TECHNICAL UNIVERSITY 1782

SUMMARY OF THE THESIS THEMES

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THE RELATIONSHIP BETWEEN THE MOLECULAR STRUCTURE AND THE SIGNAL OF THE FLAME IONIZATON DETECTOR

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Introduction

Today's quantitative analytical measurement requires providing more and more accurate and reliable results. One basis of quantitative analysis is the pure standard of measurable components, with the help of which of a measuring system's sensitivity -related to the given component- can be determined. Firstly, the purchase of these standards determinant in the costs of analytical measurements, especially when one has to determine numerous components (for instance: petrol industry). On the other hand, in many cases such components have to be measured that can not be obtained as pure standards, or the preparation of which is economically disadvantageous or technically impossible. Thanks to their signal forming mechanism flame ionization detectors used in gas chromatography provide such a solution where without using pure standards determination of the sensitivity can be done by using a simple mathematical formula.

It is well known that flame ionization detector produces a signal that is proportional to the number of carbon atoms when measuring n-hydrocarbons. In a case when a measured component contains a heteroatom as well, there can be seen a signal reduction compared to the carbon number characteristic to the heteroatom. To characterise this phenomenon at first Sternberg and his colleagues introduced the definition of effective carbon number (ECN), that related to the n- hydrocarbon with the same carbon number gives the signal intensity of the molecule containing a heteroatom. The effective carbon number increment (ECN_{inc}) gives the contribution of the atoms - building up the molecule - to the intensity of the signal. By definition ECN is proportional to the relative sensitivity of the molecule related to the n-hydrocarbon, in this way it can be used in quantitative measurements. From the early days of using detectors until today many scientists had been working on featuring ECN, but

practice shows that there are still uncertainties with which ECN can not meet the requirements of today's analytics.

In my work after searching for the causes of these uncertainties, by examining them systematically I targeted a new method, which is unlikely to the previous methods suitable for counting the relative sensitivity of the molecule with less then 1 error percentage related to the measured sensitivity.

As a first step in my work, with the help of the modern measuring techniques (dedicated equipment) I have determined the contribution of 8 different heteroatoms and functional groups by using their homologous series. By broadening my measurements for components with higher carbon number (>10) I could form a picture of the signal forming characteristics of components with bigger molecule size.

Considering my own and the results of other scientists I have stated that the uncertainties of the method can be originated from two causes. On the one part, earlier attribution values were determined without considering molecule structure, on the other part, the applied conditions showed broad variety as well. In accordance with it I had pursued my studies in these two areas.

By analysing the influencing effect of molecule structure I have determined and compared the signal decreasing effect of heteroatoms at aromatic (benzene derivatives) and open chain saturated compounds without changing any other condition.

Scientists had already been studying the conditions of measurements, but only those factors that cause ECN value changes by directly changing the mechanism of signal production. In my work I have studied the factors (mode of injection, injector, column, temperature of detector, applied concentration, quality of reference substances) that cause a change in signal ratio of the measurable substance and the reference substance (n-hydrocarbons) related to each other, in this way affecting the ECN value indirectly.

Using the results of my studies I could develop a new ECN measuring method, that takes into consideration the effect of the newly developed affecting factors as well. Thus using this method without standard substance the quantity of the measurable components can be determined with less than 1% difference compared to the experimentally determinable (with using standard) value.

Theses, results

1. thesis

I have studied the ECN changes in the function of carbon number (C_3-C_{22}) in homologous series of different compounds. At bigger carbon number ranges I have established that by increasing the carbon number ECN values monotonously decreased. In case of n-alkanes and n-alcohols on the basis of the experiments that were carried out it can be stated that this decrease is probably resulted by that increasing the molecule size the mechanism, responsible for signal production is changing.

2. thesis

During studying molecules with different molecule structure I have established that apart from the content of the molecule the signal reducing effect of different heteroatoms can be influenced by the molecule structure and the quality of the bonding between the carbon chain and the heteroatom.

2.1. ECN attributions of different heteroatoms (Cl, Br, I, -OH, -NH_2, -CO, -ester) are different in aliphatic and aromatic compounds.

2.2. The ECN values of alkyl-benzenes are continuously increasing by increasing the chain length, unlikely to the normal hydrocarbons with similar size, where building in a new methylene group doesn’t change the ECN value.

2.3. ECN values of halogenated benzene derivatives is affected by the quality of the halogen atom as well. The signal decreasing effect increases towards Cl, Br, I.

2.4. ECN values of halogen substituated benzene derivatives are continuously decreasing by increasing the number of the halogen atoms bonding to the aromatic ring. The more newer and newer halogen atom builds in the bigger the signal reducing effect.

3. thesis

At systematic analysis of the effects of measurement conditions I have established that not only conditions affecting directly the signal production of the detector but also the conditions of the whole measurement- in this way the mode of injection, the injector, the column, the detector temperature, the applied concentration and the reference substance- can affect the ECN value that can be measured. Reference substance plays an outstanding part in this, because the extent of the influencing effect of other conditions is affected by the quality of the reference substance.

4. thesis

During analysing the affecting factors of effective carbon number I have established that besides the quality and quantity of heteroatoms in the molecule the molecule structure, the bonding type of the heteroatom, furthermore the measurement conditions and the chosen reference substance can affect the ECN value. The effective carbon number calculating methods that can be found in former literatures and also the used databases did not take into considerations these affecting factors, in this way they are not suitable for satisfactory accurate determinations, which could meet today's analytical requirements. Considering the variance probabilities of affecting

factors there is no possibility for establishing such databases, needed for the previously applied ECN calculating methods, that can take into considerations the effects of all factors.

5. thesis

After surveying the ECN attribution values affecting factors there was such an ECN calculating method established, with the help of which – unlikely to the former methods- one can consider all the determined factors' effect. With this new method, more accurate one than the former ones, having less than 1 error percentage, one can get such a quantitative analysis suitable even for such molecules that can not be purchased in commerce, or their preparation can not be carried out because of economical considerations or because it is technically not possible.

Though the number of standards used in analytical measurements can not be reduced with this currently developed method, it's application provides a currently unique possibility for an accurate quantitative measurement of such molecules, the determination of which is not possible in any other way.

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Publications in the field of the theses

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2. M. Kállai, J.Balla: **The Effect of Molecular Structure upon the Response of the Flame Ionization Detector**, *Chromatographia* **2002**, *56*, p. 357-360

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