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Gas chromatography with atomic emission detection: a method for the determination of hydrocarbon mixture components

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The possibility of the determination of the elemental composition and concentrations of unknown hydrocarbon components in a mixture without performing calibration per each mixture component was shown using gas chromatography with atomic emission detection.

The most perspective features of gas chromatography with atomic emission detection (GC-AED) are the possibilities for elemental ratio determination and for quantitative analysis without calibration per each mixture component.[1,2] Earlier, we have shown that, under commonly used AED conditions, the carbon-to-hydrogen response ratios were strongly dependent on the compound structure and content in a mixture, and we have found the AED conditions for the minimization of this dependence.[3–5] Moreover, the accuracy of quantitative analysis without a calibration for the known compounds under these conditions was also higher than that under commonly used conditions.[6] Such conditions were provided by the use of maximal oxygen content in helium plasma of AED (~10%).

There was no method for the determination of unknown components of complex hydrocarbon mixtures without a calibration per each mixture component and for the determination of their elemental composition with high accuracy. However, such a method could be especially useful for meeting many important challenges in petroleum processing and petrochemistry, when the standard samples or the structures of compounds to be determined are not available, or the number of components is so high that calibration becomes unrealistic. The conventional use of a flame ionization detector leads to the inaccuracies of hydrocarbon content determination higher than 10%, which is unacceptable for the solution of such problems.

This work was aimed at the examination of the potential of GC-AED for the determination of the elemental composition of unknown hydrocarbon mixture components and their quantitation in the absence of the respective reference samples using the condition found, which provided the decrease of AED carbon and hydrogen response dependence on the component structures and concentrations in the respective mixtures. For this purpose, we used the following precisely prepared model mixture of hydrocarbons in hexane:[†]

– undecane ($C_{11}H_{24}$): 3.32×10^{-8} g μl^{-1};
– dodecane ($C_{12}H_{26}$): 2.75×10^{-8} g μl^{-1};
– tridecane ($C_{13}H_{28}$): 1.03×10^{-7} g μl^{-1};
– tetradecane ($C_{14}H_{30}$): 1.57×10^{-7} g μl^{-1};
– hexadecane ($C_{16}H_{34}$): 9.40×10^{-8} g μl^{-1}.

For the determination of n_C/n_H and m_C values (where n_C/n_H is a ratio of carbon and hydrogen atom numbers in a molecule of a mixture component and m_C is a quantity of carbon (g), respective to the AED response at carbon channel for this component) by GC-AED the common approaches were applied, which were described elsewhere.[1-6] The key point of these approaches is the comparison of the mixture component peak areas at C and H emission channels with the respective peak areas of one reference compound for all mixture components. In this case, we used not only the commonly used content of oxygen reagent gas in helium (about 1%), but also a found value (about 10%), providing the lowest AED C and H response dependence on compound structure[3,4] and concentration[5] in order to show a benefit of the conditions found.

The important feature of unknown hydrocarbon mixtures quantitative analysis without a calibration per each component by GC-AED is a possibility of their content per component determination (not per carbon or other element), because hydrocarbons are the only class of compounds for which the elemental composition can be found if the elemental ratios n_C/n_H are determined precisely. The calculation of the percentage of carbon in a hydrocarbon molecule can be performed using the GC-AED data and the equation:

$$w_C = \frac{12}{12 + (n_C/n_H)^{-1}}, \quad (1)$$

where w_C is a content of carbon in the molecule of hydrocarbon; n_C/n_H is an experimental ratio of the numbers of carbon and hydrogen atoms in the molecule of hydrocarbon, found on the basis of registered at C and H AED channels responses; 12 is the atomic weight of carbon.

Keeping in mind that n_C/n_H elemental ratios for different hydrocarbons are not less than 0.25 and not higher than 3, it can be seen from equation (1), that the inaccuracy of carbon content determination is weakly dependent on the inaccuracy of n_C/n_H

[†] Undecane, dodecane, tridecane, tetradecane and hexadecane were purchased from Polyscience corp. (USA). Hexane was purchased from Lecbiopharm (Moscow, Russia).

A microwave-induced plasma atomic emission detector, model G2350A (Agilent, Waldbronn, Germany) was coupled to a 6890N gas chromatograph equipped with a 7683 automatic sampler and a split–splitless capillary injection port. Chromatographic separation was performed on a 50 m×0.32 mm i.d. HP-1 (100% polydimethylsiloxane) capillary column (Agilent) with a 0.52 μm film thickness. The column was held at 60 °C for 2 min and then the temperature was increased to 250 °C (at a rate of 30 K min^{-1}), and held at this temperature for 3.2 min. Then, 1 μl sample was injected with an autosampler in a splitless mode at the injection port temperature of 250 °C. The flow rate of a carrier gas (helium) was 1.5 ml min^{-1}. The solvent venting began at 3.50 min after the sample injection and was finished at 6.50 min. The transfer line and detector cavity were operated at 250 °C. Carbon and hydrogen were detected at 496 and 486 nm, respectively. Helium (99.9999%), nitrogen (99.99%) and oxygen (99.999%) used by GC-AED were obtained from PromGasService (Moscow, Russia).

Table 1 Carbon content in the molecules of 'unknown' hydrocarbons, calculated on the basis of experimental n_C/n_H values (n = 3).

Oxygen content in helium (AED plasma)	Compound	n_C/n_H			Carbon content (%) in the molecule of a hydrocarbon			
		True	Calculated	Δ (%)[a]	True	Calculated	s_r	Δ (%)[a]
1% (common value)	$C_{11}H_{24}$	0.4583	0.4603	0.4	84.61	84.67	0.0001	0.07
	$C_{12}H_{26}$	0.4615	reference		84.72		reference	
	$C_{13}H_{28}$	0.4643	0.4809	3.6	84.77	85.23	0.0008	0.5
	$C_{14}H_{30}$	0.4667	0.4998	7.1	84.86	85.71	0.0009	1.0
	$C_{16}H_{34}$	0.4706	0.4748	0.9	84.97	85.07	0.0003	0.1
10% (maximum value)	$C_{11}H_{24}$	0.4583	0.4603	0.4	84.61	84.67	0.0005	0.07
	$C_{12}H_{26}$	0.4615	reference		84.72		reference	
	$C_{13}H_{28}$	0.4643	0.4775	2.8	84.77	85.14	0.0007	0.4
	$C_{14}H_{30}$	0.4667	0.4824	3.4	84.86	85.27	0.0003	0.5
	$C_{16}H_{34}$	0.4706	0.4786	1.7	84.97	85.17	0.0007	0.2

[a]The relative inaccuracies Δ of the experimental values were determined as the difference between the experimental and true values, divided to the true value and multiplied by 100%.

ratio determination because the inaccuracy of n_C/n_H determination is << 12.

Correspondingly, the quantity m of each hydrocarbon mixture component can be calculated according to the equation:

$$m = m_C/w_C, \quad (2)$$

where m_C is the respective quantity of carbon, found by GC-AED.

In order to study the possibility of the carbon percentage determination in the molecules of hydrocarbons with the use of n_C/n_H elemental ratios and the possibility of determination of the unknown hydrocarbon mixture component contents using carbon percentages in their molecules, we employed a model mixture of hydrocarbons (the composition of this mixture is given above). For the components of this mixture we determined experimentally the percentages of carbon in their molecules using n_C/n_H ratios and then, on the basis of the respective carbon percentages, we calculated the content of each mixture component. The results of carbon percentage determination in the molecules of hydrocarbons, present in the model mixture, and the respective concentrations of these hydrocarbons, which were calculated using the carbon percentage data, are given in Tables 1 and 2.

As seen in Table 1, the application of experimental n_C/n_H ratios and helium plasma enriched in oxygen allows one to determine the carbon percentages in the molecules of 'unknown' hydrocarbons with a high accuracy, in spite of the much higher n_C/n_H ratios determination inaccuracies obtained. In this case, the accuracy of carbon percentage determination in the molecules of hydrocarbon mixture components was comparable to the specified accuracy of carbon percentage determination by modern elemental analyzers when analyzing individual compounds of high purity.

Table 2 Concentrations of hydrocarbon mixture components determined without a calibration per each component on the basis of experimental w_C(%) values (n = 3).

Oxygen content in helium (AED plasma)	Compound	Hydrocarbon concentration/g μl^{-1}			
		True	Calculated	s_r	Δ (%)
1% (common value)	$C_{11}H_{24}$	3.32×10^{-8}	3.23×10^{-8}	0.004	–3
	$C_{12}H_{26}$	2.75×10^{-8}	reference		
	$C_{13}H_{28}$	1.03×10^{-7}	9.10×10^{-8}	0.004	–12
	$C_{14}H_{30}$	1.57×10^{-7}	1.30×10^{-7}	0.006	–17
	$C_{16}H_{34}$	9.40×10^{-8}	8.56×10^{-8}	0.007	–9
10% (maximum value)	$C_{11}H_{24}$	3.32×10^{-8}	3.23×10^{-8}	0.002	–3
	$C_{12}H_{26}$	2.75×10^{-8}	reference		
	$C_{13}H_{28}$	1.03×10^{-7}	9.89×10^{-8}	0.005	–4
	$C_{14}H_{30}$	1.57×10^{-7}	1.46×10^{-7}	0.002	–7
	$C_{16}H_{34}$	9.40×10^{-8}	9.04×10^{-8}	0.005	–4

As seen in Table 2, when using helium plasma enriched in oxygen and experimental values of carbon percentages in molecules of hydrocarbon mixture components, which were calculated on the basis of n_C/n_H determination data, it was possible to find the composition of hydrocarbon mixtures without a calibration per each mixture component with the relative inaccuracies of about 4%. At the same time, under the commonly used conditions such inaccuracies could be as high as 17%. The approach for the determination of w_C and hydrocarbon mixture content without a calibration per each mixture component by GC-AED was suggested by us for the first time.

The results of this work can be useful for the determination of qualitative and quantitative hydrocarbon mixture compositions in the absence of reference samples. The limitation of this approach from the viewpoint of component identification is that it is impossible to distinguish the isomers (especially if they also have identical retention times) by this method, as well as hydrocarbons of the same proportion of carbon and hydrogen atoms, because they have identical w_C values. In addition, it should be noted that in order to calculate all experimental values, we used peak areas rather than peak heights because at the preliminary experiments we observed that the respective inaccuracies were higher in the peak heights. Because of that, when working with the complex mixtures, it would be helpful to apply computer algorithms of overlapped peak areas determination, such as the one based on an approximation with modified Hook–Jeeves algorithm, which allows one to perform a highly accurate overlapping peaks separation on complex chromatograms and their areas measurement in the presence of baseline drift and high noise level.[7,8]

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