Determination of Elemental Composition and Quantitative Analysis without Calibration per Each Component Using Gas Chromatography with Atomic Emission Detection (essay)

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Nowadays the identification and quantitation of unknown organic compounds in their mixtures is a very challenging task. From this viewpoint gas chromatography with atomic emission detection (GC-AED) is attractive. It is especially promising for elemental ratio determination in mixture component molecules and for their content determination without calibration, when only one reference compound could be used for all mixture components, and therefore analysis time and cost would be drastically reduced. However, for these purposes it is necessary that AED elemental response factors for individual compounds were independent of compound structure, elemental composition and concentration.

In the publications dealing with elemental ratio determination or quantitative analysis without calibration by GC-AED the data are contradictory. In the most of publications it was shown that in a common case the AED response factor for the respective elements depends on the compound molecule structure, elemental composition and quantity of the component being determined. In spite of that there were some publications in which it was claimed that AED response was independent of these parameters. Nevertheless, in such works structure, elemental composition and/or concentration of a reference compound was similar to that of analytes or a small number of compounds was studied.

Only in a few publications found by us the AED conditions were not the same as the recommended by the manufacturer and commonly used. But in those works the optimization of the conditions was aimed at the maximal sensitivity. The accuracy of elemental ratio determination or quantitative analysis without calibration was not discussed. In spite of a high actuality of decreasing the AED signal dependence on compound structure, elemental composition and quantity, we did not find out any publications in which AED conditions were searched for less structure- and concentration-dependent response registration. None of publications dealt with the

study of the reagent gases content in helium influence on the accuracy of elemental ratios determination in the molecules of organic compounds.

As a result of this thesis work the modern state of the problem of AED response dependence on different parameters and the associated problems of elemental ratio determination and quantitation without calibration by GC-AED were studied. The literature data on these problems were critically reviewed. It was shown by the experiments that using the conditions recommended by the manufacturer in a common case the AED response depends on analyte structure, elemental composition and concentration, as well as on the detection conditions (gas flow rates, reagent gas composition).

For the first time it was shown by the example of a large number of different organic compounds (aliphatic and aromatic hydrocarbons, PAHs, PCBs, chlorophenols, alkylsulfides, trialkylphosphates, N-containing pesticides, etc.) using the same reference compound (aliphatic hydrocarbon) for all of them that it was possible to *minimize the AED carbon and hydrogen response dependence* on analyte structure, elemental composition and concentration when using helium plasma enriched by oxygen. In the conditions developed by us the relative error of n_C/n_H ratio determination was *ca*. 4% independently of the analyte and reference compound parameters. In the large majority of cases when knowing the n_C/n_H ratio and other elements presence in the analyte molecule it is possible to *confirm the presence of the supposed compound* in the mixture unambiguously and the respective standard of the compound being considered is not needed. When combining this information with retention indices the reliability of the mixture component identification or confirmation can be additionally increased. Moreover, the information on the n_C/n_H ratio, on different elements presence in molecule, and on the analyte molecular weight (found by GC/MS) permits *to find out the unknown mixture component brutto-formula*.

We have studied the possibilities for *target hydrocarbon mixture components content determination* without calibration by GC-AED under the conditions, recommended by the manufacturer, and in conditions, developed by us. It was shown that under the conditions, recommended by the manufacturer, the relative error of quantitative determination was 16%, and under the conditions, developed by us, it was *ca*. 4%.

We have proposed an approach for *carbon percentage calculation* in the molecules of *unknown hydrocarbon mixture components* based on their n_C/n_H ratios calculation. Using this approach and oxidative conditions developed by us it was possible to calculate carbon percentage in respective hydrocarbons with the relative error 0.5% or less. Therefore, due to a very low carbon percentage relative determination error it was possible to determine hydrocarbon quantities in their mixtures with the accuracy *ca*. 4%. Thus, we have proposed a method of *unknown hydrocarbon content determination* without the use of the respective standards. This method would be especially useful in such areas as petroleum quality control and standardization, in which the mixtures to be analyzed consist of hundreds of components with unknown structures and calibration is unrealistic because of the absence of respective standards and very high time consumption.

We have suggested a new method of *large volume injection into GC-AED* with the solvent removal outside of the analytical system and transfer of the whole concentrate by thermal desorption in a carrier gas flow into GC injection port. For this purposes we used a thermal desorption device made by us. This method provides decreasing the determination limits of GC-AED by more than 2 orders of magnitude. It extends the range of GC-AED application with regard to identification and quantitation of organic compounds traces in complex mixtures.

Besides, as a result of this work a new method of *fast screening of pharmaceuticals for counterfeits*, based on n_C/n_H ratio and content determination and heteroatoms registration in the molecule of the active component by GC-AED without the use of the respective standard, was proposed.

The results of this thesis work can be used for target and unknown mixture components identification and quantitation without the use of the respective standards of these compounds. The proposed approaches and methods can be successfully applied in different areas of chemistry, pharmacology, petrochemistry, environmental control, etc.