

QUANTITATIVE ANALYSIS OF AROMATIC HYDROCARBONS IN COMPLEX HYDROCARBON MIXTURES BY HIGH RESOLUTION CAPILLARY GAS CHROMATOGRAPHY

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Received October 13, 1997

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1. Introduction

Natural and synthetic hydrocarbon mixtures are complex samples containing hundreds of different aliphatic and aromatic components in widely differing concentrations. The number of components depends on a group-type composition and the range and distribution of boiling points of the components present in the mixture^{1,2}.

Hydrocarbon mixtures are characterised in two ways, by structural group analysis and boiling range determination (by distillation³ or gas-chromatographically simulated distillation⁴). The principal techniques employed for determining the content of paraffins, naphthenes, and aromatic compounds are mass spectrometry (MS)⁵, high performance liquid chromatography (HPLC)⁶⁻⁸, and capillary-column gas chromatography⁹⁻¹³.

Whereas the accuracy of MS methods for PNA (paraffin, naphthene, aromatic) determination has been shown to be sufficient for most applications, the technique does not provide information about individual components. The quantitative results obtained by HPLC are not always acceptable because of the variation of response factors for the given hydrocarbon in the sample matrix of various hydrocarbons. The HPLC technique also lacks the capacity to furnish carbon number distribution and component identification.

High resolution capillary gas chromatography (HRCGC) is the most useful general method for the analysis of complex hydrocarbon mixtures with the ultimate aim of complete component analysis. The disadvantage of this method is that every peak must be identified, or at least classified, according to the chemical group to which it belongs. Peak identification in a chromatogram is performed on the basis of retention data and the information from gas chromatography coupled with mass spectrometry (GC-MS)⁹⁻¹⁹.

Quantitation in the capillary GC by flame ionisation detection (FID) is more accurate than other techniques. The particular advantage of GC analysis is that the quantitative response of the FID is approximately the same for equal weights of any hydrocarbon, so that, to a first approximation, relative peak areas can be used directly for the determination of weight percent values^{9,10}.

Aromatic hydrocarbons are an important constituent of various petroleum products and a detailed information on their composition in feed materials, intermediates, and commercial products is required for process development and quality control programs. Low molecular weight alkylbenzenes (C₇-C₁₅) represent the whole or main part of the monoaromatic fraction which has been most frequently studied in hydrocarbon mixtures. The identification and determination of aromatic compounds is also important in environmental analysis and geochemistry.

Aromatic hydrocarbons in hydrocarbon samples may generally be analysed directly by HRGC, under isothermal and/or temperature-programmed conditions, on a single column or by multidimensional GC (ref.¹⁷). The concentrates of aromatic compounds from liquid chromatography fractions can be successfully analysed using a single column containing a stationary phase of polarity suitable for obtaining the optimum resolution of the compound of interest. The author shows in review papers¹⁷⁻¹⁹, that the detailed analysis (separation, identification, and quantitation) of individual aromatic hydrocarbons in hydrocarbon mixtures has been most frequently performed with single columns. Highly efficient non-polar phases are applied when information is required about all components of the mixture. Moderately polar or highly polar stationary phases have been employed for the estimation of aromatic com-

pounds in the presence of C₁-C₁₂ saturated hydrocarbons, which elute very rapidly under either isothermal or temperature-programmed conditions. When the sample is very complex, polar columns are unable to separate aromatics from the other hydrocarbon groups. A usual approach to such analysis has been either the fractionation into narrower cuts and the subsequent analysis of the cuts on different columns, or the pre-separation of aromatics from other hydrocarbons followed by the analysis on a suitable highly efficient non-polar column.

2. Response factors

Determination of concentration and mass of individual compounds in samples separated by HRGC is based on the measurements of areas and/or heights of peaks (in the dependence on the used method of quantitative analysis). As the dependence of areas or heights on concentration (for concentration detectors), or on mass (for mass detectors), is not known, it is necessary to find it by calibration which, however, requires pure standards. In regard to the great number of compounds which can be analysed by gas chromatography, only a small percentage of compounds is available in pure state. If pure components are not available, the published data could be utilised for the calibration of detectors.

Hydrocarbon mixtures have been detected by FID (ref.⁹⁻²⁸). The quantitative evaluation of a gas chromatogram is generally based on the assumption that the relative response of the individual hydrocarbons on an equal weight basis is the same when using a FID. Thus, area per cent values may be taken directly as concentrations in weight per cent.

In the early sixties a number of researchers investigated the problem of the FID response for hydrocarbons²⁰. These studies have shown the general validity of this rule for the majority of compounds assuming that their carbon atom number does not vary greatly. For example, according to the data of Durrett et al.²¹, if the response of n-heptane is taken as 1.00, then there is a $\pm 4\%$ variation in the C₅-C₁₀ range of paraffins and cycloparaffins. Generally, aromatics follow the same rule, the variation being within $\pm 4\%$, except for benzene and toluene.

According to the literature sources, the detector response factors can be calculated in different ways. In the first way, the response factor (f_i) is equal to the peak area for unit of mass or concentration (this is, according to the definition, the sensitivity of detector) :

$$f_i = A_i/m_i(c_i) \quad (1)$$

where m_i is the mass (c_i the concentration) of the compound of interest in the sample and A_i is the corresponding peak area. The mass, or concentration of an unknown mixture is calculated by dividing the individual peak area by the corresponding response factor (sensitivity), resulting in the corrected peak area. After normalisation of these values, the area per cent values for hydrocarbons obtained with FID are taken as weight per cents.

The second way of the calculation of response factors is the calculation of mass (concentration) for unit peak area, i.e. the reciprocal value of the equation (2):

$$f_i = m_i(c_i)/A_i \quad (2)$$

In this case, the corrected peak area is obtained by multiplying the original area by the response factor. Most data systems operate in this second mode, whereas most of the early works utilised the first mode (the sensitivity).

For the studies of the relative responses of a detector, it is most convenient to express the response factor relative to the response factor of a selected compound. According to the second way of calculation, the relative response factor (RRF_i) can be calculated as:

$$RRF_i = \frac{m_i(c_i)/A_i}{m_{st}(c_{st})/A_{st}} = \frac{A_{st}}{A_i} \cdot \frac{m_i(c_i)}{m_{st}(c_{st})} \quad (3)$$

where A_{st} is the peak area and $m_{st}(c_{st})$ is the mass (concentration) of the compound selected as a reference standard material. (As FID is the mass detector, masses have been utilised in the calculations.) This equation is based on the factor equal to 1.00 for referent compounds, according to the definition. On this base, the numerical value of a compound is the mass of a compound necessary to give the same response (area) as the reference compound. The reciprocal value of relative response factor is the relative sensitivity of FID (which can be also utilised as the response factor, where the peak area is necessary to divide by response factor). As it is defined in equation (3), the $RRF_i > 1$ means that the detector is less sensitive to the searched compounds compared to the reference standard and, therefore, the obtained peak area has to be multiplied by the higher number as 1, resulting in the same area per mass unit for the compound i and for the reference standard material.

Table I
Published relative response factors RRF_i of aromatic hydrocarbons

Alkyl	RRF_i Alkylbenzenes (Alkyl Be)			
	ref. ^{22,a}	ref. ^{20,b}	ref. ^{23,c}	ref. ²⁶
H	0.893	-	-	0.92
Me	0.935	0.893	-	0.93
Et	0.971	0.926	0.870	0.94
1,4-Me ₂	1.000	0.924	-	0.94
1,3-Me ₂	0.962	-	-	0.94
1,2-Me ₂	0.980	-	1.000	0.94
1-Me-2-Et	0.980	-	-	-
1-Me-3-Et	0.990	-	-	-
1-Me-4-Et	1.000	-	-	-
1,2,3-Me ₃	1.020	-	-	-
1,2,4-Me ₃	1.031	-	1.072	-
1,3,5-Me ₃	1.020	-	-	-
i-Pr	1.031	-	0.864	-
n-Pr	0.990	-	-	-
1-Me-2-i-Pr	1.010	-	-	-
1-Me-3-i-Pr	0.990	-	-	-
1-Me-4-i-Pr	1.010	-	-	-
s-Bu	1.000	-	-	-
t-Bu	0.980	-	-	-
n-Bu	1.020	-	-	-

RRF_i Polyaromatic Hydrocarbons		
	ref. ^{24,d}	ref. ^{25,e}
Naphthalene	1.047	0.921
2-Me-naphthalene	1.068	-
2,6-diMe-naphthalene	1.078	-

^a Relative to n-pentane (Pe), ^b relative to 2,2,4-TriMePe, ^c relative to 1,2-dimethylbenzene, ^d relative to n-C₁₄, ^e relative to n-alkane

In Table I, there are summarised RRF_i values of aromatic compounds from the literature^{20,22-25} published within the period of 21 years. It follows that the relative response factors of aromatic compounds for the majority of searched compounds are close to 1. We have determined the response factors of aromatic hydrocarbons at trace level concentrations. The results relative to n-C₁₄ are presented in Table II. The numerical values of response factors for the

same compounds published by different authors are not in the full agreement, owing to the difference in the purity of the used standard, reference material selected, injection system, and concentration level as measured by capillary GC (ref.^{20-23,26}).

Table II
Response factors of aromatic hydrocarbons relative to n-C₁₄

Compound ^a	RRF_i	RSD [%] ^b
Isopropylbenzene	1.022	4.11
Propylbenzene	0.986	3.45
1,3,5-Trimethylbenzene	1.002	3.19
1,2,4-Trimethylbenzene	0.986	4.97
Indane	0.977	3.78
Indene	1.003	3.89
n-Butylbenzene	1.006	3.97
2,2-Dimethylpropylbenzene	0.980	2.35
1,2,4,5-Tetramethylbenzene	1.074	3.82
n-Pentylbenzene	1.005	3.78
1,3-Dimethyl-5-tert.butylbenzene	0.960	2.50
Phenylcyclohexane	1.003	3.79
2,6-Dimethylnaphthalene	1.057	3.50
2,3-Dimethylnaphthalene	1.049	2.29
Hexamethylbenzene	1.099	3.82
Acenaphthene	1.042	4.12
Fluorene	1.006	4.37

^a Injected amount in splitless injection: 15 ng; n = 3; ^b relative standard deviation, other abbreviations as in Table I

3. Methods of quantitative analysis

In the published papers connected with the quantitative analysis, the determination of aromatic hydrocarbons was performed at various concentration levels after previous compound identification or group type analysis²⁷:

- in multicomponent hydrocarbon mixtures (a) after separation of hydrocarbons on column with non-polar stationary phase^{11,12} and (b) after separation of other hydrocarbon groups on column with a polar stationary phase and resolution of individual aromatic hydrocarbons^{11,12};
- in aromatic fractions after column LC at trace level concentration^{16,26}.

The most common method used in the analysis of hydrocarbon mixtures using FID has been the "area per cent technique". The accuracy is the higher, the more similar are the hydrocarbons in the mixture and the narrower is their boiling-point range. A disadvantage of this method is the necessity to elute all mixture components. In the paper¹¹, we compared various approaches to the peaks area evaluation of the constituents of a gasoline fraction of crude oil after their separation on a highly efficient squalane capillary column under isothermal conditions. The quantitation of 238 constituents was performed, whose concentration was in the range of 0.005-8 %. The problems connected with peaks coelutions under isothermal and temperature-programmed conditions were shown^{11,12}. The best resolution of compounds was obtained under isothermal conditions. Economical demands, however, require a shorter analysis and, therefore, temperature programming is preferred to isothermal operations because narrow peaks are normally obtained throughout the chromatogram and compounds with a wide range of boiling points can be chromatographed in a single run, which is essential for the analysis of complex hydrocarbon mixtures^{9,10,12-15,17,19}. The most of hydrocarbons exhibit a change in retention relative to the normal hydrocarbons as elution temperature is changed. The practical result is that the relative elution times and even elution orders can change under different chromatographic conditions causing problems with compound identification and quantitation. Using the temperature programming, coelution occurs more frequently compared to the isothermal conditions, making quantitative as well as qualitative analysis more complicated. The number of unresolved peaks and time of analysis are highly dependent on the used temperature-program conditions often comprising a multi step program incorporating both isothermal and programmed periods^{10,13,17,27}. It is evident that, for the sufficient separation of components and for the preceding group analysis, it is necessary to optimise the experimental conditions, such as column length (efficiency), film thickness, temperature gradient, time of analysis, etc, with respect to the number of resolved peaks. It influences the precision and the reproducibility of the results of quantitative analysis.

A disadvantage of "the area per cent technique" 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 peaks area may be loaded with a large systematic error. To determine the correct content of compounds we introduced "the modified standard addition method"¹¹.

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. Both methods are based on the assumption that the relative mass responses of hydrocarbons are nearly constant for the series of hydrocarbons. In contrast to the standard addition method, "the modified standard addition method" does not require a precise and reproducible injection. The results obtained by "the modified standard addition method" showed unambiguously that the sum of components determined by "the area per cent technique" did not include fairly high per cent of constituents (e.g. in gasoline > 5 %; (ref.¹¹)). In the analysis of individual aromatic hydrocarbons on polar stationary phases TCEP11 and SP-2340 (ref.¹²), a very good agreement of results was obtained with the results of quantitative analysis on non-polar stationary phase.

Possibilities and difficulties of trace analysis of complex organic mixtures has been demonstrated by the analysis of traces of numerous aromatic hydrocarbons in an n-alkane matrix with boiling point range of 151-270 °C. Much attention was given to the evaluation of the pre-separation process of aromatics, which was performed by an off-line LC pre-separation step, and the reproducibility of compounds resolution by HRGC on HP PONA column^{16,17}. The gas chromatographic quantitation of 191 identified aromatic compounds was performed by an internal standard method. Percentage by weight of individual aromatic compounds (mainly alkylbenzenes, indanes, naphthalenes, and acenaphthenes) was in the range 10⁻³ to 10⁻⁶. The precision and reproducibility were studied both for the GC determination and overall analysis, including pre-separation¹⁷. Relative standard deviations of the GC determination of the individual aromatic compounds, which represent errors of the GC measurements and integration, were found to be in the range 3-6 % in most cases. Extremely high values (up to 30 %) were found for poorly resolved peaks, small peaks, and pairs of compounds which, in some analyses, were integrated as individual peaks and in other analyses were integrated as one peak.

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E. Matisová (*Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Bratislava, Slovak Republic*): **Quantitative Analysis of Aromatic Hydrocarbons in Complex Hydrocarbon Mixtures by High Resolution Capillary GC**

The scope of the principal techniques employed for the quantitative analysis of hydrocarbons in complex mixtures is discussed with the emphasis on the analysis of one- and two-ring aromatic compounds by single column capillary gas chromatography. The questions related to the analysis of complex hydrocarbon samples are outlined. The paper considers quantitative evaluation of a gas chromatogram when analysing a hydrocarbon mixture with a flame ionisation detector (FID). Response factors and methods of quantitative analysis are discussed in detail.