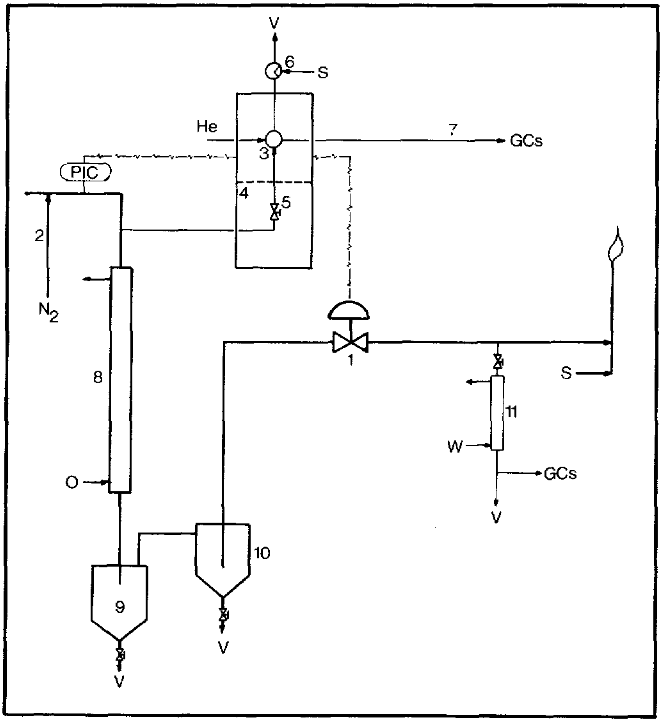

Fig. 1. Reactor outlet and sampling system. O = oil, S = steam, V = vent, W = water.

flushed with steam (6). From the sampling valves, the sample is led to the C_5^+ gas chromatographs for separation through stainless-steel capillary transfer lines (7). Internal coating with OV-1 prevents adsorption of the aromatic species on the stainless-steel piping. The temperature of these lines is limited to 275°C to prevent deterioration of the coating.

The reactor effluent is cooled to *ca.* 150°C in an oil cooler (8). Condensed hydrocarbons and coke particles are removed in a liquid separator (9) and a cyclone (10). The effluent then flows through traced piping to a flare, where it is burned. A fraction of the product stream is withdrawn for on-line analysis of the C_4^- fraction. The C_4^- fraction is analysed after removal of water and pyrolysis gasoline in a water cooler (11) at 45°C.

C_4^- *Analysis*

The C_4^- sample is analysed on two gas chromatographic (GC) systems simultaneously. Only hydrogen is not detected twice. The use of two different units for the same analysis improves the reliability of the results.

The first system is a set of three Packard 417 gas chromatographs, which perform an analysis designed at the Laboratorium voor Petrochemische Techniek[2]. The operating conditions for the three chromatographs are listed in Table I. All three instruments are equipped with precolumns to allow backflushing of higher boiling products. C_4^- chromatograms are shown in Fig. 2. The first chromatograph determines the nitrogen, carbon monoxide and methane contents of the product stream; C_2 and heavier components are backflushed. Methane is used as a secondary standard, because nitrogen cannot be detected by FID. The second chromatograph separates nitrogen and carbon monoxide, methane, carbon dioxide, ethene and ethane after backflush of C_3^+; all C_3 and C_4 saturates, mono-olefins, di-olefins and acetylenes are separated on the third chromatograph.

The second system consists of a Carle CGC 530 automated refinery gas analyser. This multicolumn instrument, equipped with eight columns and five switching valves, performs a similar analysis. The carrier gas is helium. Nitrogen, carbon monoxide, carbon dioxide and hydrocarbons up to C_2 are detected by thermal conductivity detection (TCD), C_3 and C_4 by FID. This chromatograph is also equipped

TABLE I

OPERATING CONDITIONS FOR THE PACKARD 417 CHROMATOGRAPHS

	Packard 417 GC1	*Packard 417 GC2*	*Packard 417 GC3*
Precolumn	Porapak N 1.0 m, 1/8 in.	Porapak N 1.0 m, 1/8 in.	Durapack *n*-octane 0.65 m, 1/4 in.
Analysis column	Carbosphere 1.8 m, 1/8 in.	Porapak N 6.0 m, 1/8 in.	17% Sebaconitrile on Chromosorb P-AW 10.0 m, 1/4 in.
Oven temp. (°C)	50	35	20
Carrier gas (ml/min)	H_2 (20)	H_2 (30)	N_2 (35)
Detection	TCD	TCD	FID

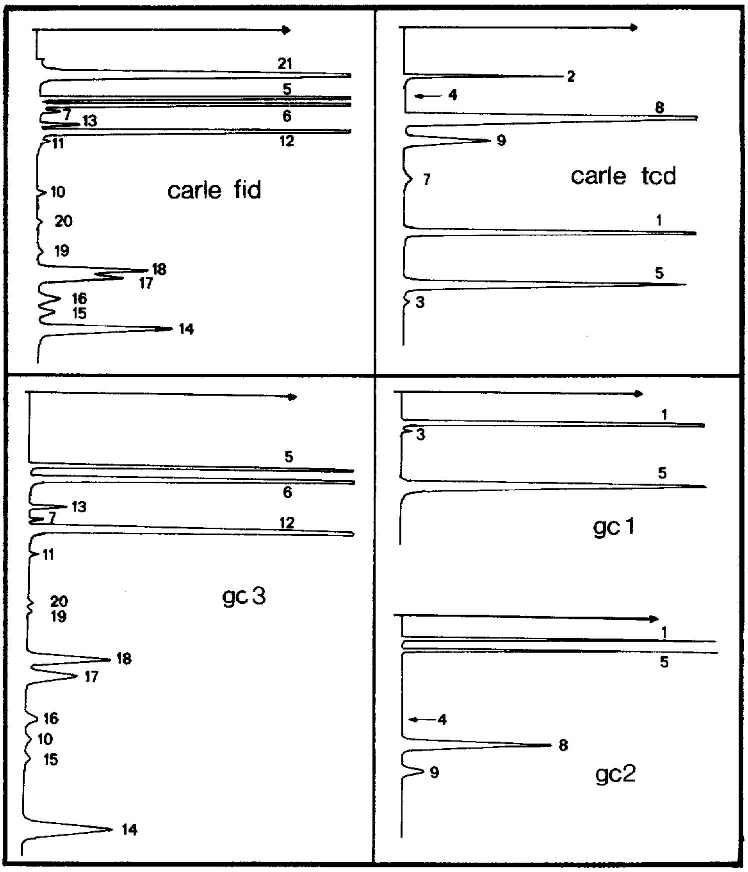

Fig. 2. C_4^- chromatograms. Peaks: 1 = N_2; 2 = H_2; 3 = CO; 4 = CO_2; 5 = CH_4; 6 = sumC_2; 7 = C_2H_2; 8 = C_2H_4; 9 = C_2H_6; 10 = C_3H_4(MA); 11 = C_3H_4(PD); 12 = C_3H_6; 13 = C_3H_8; 14 = 1,3-C_4H_6; 15 = *cis*-2-C_4H_8; 16 = *trans*-2-C_4H_8; 17 = *i*-C_4H_8; 18 = 1-C_4H_8; 19 = *n*-C_4H_{10}; 20 = *i*-C_4H_{10}; 21 = C_5^+ backflush.

with a hydrogen transfer system, a palladium tube that allows migration of hydrogen from helium into nitrogen carrier gas. In nitrogen, the hydrogen is easily detected by TCD.

$C_5{}^+$ Analysis

The C_4^- analysis takes 32 min on the Carle and 38 min on GC3. Since a C_5^+ analysis lasts more than 90 min, two C_5^+ chromatographs (Packard 428 and Packard 437A) are used in alternate operation. Each has two columns, inserted in the same injection port, and two flame ionization detectors. Both columns are fused-silica capillaries (30 m × 0.32 mm I.D.) and coated with DB1-30W (polymethylsiloxane). The only difference between them is the thickness of the coating: 0.25 μm for one and 5.0 μm for the other. The temperature is kept at -20°C for 1 min and is then programmed to 250°C at 3°C/min.

Fig. 3 shows chromatograms obtained from one of the two C_5^+ chromato-

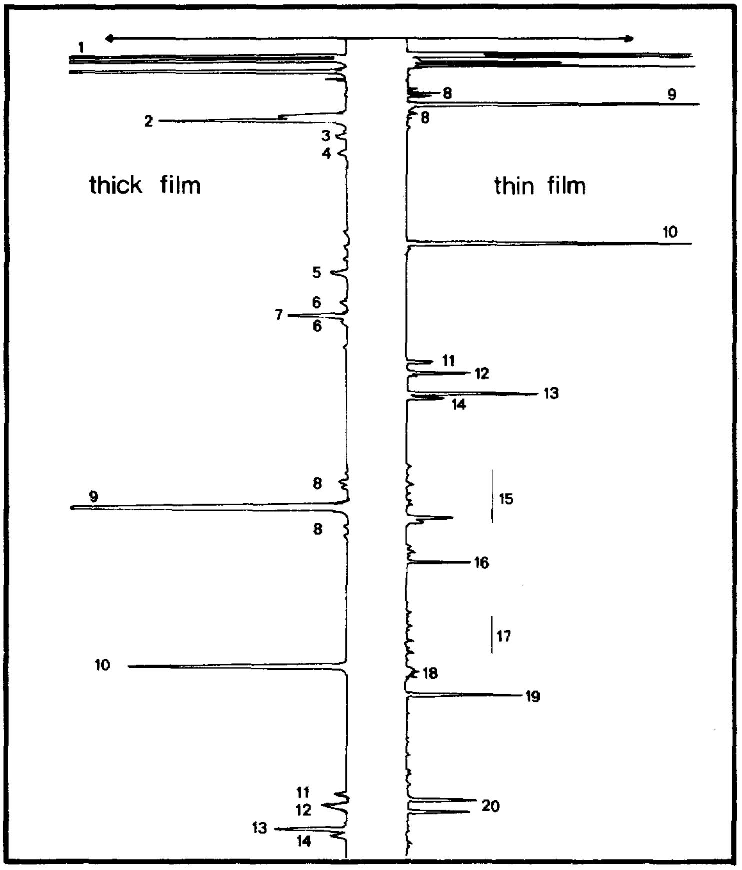

Fig. 3. C_5^+ chromatograms. Peaks: 1 = CH_4; 2 = 1,3-C_4H_6; 3 = *trans*-2-C_4H_8; 4 = *cis*-2-C_4H_8; 5 = isoprene; 6 = 1,3-pentadienes; 7 = 1,3-cyclopentadiene; 8 = methylcyclopentadienes and cyclohexadienes; 9 = benzene; 10 = toluene; 11 = ethylbenzene; 12 = *para*- and *meta*-xylene; 13 = styrene; 14 = *ortho*-xylene; 15 = C_9 aromatics and indane; 16 = indene; 17 = C_{10} aromatics; 18 = methylindenes; 19 = naphthalene; 20 = methylnaphthalenes.

graphs. On the thick-film column, methane is separated from ethene and ethane. It is used as a secondary standard for calculation of the yields of C_5 and C_6 components. This column, however, does not achieve a sufficient resolution in the higher boiling point range. Therefore, benzene is used as a tertiary standard for the analysis of C_6 to C_{30} hydrocarbons on the thin-film column.

Data treatment

A Data General S140 real-time process computer controls reactor temperatures and feed flow-rates, switches GC injection and backflush valves and acquires and digitizes GC outputs. Peak areas are computed by an integration and peak detection program. Both C_4^- and C_5^+ peaks are identified on-line, and a full report containing kinetic data and the product distribution is generated.

Calculations are based on the absolute flow-rates of the effluent components.

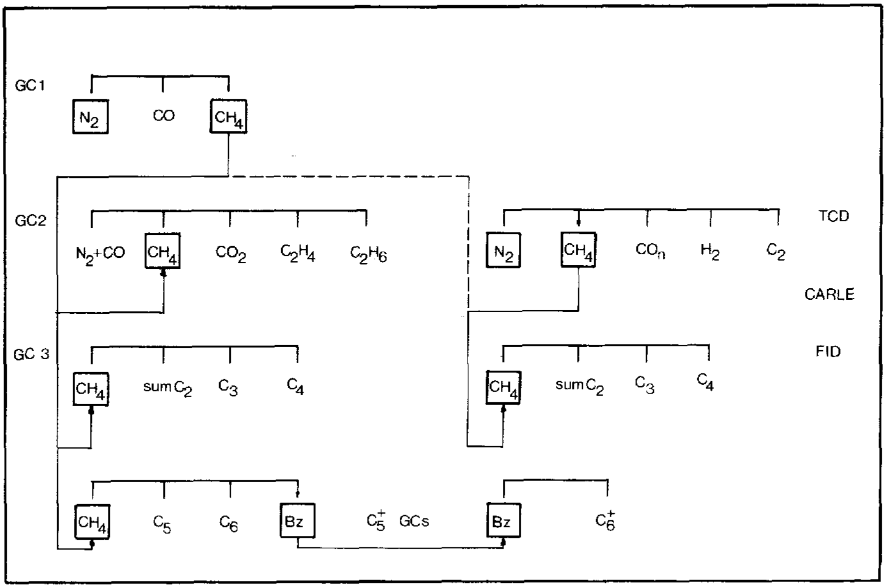

Fig. 4. Calculation procedure for the product yields.

This is made possible by the injection of a precisely known nitrogen flow at the reactor exit. The use of reference components is illustrated in Fig. 4. From the peak areas of the Packard GC1, the experimentally determined calibration factors on this instrument and the known amount of nitrogen, the flows of methane and carbon monoxide are calculated. Using the methane flow thus calculated, the flows of ethane, ethene and carbon dioxide are calculated from the data of GC2. The methane peak is used, because nitrogen and carbon monoxide are not always separated on GC2. The remaining C_4^- components are referred to methane on GC3, because nitrogen is not detected by FID. The results on the Carle can be calculated in two ways: by referring either to the known nitrogen flow or to the methane flow determined on GC1. The C_5^+ results of the thick film column are calculated in the same way as the results of GC3. Then benzene is used as a standard to calculate the flows of the components analysed on the thin-film column.

With these data, a product distribution in terms of weight percentages can be determined. As the feed flow-rate is known, yields (kilograms of product per kilogram of hydrocarbon fed) and a material balance can also be calculated. By way of example, the calibrated analysis of an effluent of the thermal cracking of an atmospheric gas oil is given in Table II. The total material balance and the agreement between the two C_4^- analyses are excellent.

RESULTS

Since the above calculations are based on mass flows, weight calibration factors are preferred to molar calibration or response factors. A calibration factor (CF) is the number by which the peak area (PA) has to be multiplied to obtain a measure

TABLE II

EFFLUENT ANALYSIS REPORT

Yields in weight percent.

Packard	N_2	10.417			
417	CO	0.124			
GC1	CH_4	11.472			
			0.623	H_2	Carle TCD
Packard	N_2 + CO	10.726	10.416	N_2	Carle TCD
417		–	0.103	CO	
GC2	CH_4	11.472	11.472	CH_4	
	CO_2	0.000	0.000	CO_2	
	C_2H_4	21.933	21.874	C_2H_4	
	C_2H_6	3.325	3.406	C_2H_6	
Packard	CH_4	11.472	11.472	CH_4	Carle FID
417	sumC_2	24.914	25.078	sumC_2	
GC3	C_3H_8	0.398	0.375	C_3H_8	
	C_2H_2	0.257	0.270	C_2H_2	
	C_3H_6	12.285	12.352	C_3H_6	
	i-C_4H_{10}	0.024	0.028	i-C_4H_{10}	
	n-C_4H_{10}	0.046	0.042	n-C_4H_{10}	
	C_3H_4(PD)	0.184	0.192	C_3H_4(PD)	
	1-C_4H_8	0.868	0.842	1-C_4H_8	
	i-C_4H_8	1.550	1.568	i-C_4H_8	
	t-2-C_4H_8	0.306	0.297	t-2-C_4H_8	
	C_3H_4(MA)	0.219	0.231	C_3H_4(MA)	
	c-2-C_4H_8	0.086	0.075	c-2-C_4H_8	
	C_4H_6	4.125	4.119	C_4H_6	
	C_4^-	57.624	57.869	C_4^-	
C_5^+ from thick-film column, up to benzene:				16.06	
of which: isoprene:				1.11	
1,3-cyclopentadiene:				2.13	
benzene:				9.63	
C_5^+ from thin-film column, up to naphthalene:				11.86	
of which: toluene:				4.84	
ethylbenzene:				0.31	
xylenes:				1.20	
styrene:				1.09	
C_5^+ higher than naphthalene, pyrolysis fuel oil:				14.02	
Total material balance		99.56	99.81		

for the weight flow or weight percentage (wt) of the component *i*:

$$\mathrm{wt}(i) = \frac{\mathrm{CF}(i) \cdot \mathrm{PA}(i)}{\mathrm{CF(ref)} \cdot \mathrm{PA(ref)}} \cdot \mathrm{wt(ref)}$$

The CF of the reference component is chosen to be unity. Methane is the reference for the calibration factors on all detectors, except for the flame ionization detectors of the thin-film columns, on which CFs are referred to benzene. Thus, the CF is:

$$\mathrm{CF}(i) = \frac{\mathrm{PA(ref)} \cdot \mathrm{wt}(i)}{\mathrm{PA}(i) \cdot \mathrm{wt(ref)}} \tag{1}$$

This CF is the reciprocal of the relative weight response factor (RWR). Taking into account the molecular weights (MW) of *i* and (ref), the relative molar response factor (RMR) is easily derived:

$$\mathrm{RMR}(i) = \frac{\mathrm{MW}(i)}{\mathrm{MW(ref)}} \cdot \frac{1}{\mathrm{CF}(i)} \tag{2}$$

For on-line analyses, three sets of calibration factors are needed. The set of C_4^- calibration factors and the set of calibration factors for the thick-film columns are referred to methane. The C_5^+ calibration factors on the thin-film columns are referred to benzene. For off-line injections of hydrocarbon mixtures, such as naphtha or gas oil, internally consistent sets of C_5^+ calibration factors are also needed, in particular on the thin-film columns.

C_4^- Calibration

For C_4^- calibrations, certified standards containing up to nineteen components in concentrations as close as possible to the expected effluent composition, were pur-

TABLE III

C_4^- CALIBRATION FACTORS

Packard	N_2	1.460			
417	CO	1.520			
GC1	CH_4	1.000			
			0.295	H_2	Carle TCD
Packard	N_2 + CO	1.450	1.390	N_2	Carle TCD
417		–	1.400	CO	
GC2	CH_4	1.000	1.000	CH_4	
	CO_2	1.875	1.881	CO_2	
	C_2H_4	1.290	1.225	C_2H_4	
	C_2H_6	1.330	1.215	C_2H_6	
Packard	CH_4	1.000	1.000	CH_4	Carle FID
417	sumC_2	0.934	0.868	sumC_2	
GC3	C_3H_8	0.899	0.826	C_3H_8	
	C_2H_2	0.792	0.446	C_2H_2	
	C_3H_6	0.937	0.862	C_3H_6	
	i-C_4H_{10}	0.815	0.834	i-C_4H_{10}	
	n-C_4H_{10}	0.917	0.790	n-C_4H_{10}	
	C_3H_4(PD)	0.847	0.548	C_3H_4(PD)	
	1-C_4H_8	0.929	0.853	1-C_4H_8	
	i-C_4H_8	0.947	0.818	i-C_4H_8	
	t-2-C_4H_8	0.981	0.835	t-2-C_4H_8	
	C_3H_4(MA)	1.050	0.812	C_3H_4(MA)	
	c-2-C_4H_8	1.022	0.847	c-2-C_4H_8	
	C_4H_6	0.929	0.831	C_4H_6	

chased from Matheson. Consistence of CFs in time was checked. Standards with widely different compositions are available for flame ionization detector and electrometer linearity checks. CFs on a linear flame ionization detector are constant over a wide concentration range. Unfortunately, "linear" detectors are often linear only in a log–log plot of response *versus* concentration, with a slope that is not necessarily equal to one[8]. This results in variations of the CF with the concentration in the sample of the component concerned. This has been observed for some C_3 and C_4 hydrocarbons on the flame ionization detectors of the Packard GC3 and the Carle. It was noticed that the slope in the log–log diagram can be brought closer to unity by increasing the ratio of hydrogen to air in the detector flame. In Table III, a set of C_4^- calibration factors is listed. These results are compared with expected values derived from literature data and prediction methods as a test for GC tuning and accuracy of the standards. Correlations are less accurate for predicting the calibration factors for methane and highly unsaturated light hydrocarbons, such as ethyne[9,10] and propadiene.

C_5^+ Calibration

The C_5^+ calibration was performed in two steps. First, a set of C_5^+ CFs is determined for each detector by syringe injection of liquid calibration mixtures. They are referred to benzene. Then, the CF of benzene referred to methane on the thick-film columns was determined by means of on-line injection of methane–benzene mixtures. This method is preferred to the on-line determination of all C_5^+ calibration factors, because it is less sensitive to fractionation of the sample.

In order not to introduce uncertainties exceeding the GC reproducibility in the composition of the liquid calibration mixtures, extreme care is required in their preparation. Therefore, only products with a purity higher than 99% were used. All of them were analysed quantitatively (GC–FID) and qualitatively (GC–MS), to check for possible cross-contamination of components by impurities in other products. Some 25 hydrocarbons with widely varying molecular weights and structures were mixed on a digital balance, starting with the higher boiling products. The components of the calibration mixtures were also chosen in order to achieve a baseline-to-baseline separation of all peaks. Several mixtures with different compositions were prepared to check for detector non-linearity and for bias of the results by errors in the mixture composition. For syringe injection, some of the mixtures were diluted with a highly volatile solvent that does not disturb the analysis, such as pentane or acetone. The solvent is added to ensure a fast and complete evaporation of the mixture in the GC injector, to improve separation and to reduce inlet splitter influence to a minimum. The composition of one of the mixtures is given in Table IV.

For the determination of the calibration factors of C_5^+ referred to benzene, 0.1 μl of the calibration mixtures was injected with a Hamilton 1.0-μl syringe. When an internal standard is used, an exact reproduction of the injected amount is not required. In Table IV, experimental values of the CFs, averaged over five injections, are listed. No significant changes in CFs were noticed for the different calibration mixtures. The discussion below is based on the set of CFs given in Table IV, the conclusions being the same, whatever set, including C_4^-, is used. Typical values of CFs are 1.15 for paraffins and 1.12 for naphthenes. The CFs of aromatics range from 1.00 for benzene up to values that are typical of aliphatic compounds as the number

TABLE IV

CALIBRATION MIXTURE COMPOSITION AND C_5^+ CALIBRATION FACTORS

Component	*wt.%*	*CF*
n-Hexane	3.747	1.151
n-Heptane	4.154	1.151
n-Octane	4.402	1.130
n-Decane	3.798	1.148
n-Dodecane	3.980	1.145
n-Hexadecane	4.080	1.146
2,2-Dimethylbutane	3.956	1.182
2,3-Dimethylbutane	5.172	1.167
2,2,4-Trimethylpentane	2.687	1.131
1-Hexene	4.227	1.182
1-Octene	4.940	1.147
Cyclohexene	3.674	1.069
Methylcyclopentane	2.652	1.142
Cyclohexane	3.457	1.123
Methylcyclohexane	5.938	1.115
Decalin	4.026	1.127
Benzene	4.700	1.000
Toluene	3.697	1.019
Ethylbenzene	3.945	1.043
meta-Xylene	2.981	1.051
ortho-Xylene	4.460	1.045
ortho-Ethyltoluene	4.076	1.074
para-Diisopropylbenzene	4.874	1.146
Tetralin	3.372	1.078
Naphthalene	1.676	1.063
Biphenyl	1.309	1.021

of carbon atoms in the side-chains increases. Table IV clearly demonstrates that when CFs are not applied in the analysis of petroleum fractions, the aromatics content is overestimated. In naphtha analysis for instance, relative errors of 9–12% are typical, depending on the average molecular weight and composition. For mixtures with higher aromatics content, such as reformates or extracts, the relative error is smaller, but the absolute error on the aromatics content reaches a maximum of 2 to 3 percentage points for fractions containing 50% aromatics, as encountered in pyrolysis gasoline.

The on-line determination of the CF of benzene with respect to methane is much more complicated from the experimental point of view. The methane and benzene concentrations in the sample loop have to be reduced to an appropriate level, corresponding approximately to the expected effluent composition. Therefore, the sample is diluted with steam and hydrocarbon gases. The internal standard, nitrogen, is added as well to check the methane flow-rate on the C_4^- chromatographs. All gas flows are controlled by means of thermal mass flow controllers; liquids are fed from balances and their flow-rates are controlled by the process computer. Water and benzene are evaporated separately in the furnace and are mixed with the hydrocarbon gases in the gas phase. To obtain reproducible results, the system is rigorously maintained at constant conditions. This means, in particular, that pulsations of the feed pumps for benzene and water should be absent or have a period that is at least one order smaller than the residence time of the products in the whole system. The reactor is kept at a temperature that is sufficiently high to prevent condensation, without causing thermal decomposition of the hydrocarbons, however. A temperature of 300–350°C at the reactor outlet was found to be appropriate. The CF of benzene with respect to methane differs significantly from one: 0.716 on the one instrument and 0.856 on the other. Along with the values listed in Tables III and IV, this illustrates the necessity of using CFs in quantitative FID analyses, even for hydrocarbons. CFs for C_2^+ components follow similar patterns on different, but decently operated flame ionization detectors. This rule does not apply to methane, as is clearly illustrated by the values in Table III.

Correlations

A number of correlations for RMRs or CFs on flame ionization detectors have been presented in the literature. In this paper, a new type of correlation is introduced. All of the correlations are then confronted with the experimental data of Table IV. Model discrimination, based on the statistical *F*- and *t*-tests, allows for the selection of the best correlation.

A first set of correlations is based on the observation that a flame ionization detector is essentially a carbon atom counter[9,11]. RMRs of hydrocarbons are approximately proportional to the number of carbon atoms in the component detected. In terms of calibration factors, this can be expressed as (*viz.* eqn. 2):

$$\frac{\mathrm{MW}(i)}{\mathrm{CF}(i)} = AN_\mathrm{C} \qquad \text{(correlation I)}$$

where N_C is the number of carbon atoms in the molecule *i*.

It was soon recognized that some dependence on the hydrocarbon structure has to be accounted for, and effective carbon number contributions were introduced[12]:

$$\frac{\mathrm{MW}(i)}{\mathrm{CF}(i)} = AN_{\mathrm{C,aliphatic}} + BN_{\mathrm{C,olefinic}} + CN_{\mathrm{C,aromatic}} \qquad \text{(correlation II)}$$

This method was further developed for oxygenated compounds[13,14]. For hydrocarbons, all contributions were found to be approximately equal[12]. From the present data, it is clear that this is not true. It has also been suggested that the relative weight response is proportional to the weight percent of carbon in the molecule[7]. This method is equivalent to correlation I, however:

$$\mathrm{RWR}(i) = [\mathrm{CF}(i)]^{-1} = A' \frac{12N_\mathrm{C}}{\mathrm{MW}(i)} = A \frac{N_\mathrm{C}}{\mathrm{MW}(i)}$$

It can also be investigated whether hydrogen atoms contribute to the RMR:

$$\frac{\mathrm{MW}(i)}{\mathrm{CF}(i)} = AN_\mathrm{C} + BN_\mathrm{H} \qquad \text{(correlation III)}$$

A different type of correlation was proposed by Bulewicz[10], who suggested that the RMR is proportional to the standard enthalpy change $(-\Delta H^0)_{\mathrm{ox}}(\mathrm{H_2})$ at 298 K of the hypothetical combustion reaction

$$\mathrm{C}_n\mathrm{H}_m + n\mathrm{O}_2 \rightarrow n\mathrm{CO}_2 + m/2\ \mathrm{H}_2$$

$$\frac{\mathrm{MW}(i)}{\mathrm{CF}(i)} = A(-\Delta H^0)_{\mathrm{ox}}(\mathrm{H_2}) \qquad \text{(correlation IV)}$$

The value of this model as an attempt to explain the mechanism of ion formation in the flame has been questioned[15–17]. Nevertheless, this kind of approach may be of some practical use.

Below, a new type of correlation, based on the standard Gibbs energy change $(-\Delta G^0)_{\mathrm{ox}}$[18] at 298 K of the complete oxidation reaction to carbon dioxide and water, is introduced. It is based on the observation that the molar FID responses of homologous series of organic compounds are straight lines when plotted against the carbon number, the slope being the response of a single methylene group[10,19]. In other words:

$$\mathrm{PA}(i) = (a + bN_\mathrm{C}) \cdot \mathrm{mol}(i) \qquad (3)$$

For hydrocarbons, the parameter a is a small number, since their responses are nearly proportional to N_C. For paraffins for instance, the parameter a is twice the difference in response between a methyl and a methylene group; for aromatics, it is six times the difference in response between an aromatic carbon atom and a methylene group. The contribution for a methylene group, b, is constant for all homologous series and depends solely on detector construction and operation.

In weight units, eqn. 3 becomes:

$$\mathrm{PA}(i) = (a + bN_\mathrm{C})/(c + dN_\mathrm{C}) \cdot \mathrm{wt}(i) \qquad (4)$$

with $(c + dN_\mathrm{C}) = \mathrm{MW}(i)$ and $d = 14$, the molecular weight of a methylene group. The parameter c depends on the type of hydrocarbon, but it is relatively small. From eqn. 4 and the definition of the calibration factor (eqn. 1):

$$\mathrm{CF}(i) = k(c + dN_\mathrm{C})/(a + bN_\mathrm{C}) \qquad (5)$$

For a homologous series, the standard Gibbs energy of formation[18] can be expressed as

$$\Delta G^0_{\mathrm{f,HC}} = u + vN_\mathrm{C}$$

with v again the constant contribution of a methylene group. Hence, the standard Gibbs energy change of the combustion reaction

$$C_nH_m + (n + m/4)O_2 \rightarrow nCO_2 + m/2\ H_2O$$

is

$$\begin{aligned}(-\Delta G^0)_{ox} &= -[N_C \Delta G^0_{f,CO2} + (2N_C + c)/2 \cdot \Delta G^0_{f,H_2O} - \Delta G^0_{f,HC}] \\ &= e + fN_C\end{aligned}$$

or

$$N_C = [(-\Delta G^0)_{ox} - e]/f \tag{6}$$

The parameter f is the contribution of a methylene group to the standard Gibbs energy change of the combustion reaction and is independent of the nature of the hydrocarbon. Substituting eqn. 6 into eqn. 5 yields

$$\mathrm{CF}(i) = k\,\frac{(fc - de) + d(-\Delta G^0)_{ox}}{(fa - be) + b(-\Delta G^0)_{ox}} \tag{7}$$

$(-\Delta G^0)_{ox}$ covers a wide range of values (linear in N_C), while all CFs lie within a limited range. To estimate the parameters more conveniently, eqn. 7 is multiplied by the molecular weight of the component:

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = k\,\frac{[(fc - de) + d(-\Delta G^0)_{ox}]^2}{(fa - be) + b(-\Delta G^0)_{ox}} \tag{8}$$

or

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = A[B + (-\Delta G^0)_{ox}]^2/[C + (-\Delta G^0)_{ox}] \qquad \text{(correlation V)}$$

Simplification of eqn. 8 is possible, since both CFs and $(-\Delta G^0)_{ox}/\mathrm{MW}(i)$ are approximately constant within a homologous series. Hence,

$$\mathrm{CF}(i) = \frac{c + dN_C}{a + bN_C} = k_1 \quad \text{and} \quad \frac{(-\Delta G^0)_{ox}}{\mathrm{MW}(i)} = \frac{e + fN_C}{c + dN_C} = k_2$$

for all N_C, and in particular for $N_C = 0$ and $N_C = \infty$:

$$c/a = d/b = k_1 \tag{9a}$$

and

$$e/c = f/d = k_2 \tag{9b}$$

From eqns. 9a and 9b, it follows that, with sufficient approximation

$$fa - be = 0 \tag{10a}$$

and

$$fc - de = 0 \tag{10b}$$

Using eqns. 10a and 10b, the dependence on the nature of the hydrocarbon, which appears in eqn. 8 through a, c and e, can be eliminated; eqn. 8 then becomes:

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = kd^2/b(-\Delta G^0)_{\mathrm{ox}} = A(-\Delta G^0)_{\mathrm{ox}} \qquad \text{(correlation VI)}$$

From this basic correlation, two further ones are derived. First, it is investigated whether $(-\Delta G^0)_{\mathrm{ox}}$ can be substituted by $(-\Delta H^0)_{\mathrm{ox}}$, the lower heat of combustion, which may be more accessible than the standard Gibbs energy values, so that

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = A(-\Delta H^0)_{\mathrm{ox}} \qquad \text{(correlation VII)}$$

As a further simplification, $(-\Delta G^0)_{\mathrm{ox}}$ is expanded into a linear combination of the number of carbon and hydrogen atoms in the molecule:

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = AN_{\mathrm{C}} + BN_{\mathrm{H}} \qquad \text{(correlation VIII)}$$

Correlations II and VI can be expanded into group contribution methods, as is done for the estimation of thermodynamic properties[20]. In the present case, ten contributions are considered. They are listed in Table V. The following ways of calculating calibration factors by means of group contributions (a_j) are investigated:

$$\mathrm{CF}(i) = \sum_j n_{j,i} a_j \qquad \text{(correlation IX)}$$

TABLE V

GROUP CONTRIBUTIONS

1	CH_3	Methyl group in an aliphatic chain
2	CH_2	Methylene group in an aliphatic chain
3	CH	Tertiary carbon atom in an aliphatic chain
4	C	Quaternary carbon atom in an aliphatic chain
5	(5)	Additional contribution for a 5-membered naphthenic ring
6	(6)	Additional contribution for a 6-membered naphthenic ring
7	C_{aro}–H	Aromatic carbon atom, connected to a hydrogen atom
8	C_{aro}–C	Aromatic carbon atom, connected to another carbon atom
9	$C{=}H_2$	Olefinic carbon atom, connected to two hydrogen atoms
10	C=CH	Olefinic carbon atom, connected to a hydrogen and a carbon atom

TABLE VI

RELATIONS BETWEEN THE DIFFERENT CORRELATIONS

Correlation numbers are given in brackets.

	Basic correlation	*Derived correlations*			*Derived group contributions*
MW(i)/CF(i) as a function of contributions for types of carbon atom	N_C (I)	N_C, N_H (III)	*ECNC* (II)		$\sum_j n_{j,i}a_j$ (XI)
MW(i)/CF(i) as a function of the heat of reaction of a partial combustion	$(-\Delta H^0)_{ox}(H_2)$ (IV)				
CF(i) as a function of contributions for types of carbon atom					$\sum_j n_{j,i}a_j$ (IX)
CF(i) · MW(i) as a function of the Gibbs energy change of the complete combustion	$(-\Delta G^0)_{ox}$ (VI)	$(-\Delta H^0)_{ox}$ (VII)	N_C, N_H (VIII)	$(-\Delta G^0)_{ox}$ (V)	$\sum_j n_{j,i}a_j$ (X)

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = \sum_j n_{j,i}a_j \qquad \text{(correlation X)}$$

$$\mathrm{MW}(i)/\mathrm{CF}(i) = \sum_j n_{j,i}a_j \qquad \text{(correlation XI)}$$

Correlation XI is nothing but an extended effective carbon number contribution method, while correlation X is an extension of correlation VI. The different correlations are interrelated as is shown in Table VI. The number of parameters and the amount of calibration effort required increase from left to right. The quality of the fit can be expected to follow the same trend. The preferred type of correlation, a group contribution method or one of the other correlations, depends on the specific requirements of each analysis problem. In the next section, the most appropriate correlations for calculating hydrocarbon calibration factors on a flame-ionization detector are selected on the basis of a detailed statistical check.

DISCUSSION

The parameters in the different correlations were estimated by minimizing the following sum of squares:

$$\sum_{i=1}^{k} \sum_{j=1}^{n_i} [\mathrm{CF}(i)_j - \hat{\mathrm{C}}\mathrm{F}(i)]^2$$

where k is the total number of components in the mixture and n_i the number of replicate experiments for component i. $\hat{\mathrm{C}}\mathrm{F}(i)$ is the predicted value of the calibration factor. For parameter estimation in the non-linear correlation V, a Marquardt minimization routine was used.

The discrimination between the different correlations (I–XI) is based on rigorous statistical testing.

First, model adequacy is tested by means of the lack-of-fit F-test[21]. This F-test can be used when replicate experiments are available. The total residual sum of squares is broken down into the pure-error sum of squares, which arises from experimental scatter, and the lack of fit sum of squares, which is caused by model inadequacy. The pure-error sum of squares is given by

$$\sum_{i=1}^{k} \sum_{j=1}^{ni} [\mathrm{CF}(i)_j - \overline{\mathrm{CF}(i)}]^2$$

in which $\overline{\mathrm{CF}(i)}$ is the average experimental value of the calibration factor for component i. This sum of squares has

$$\sum_{i=1}^{k} (n_i - 1) = \sum_{i=1}^{k} n_i - k$$

degrees of freedom. The lack-of-fit sum of squares is obtained from the total sum of squares by substraction of the pure-error sum of squares. The F-value is calculated from

$$F_{\mathrm{calc}} = \frac{\text{lack-of-fit sum of squares/[total degrees of freedom} - (\Sigma n_i - k)]}{\text{pure error sum of squares/}(\Sigma n_i - k)}$$

The calculated F-value is compared with the tabulated 95% value of the F-distribution. If the calculated F-value is above the significance level, in other words, exceeds the tabulated one, there is a probability of 95% that the correlation is inadequate. It is then rejected because of lack of fit.

In a second step, the parameters are tested for significance. The actual parameter estimates are compared to zero, and the significance of the difference is tested on the t-distribution. Parameters that are not significantly different from zero at the 95% level are deleted. An inspection of the significance of the parameters is an additional tool in the discrimination between the rival correlations.

Among the resulting correlations, the one offering the best fit with the smallest number of significant parameters is finally selected. A distinction is made between group contribution methods (correlations IX to XI) and the other correlations (I to VIII), since they exhibit a different degree of complexity and may have different areas of application. Group contribution methods are more appropriate for high precision measurements, while the more simplified correlations, which are less demanding in calibration effort, can be used for automated routine analyses.

The results of the parameter estimation and of the statistical tests are given in Table VII.

TABLE VII

PARAMETER ESTIMATION AND RESULTS OF STATISTICAL TESTS

Correlation	*Parameter estimates 95% confidence limits*	*t-values*	*Lack-of-fit F-value*	*Average % error*
I	$A = 12.46 \pm 0.16$	155.0	0.5344	1.694
II	$A = 12.43 \pm 0.21$	121.6		
	$B = 11.97 \pm 1.31$	18.21	0.3642	1.234
	$C = 12.83 \pm 0.39$	65.32		
III	$A = 12.79 \pm 0.63$	40.75	0.5015	1.603
	$B = -0.180 \pm 0.324$	−1.112		
IV	$A = 7.272 \pm 0.106$	137.8	1.8399	3.402
V	$A = 0.1045 \pm 0.0169$	12.36		
	$B = 2.07 \pm 20540$	0.00	0.2628	1.134
	$C = -3.07 \pm 40700$	0.00		
VI	$A = 0.1052 \pm 0.0013$	161.9	0.2375	1.128
VII	$A = 0.1068 \pm 0.0016$	158.0	0.4479	1.482
VIII	$A = 11.01 \pm 0.70$	31.75	0.5108	1.614
	$B = 2.418 \pm 0.378$			
IX	$(CH_3) = 0.580 \pm 0.030$	38.84		
	$(CH_2) = -0.002 \pm 0.008$	−0.49		
	$(CH) = -0.583 \pm 0.062$	−19.01		
	$(C) = -1.163 \pm 0.111$	−21.06		
	$(5) = 1.151 \pm 0.186$	26.89	0.2955	0.888
	$(6) = 1.130 \pm 0.069$	32.76		
	$(C_{aro}\text{–}H) = 0.167 \pm 0.009$	38.38		
	$(C_{aro}\text{–}C) = -0.385 \pm 0.039$	−19.56		
	$(C{=}H_2) = 0.618 \pm 0.061$	20.36		
	$(C{=}CH) = -0.027 \pm 0.040$	−1.34		
X	$(CH_3) = 18.59 \pm 3.48$	10.66		
	$(CH_2) = 15.62 \pm 1.16$	26.92		
	$(CH) = 12.70 \pm 8.93$	3.66		
	$(C) = 10.23 \pm 12.55$	1.63		
	$(5) = 2.33 \pm 9.38$	0.50	0.1857	0.695
	$(6) = 0.52 \pm 8.65$	0.12		
	$(C_{aro}\text{–}H) = 12.99 \pm 0.71$	36.23		
	$(C_{aro}\text{–}C) = 11.31 \pm 4.19$	5.41		
	$(C{=}H_2) = 20.86 \pm 6.03$	6.93		
	$(C{=}CH) = 12.43 \pm 3.56$	6.98		
XI	$(CH_3) = 12.06 \pm 2.68$	8.98		
	$(CH_2) = 12.60 \pm 0.91$	27.74		
	$(CH) = 13.11 \pm 5.32$	4.92		
	$(C) = 13.26 \pm 9.58$	2.77		
	$(5) = -1.85 \pm 7.24$	−0.51	0.1838	0.697
	$(6) = -0.44 \pm 6.74$	−0.13		
	$(C_{aro}\text{–}H) = 13.05 \pm 0.71$	36.46		
	$(C_{aro}\text{–}C) = 12.26 \pm 3.51$	6.99		
	$(C{=}H_2) = 8.43 \pm 4.68$	3.60		
	$(C{=}CH) = 13.42 \pm 2.98$	9.04		

Correlation IV, in which the RMR is taken to be proportional to the heat of reaction of the oxidation of the hydrocarbon into carbon dioxide and hydrogen[10], is the only one to be rejected because of lack of fit. It has a very pronounced tendency to overestimate the calibration factors for saturates, and to underestimate those for aromatic hydrocarbons. Since the correlation is inadequate for hydrocarbons, it is not likely to be valid for oxygenated compounds[10].

A number of other correlations can be eliminated on the basis of the non-significance of some of the parameters, as revealed by their small t-values. This is the case for correlations III and V. In correlation III, the contribution of hydrogen atoms to the RMR of hydrocarbons appears to be non-significant. The correlation is reduced to correlation I by eliminating this parameter:

$$\frac{\mathrm{MW}(i)}{\mathrm{CF}(i)} = AN_{\mathrm{C}} + BN_{\mathrm{H}} = AN_{\mathrm{C}}$$

by eliminating the parameter B.

In the same way, correlation V turns into correlation VI:

$$\mathrm{CF}(i) \cdot \mathrm{MW}(i) = A\,\frac{[B + (-\Delta G^0)_{\mathrm{ox}}]^2}{[C + (-\Delta G^0)_{\mathrm{ox}}]} = A(-\Delta G^0)_{\mathrm{ox}}$$

by eliminating the parameters B and C.

In the group contribution methods X and XI, the number of contributions can be reduced by two, since the presence of a naphthenic ring apparently does not affect the response of an aliphatic carbon atom.

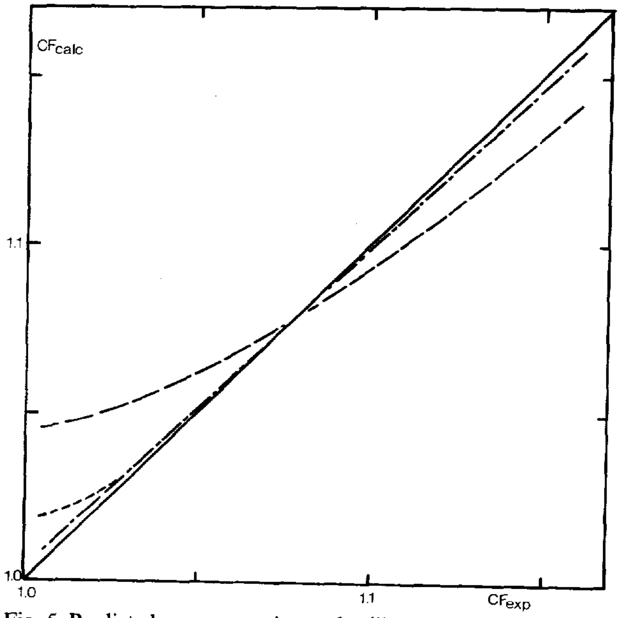

Fig. 5. Predicted *versus* experimental calibration factors. — —, Correlations I and VII; ----, Correlations II, VI and VIII; — · —, Correlations IX, X and XI.

As far as the group contribution methods are concerned, the best fit is obtained with correlations X and XI.

Further discrimination between these two is impossible. Since these correlations are derived from others that are already adequate (correlations VI and II, respectively) simply by adding parameters, intercorrelation between the parameters is high. This leads to extremely wide confidence intervals for the parameter estimates, as can be seen in Table VII. On the other hand, group contribution methods allow the closest prediction of CFs, as is evident from the average percentage error in Table VII and from Fig. 5. This figure also reveals that some of the remaining simplified correlations (I and VII) show a tendency to overestimate the CFs for aromatics. Correlation I (RMR proportional to N_C) is clearly an oversimplification. Since one of the main goals of calibrating is to arrive at an accurate ratio of saturates to aromatics, these correlations are discarded in favour of the correlations II (effective carbon number contributions), VI [$(-\Delta G^0)_{ox}$] and VIII (extension of VI). From the three resulting ones, correlation VI turns out to be the most efficient, combining a good fit with the lowest possible number of parameters.

CONCLUSIONS

It has been demonstrated that, in a reliable and precise analysis of complex hydrocarbon mixtures, calibration of detectors (flame ionization as well as thermal conductivity) is an absolute necessity. Calibration is even more necessary if heavier compounds are to be referred to a low-molecular-weight standard. It is not necessary to determine CFs for all the hydrocarbons analysed, as CFs on flame ionization detectors can be correlated. A new correlation, based on $(-\Delta G^0)_{ox}$ at 298K, has been presented and turns out to be very efficient. The use of detailed structural group contribution methods allows a very accurate prediction of CFs on flame ionization detectors from a limited number of calibration experiments.

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