

Determination of Atomic Fraction of Isotope Carbon-13 Directly in Urea, Benzophenone, Nitrobenzene, Benzoic Acid and 2-Hydroxybenzoic Acid

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Abstract

The possibility of determining atomic fractions of the isotopes of carbon directly in urea, nitrobenzene, benzophenone, benzoic acid and 2-Hydroxybenzoic acid in compounds isotopically modified by all carbon centers, as well as by one or several identical carbon centers is considered. The mass peaks of the mass spectrum that allows determining the atomic fraction of carbon isotopes are selected. The respective formulas are proposed. Until now, isotope analysis of these compounds has been carried out by converting them to carbon monoxide or dioxide, and it has been impossible to determine the atomic fraction of carbon at individual centers.

Keywords

Atomic Fraction, Isotopically Modified Centers, Monoisotopic Form, Molecular Ions, Mass Spectrometer, Mass Spectrum

1. Introduction

The scope of use of compounds isotopically modified by the isotope carbon-13 is gradually widening. The compounds isotopically modified by the carbon-13 allow for conducting a wide range of scientific research in clinical medicine, biology, chemistry and various fields of science. The compounds modified by the isotope carbon-13 allow us to study such important problems as the processes of metabolism, to determine optimal doses of medicinal preparations, metabolism of medications, and their exchange rates in various organs of humans. The scope of use of isotopically modified compounds is gradually widening that needs the

availability of relatively simple and less time-consuming methods of determination of the atomic fraction of carbon isotopes. [1]

As it is known, the compounds modified by the isotope carbon-13 for conducting the mass-spectrometric analysis are converted into the compounds “convenient” for mass-spectrometric analysis: carbon oxide or carbon dioxide. [2]

Organic compounds may be isotopically modified by one or several carbon centers. The atomic fraction of the isotope carbon-13 may differ in different carbon isotope centers. During the conversion, information about the modification centers and the atomic fraction of carbon-13 in these centers is being lost. Therefore, its average content in the whole compound is determined.

The authors of the paper [3] have proposed the mathematical model of the possibility of direct (immediate) mass-spectrometric analysis of organic compounds to be researched. In the patent [4], the possibility of its use is proposed: the method of determination of the atomic fraction of the isotope carbon-13 in methanol. [5]

The given paper considers the possibility of determination of the atomic fraction of the isotope carbon-13 directly in urea, nitrobenzene, benzophenone, benzoic acid and 2-Hydroxybenzoic acid. For each compound, it is necessary to study the mass-spectra recorded on the isotope mass spectrometer in given conditions, study possible secondary processes and determine the mechanism of formation of each fragment.

2. Experimental

The mass spectrum of urea, recorded on the isotope mass spectrometer МИ-1201, is given in Figure 1.

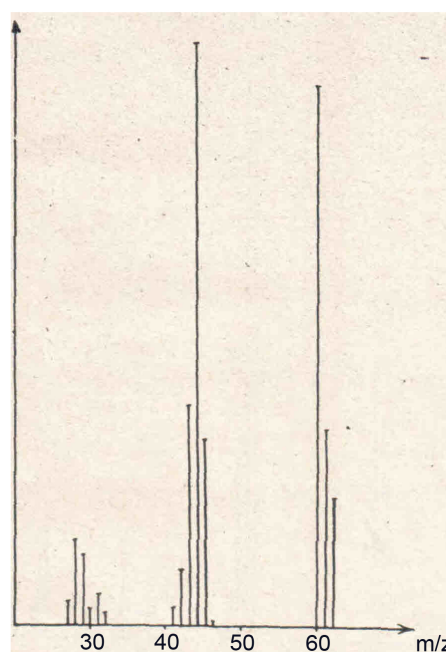


Figure 1. The mass spectrum of Urea, МИ-1201.

The sample was inserted into the mass spectrometer by means of the system for insertion in the mass spectrometer of the solid phase, invented by us [3].

As it is known, at ionization of urea by electron bombardment, the positive charge is localized primarily on one amino group that determines the character of the spectrum. The molecular ion of urea is stable, and the peak $m/z = 60$ is maximal. The ions NH_2^+ , which $m/z = 16$ and $\text{NH}_2\text{-C} = \text{O}^+$ with the mass number $m/z = 44$ are intensive. The localization of the charge on the oxygen atom is less probable. Therefore the peak of ions $m/z = 28$ (ions CO^+) is of small intensity.

Proceeding from the aforementioned, the atomic fraction of carbon isotopes may be determined by means of molecular ions, because background superposition is possible at the peak of ions $\text{NH}_2\text{-C} = \text{O}^+$. The formulas that determine the atomic fractions of carbon isotopes in percent are of the following form:

$$X^{13}\text{C}\% = \frac{1}{1 + \frac{I_{60}}{I_{61} - 0.0083I_{60}}} \cdot 100\% \quad (1)$$

whereas,

$$X^{12}\text{C}\% = \frac{\frac{I_{60}}{I_{61} - 0.0083I_{60}}}{1 + \frac{I_{60}}{I_{61} - 0.0083I_{60}}} \cdot 100\% \quad (2)$$

where I_{60} and I_{61} are the intensities of the ion peaks $m/z = 60, 61$. The numerical coefficient takes into account the natural distribution of heavy isotopes of nitrogen and hydrogen.

The samples of urea have been measured; with the natural distribution of carbon isotopes and with a certified atomic fraction of the isotope carbon-13 equal to 80.8%. The obtained results are 1.09% and 80.8%, respectively.

The mass spectrum of nitrobenzene, recorded on the isotope mass spectrometer MI-1201, is given in **Figure 2**.

As it is known, nitrobenzene has a specific mass spectrum. The maximal is the peak, obtained by elimination of the nitro group, ions (M-46) are obtained, that have the phenol-cation structure, from which by elimination of the molecule of acetylene C_4H_3^+ is produced, its mass number is 51. The ionic peak $m/z = 93$ is

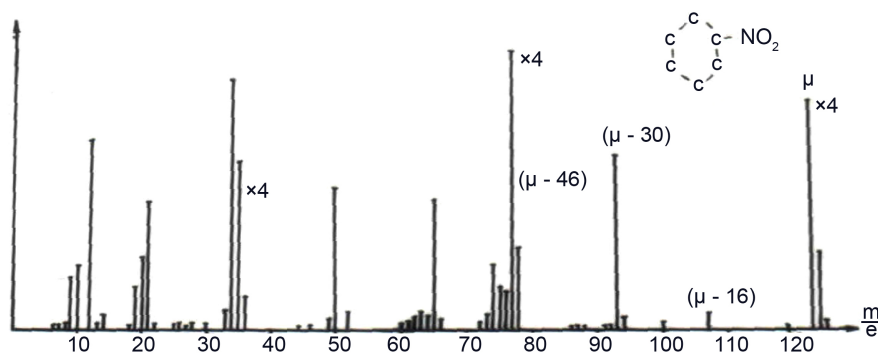


Figure 2. The mass spectrum of Nitrobenzene, MI-1201.

produced from the molecular ion after elimination of NO by non-standard rearrangement and ions $(C_6H_5-O)^+$ are obtained, from which by elimination of carbon oxide $C_5H_5^+$ is obtained with $m/z = 65$. Fragmentation from a molecular ion with hydrogen abstraction has been studied with especial attention; such ions have not been discovered in the spectrum.

Proceeding from the aforesaid, the calculation of the atomic fractions of carbon isotopes should be made by means of peaks of the molecular ions. In this case

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{123}}{I_{124} - 0.00515I_{123}}} \cdot 100\% \quad (3)$$

$$X^{12}C\% = \frac{\frac{I_{123}}{I_{124} - 0.00515I_{123}}}{1 + 6 \cdot \frac{I_{123}}{I_{124} - 0.00515I_{123}}} \cdot 100\% \quad (4)$$

where I_{123} and I_{124} respectively are the intensities of ions with mass number $m/z = 123$ and $m/z = 124$. The numerical coefficient takes into account the presence of heavy isotopes of nitrogen, oxygen and hydrogen entering the composition of the ion. The atomic fraction of carbon isotopes may be determined by using intensive ions ($C_6H_5^+$, $C_5H_5^+$), but in this case, the ions formed by the abstraction of hydrogen are to be taken into account. The atomic fraction of the carbon isotopes is determined by the high-order equations.

The mass spectrum of benzophenone, recorded on the isotope mass spectrometer МИ-1201, is given in **Figure 3**.

The electronic bombardment of benzophenone gives an intensive molecular peak with $m/z = 182$.

The peak that is produced by α -abstraction is maximal in the spectrum, and then the abstraction of the carboxylic group occurs $m/z = 77$ with the formation of fragmentary ions with mass peak, which further fragmentation proceeds according to the decay of the benzene group. Based on the conducted research, we

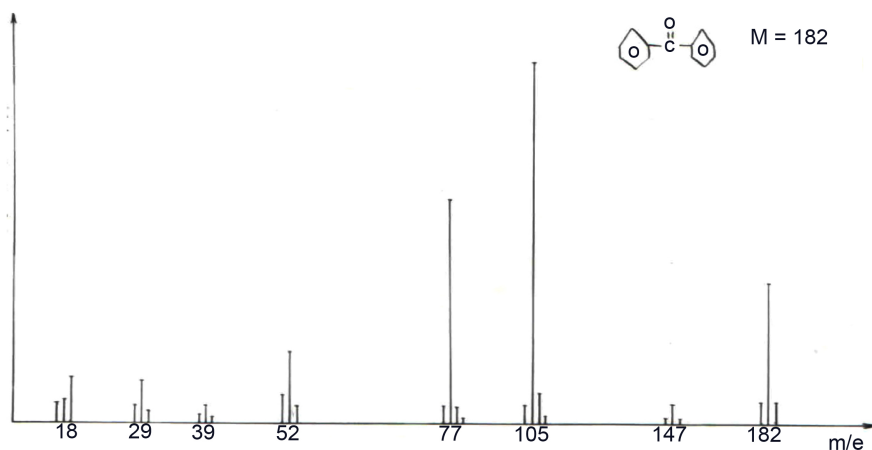


Figure 3. The mass spectrum of Benzophenone, МИ-1201.

have concluded that the isotopic analysis of carbon may be carried out by means of the peaks of molecular ions, as well as by ions with mass numbers $m/z = 105$, 106 and $m/z = 77$, 78 .

Benzophenone is so stable compound that the probability of abstraction of hydrogen from molecular ions is small; therefore, when the atomic fraction of the isotope carbon-13 is less than 90%, it is possible to not take it into account in calculations and to confine ourselves only with ionization process. In this case, if the distribution of carbon isotopes is uniform among all carbon centers, then:

$$X^{13}C\% = \frac{1}{1 + 13 \cdot \frac{I_{182}}{I_{183} - 0.00185I_{182}}} \cdot 100\% \quad (5)$$

$$X^{12}C\% = \frac{13 \cdot \frac{I_{182}}{I_{183} - 0.00185I_{182}}}{1 + 13 \cdot \frac{I_{182}}{I_{183} - 0.00185I_{182}}} \cdot 100\% \quad (6)$$

where I_{183} and I_{182} are the intensities of the ion peaks $m/z = 183$, 182 ; whereas when the atomic fraction of the isotope carbon-13 $> 90\%$, it is necessary to take into account the fragmentation with hydrogen abstraction. In this case,

the ratio of carbon isotopes $Y = \frac{X^{13}C}{X^{12}C}$ is determined by the equation:

$$9I_{181}Y^2 - (13I_{182} - 0.02406I_{181})Y + (I_{183} - 0.00185I_{182} - 0.00204I_{81}) = 0 \quad (7)$$

When the atomic fraction of the isotope carbon-13 $> 90\%$, then the atomic fraction of carbon isotopes by ionic currents with mass number $m/z = 105$, 106 is calculated by the formula:

$$X^{13}C\% = \frac{1}{1 + 7 \cdot \frac{I_{105}}{I_{106} - 0.00111I_{105}}} \cdot 100\% \quad (8)$$

$$X^{12}C\% = \frac{7 \cdot \frac{I_{105}}{I_{106} - 0.00111I_{105}}}{1 + 7 \cdot \frac{I_{105}}{I_{106} - 0.00111I_{105}}} \cdot 100\% \quad (9)$$

where I_{106} and I_{105} are the intensities of the ion peaks $m/z = 106$, 105 .

When the atomic fraction of the isotope carbon-13 $> 90\%$,

$$28I_{104}Y^2 - (7I_{105} - 0.00777I_{104})Y + (I_{106} - 0.00111I_{105} - 0.00204I_{104}) = 0 \quad (10)$$

Similarly the atomic fraction of carbon isotopes may be determined by the peaks with the mass number $m/z = 77$, 78

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{77}}{I_{78} - 0.00074I_{77}}} \cdot 100\% \quad (11)$$

when $X^{13}C\% < 90\%$,

$$X^{12}C\% = \frac{6 \cdot \frac{I_{77}}{I_{78} - 0.00074I_{77}}}{1 + 6 \cdot \frac{I_{77}}{I_{78} - 0.00074I_{77}}} \cdot 100\% \quad (12)$$

and by the equation:

$$21I_{76}Y^2 - (6I_{77} - 0.00445I_{76})Y + (I_{78} - 0.00075I_{77} - 0.00204I_{76}) = 0 \quad (13)$$

where I_{77} and I_{76} are the intensities of the ion peaks $m/z = 77, 76$ when $X^{13}C\% > 90\%$,

If benzophenone is isotopically modified only in carboxylic group, then

$$X^{13}C\% = \frac{1}{1 + \frac{I_{182}}{I_{183} - 0.13628I_{182}}} \cdot 100\% \quad (14)$$

$$X^{12}C\% = \frac{\frac{I_{182}}{I_{183} - 0.13628I_{182}}}{1 + \frac{I_{182}}{I_{183} - 0.13628I_{182}}} \cdot 100\% \quad (15)$$

Similarly the atomic fraction of carbon isotopes is determined according to the intensities of ionic currents of the mass peaks $m/z = 105, 106$:

$$X^{13}C\% = \frac{1}{1 + \frac{I_{105}}{I_{106} - 0.06833I_{105}}} \cdot 100\% \quad (16)$$

$$X^{12}C\% = \frac{\frac{I_{105}}{I_{106} - 0.06833I_{105}}}{1 + \frac{I_{105}}{I_{106} - 0.06833I_{105}}} \cdot 100\% \quad (17)$$

If nitrobenzene is isotopically modified by carbon centers of the benzene group, then the atomic fraction of carbon isotopes is calculated by the formula

$$X^{13}C\% = \frac{1}{1 + 12 \cdot \frac{I_{183}}{I_{182} - 0.01306I_{183}}} \cdot 100\% \quad (18)$$

$$X^{12}C\% = \frac{12 \cdot \frac{I_{183}}{I_{182} - 0.01306I_{183}}}{1 + 12 \cdot \frac{I_{183}}{I_{182} - 0.01306I_{183}}} \cdot 100\% \quad (19)$$

Also,

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{105}}{I_{106} - 0.01232I_{105}}} \cdot 100\% \quad (20)$$

$$X^{12}C\% = \frac{6 \cdot \frac{I_{105}}{I_{106} - 0.01232I_{105}}}{1 + 6 \cdot \frac{I_{105}}{I_{106} - 0.01232I_{105}}} \cdot 100\% \quad (21)$$

The most convenient calculation is by the formulas (11)-(13) in the sample, where benzophenone was isotopically modified by carboxylic carbon center and was certified 25.3%, the calculation by the formula (14) gave 25.4% and by (16) – 25.4%. Thus, atomic fractions of the isotope carbon-13 calculated by different mass peaks within the measurement accuracy coincide with the certified data. In that way, it is possible to check the results.

The mass spectrum of the benzoic acid, recorded on the isotope mass spectrometer MI-1201, is given in **Figure 4**. The maximal in the spectrum is the ion peak with $m/z = 105(\text{M-OH})^+$, but the molecular peak is also intensive in the mass spectrum. The peak of fragmentary ions is quite intensive that is obtained by breaking of α -bond and the ion peak with $m/z = 77(\text{C}_6\text{H}_5^+)$ is produced. Further, this fragment is fragmented in a standard way. The peaks with $m/z = 44, 45$ are of low intensity because the charge is primarily localized on the benzene ring.

Proceeding from the aforementioned, all carbon centers isotopically modified in benzoic acid can be defined by means of molecular ions. When the atomic fraction of the isotope carbon-13 is less than 90%, it is calculated by the formula:

$$X^{13}\text{C}\% = \frac{1}{1 + 7 \frac{I_{122}}{I_{123} - 0.00164I_{122}}} \cdot 100\% \quad (22)$$

$$X^{12}\text{C}\% = \frac{7 \frac{I_{122}}{I_{123} - 0.00164I_{122}}}{1 + 7 \frac{I_{122}}{I_{123} - 0.00164I_{122}}} \cdot 100\% \quad (23)$$

where I_{123} and I_{122} are the intensities of the ion peaks $m/z = 123, 122$; whereas when the atomic fraction of the isotope carbon-13 $> 90\%$, it is necessary to take into account the low probable process of hydrogen abstraction from the molecular ion, then $Y = \frac{X^{13}\text{C}}{X^{12}\text{C}}$ will be determined by the formula:

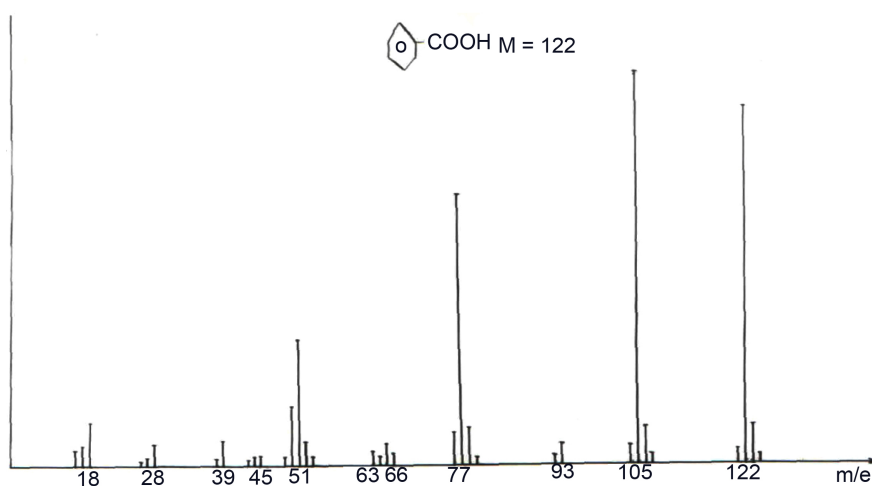


Figure 4. The mass spectrum of the benzoic acid, MI-1201.

$$28I_{121}Y^2 - (7I_{122} - 0.01141I_{121})Y + (I_{123} - 0.00165I_{122} - 0.00409I_{121}) = 0 \quad (24)$$

The atomic fraction of the isotope carbon-13 may be determined according to the intensities of the mass peaks $m/z = 105, 106$. When $X^{13}C\% < 90\%$, then

$$X^{13}C\% = \frac{1}{1 + 7 \frac{I_{105}}{I_{106} - 0.00111I_{105}}} \cdot 100\% \quad (25)$$

$$X^{12}C\% = \frac{7 \frac{I_{105}}{I_{106} - 0.00111I_{105}}}{1 + 7 \frac{I_{105}}{I_{106} - 0.00111I_{105}}} \cdot 100\% \quad (26)$$

whereas when $X^{13}C\% > 90\%$, then $Y = \frac{X^{13}C}{X^{12}C}$ is determined by the equation;

$$28I_{104}Y^2 - (7I_{105} - 0.00777I_{104})Y + (I_{106} - 0.00111I_{105} - 0.00204I_{104}) = 0 \quad (27)$$

whereas by the fragmentary ions $m/z = 77, 78$ is determined by the formula:

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{77}}{I_{78} - 0.00075I_{77}}} \cdot 100\% \quad (28)$$

$$X^{12}C\% = \frac{6 \cdot \frac{I_{77}}{I_{78} - 0.00075I_{77}}}{1 + 6 \cdot \frac{I_{77}}{I_{78} - 0.00075I_{77}}} \cdot 100\% \quad (29)$$

The results of isotopic analysis directly in benzophenone acid with certificate data 24.3% at. contain the isotope carbon-13, such in the formula is (22) 26.0% at., and in the formula (25) 26.1% at., and in the benzophenone acid with natural distribution 1.11% and 1.12% have been obtained, respectively.

The mass spectrum of 2-Hydroxybenzoic acid recorded on the mass spectrometer MI-1201, is given in **Figure 5**. The presence of a benzene nucleus in it determines the character of the mass spectrum. The maximal in the spectrum is the peak of ions, obtained as a result of dehydration of the molecular peak. In the ionization process, migration of hydrogen atom on carboxylic group and elimination of water molecule occur. The further fragmentation takes place by the eruption of carbon oxide from the benzene nucleus and the formation of the ion with the mass number $m/z = 92$. This mechanism of fragmentation has been determined by the analysis of the compound isotopically modified by carboxylic carbon. The molecular peak with the mass number $m/z = 138$ is intensive in the spectrum. The abstraction of the carboxylic group is a less probable process; it is unstable and undergoes further fragmentation. These peaks are of low intensity and are not interesting from the point of view of isotopic analysis.

Determination of the atomic fractions of carbon isotopes may be made by means of molecular ions. Abstraction of hydrogen atoms out of molecular ion is insignificant; therefore, when the atomic fraction of the isotope carbon-13 is less than 98%, the inaccuracy caused by this process may be neglected, and the atomic

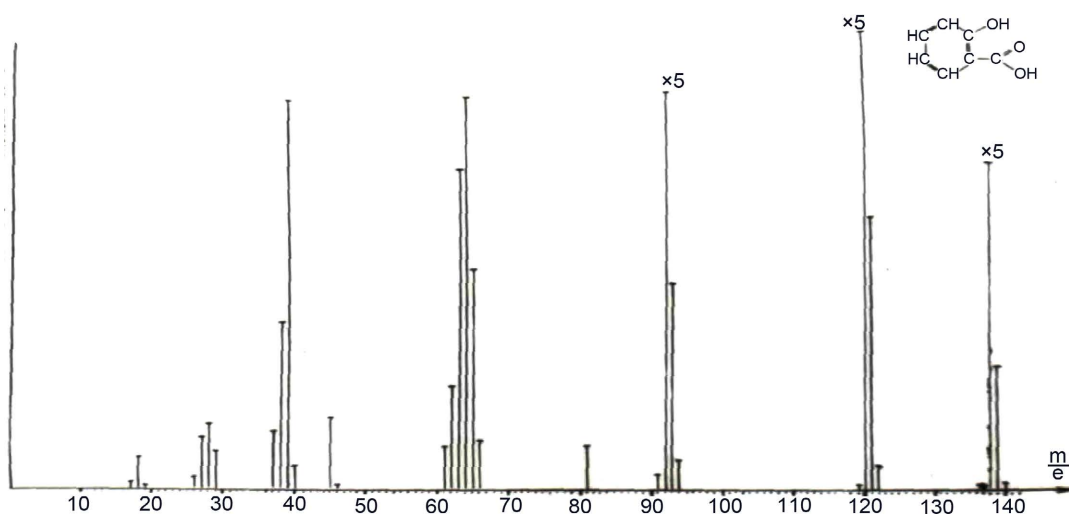


Figure 5. The mass spectrum of 2-Hydroxybenzoic acid, MI-1201.

fraction of carbon isotopes can be calculated by the formula:

$$X^{13}C\% = \frac{1}{1 + 7 \cdot \frac{I_{138}}{I_{139} - 0.00200I_{138}}} \cdot 100\% \quad (30)$$

$$X^{12}C\% = \frac{7 \cdot \frac{I_{138}}{I_{139} - 0.00200I_{138}}}{1 + 7 \cdot \frac{I_{138}}{I_{139} - 0.00200I_{138}}} \cdot 100\% \quad (31)$$

where I_{139} and I_{138} are the intensities of the ion peaks $m/z = 139, 138$.

The atomic fraction of carbon isotopes may be calculated by means of ions $(M-H_2O)^+$, then

$$X^{13}C\% = \frac{1}{1 + 7 \cdot \frac{I_{120}}{I_{121} - 0.00133I_{120}}} \cdot 100\% \quad (32)$$

$$X^{12}C\% = \frac{7 \cdot \frac{I_{120}}{I_{121} - 0.00133I_{120}}}{1 + 7 \cdot \frac{I_{120}}{I_{121} - 0.00133I_{120}}} \cdot 100\% \quad (33)$$

where I_{120} and I_{121} are the intensities of the ion peaks $m/z = 120, 121$.

The atomic fractions of carbon isotopes may also be determined by ions with the mass peaks $m/z = 92, 93$.

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{92}}{I_{93} - 0.00096I_{92}}} \cdot 100\% \quad (34)$$

$$X^{12}C\% = \frac{6 \cdot \frac{I_{92}}{I_{93} - 0.00096I_{92}}}{1 + 6 \cdot \frac{I_{92}}{I_{93} - 0.00096I_{92}}} \cdot 100\% \quad (35)$$

where I_{92} and I_{93} are the intensities of the ion peaks $m/z = 92, 93$.

If salicylic acid is isotopically modified only by the carbon centers of benzene nucleus, then the atomic fraction of isotopes may be determined by the formulas:

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{138}}{I_{139} - 0.01321I_{138}}} \cdot 100\% \quad (36)$$

$$X^{12}C\% = \frac{6 \cdot \frac{I_{138}}{I_{139} - 0.01321I_{138}}}{1 + 6 \cdot \frac{I_{138}}{I_{139} - 0.01321I_{138}}} \cdot 100\% \quad (37)$$

$$X^{13}C\% = \frac{1}{1 + 6 \cdot \frac{I_{120}}{I_{121} - 0.01254I_{120}}} \cdot 100\% \quad (38)$$

$$X^{12}C\% = \frac{6 \cdot \frac{I_{120}}{I_{121} - 0.01254I_{120}}}{1 + 6 \cdot \frac{I_{120}}{I_{121} - 0.01254I_{120}}} \cdot 100\% \quad (39)$$

$$X^{13}C\% = \frac{1}{1 + 5 \cdot \frac{I_{92}}{I_{93} - 0.01217I_{92}}} \cdot 100\% \quad (40)$$

$$X^{12}C\% = \frac{5 \cdot \frac{I_{92}}{I_{93} - 0.01217I_{92}}}{1 + 5 \cdot \frac{I_{92}}{I_{93} - 0.01217I_{92}}} \cdot 100\% \quad (41)$$

If the 2-Hydroxybenzoic acid is isotopically modified only by carboxylic carbon center, then

$$X^{13}C\% = \frac{1}{1 + \frac{I_{138}}{I_{139} - 0.06923I_{138}}} \cdot 100\% \quad (42)$$

$$X^{12}C\% = \frac{\frac{I_{138}}{I_{139} - 0.06923I_{138}}}{1 + \frac{I_{138}}{I_{139} - 0.06923I_{138}}} \cdot 100\% \quad (43)$$

also

$$X^{13}C\% = \frac{1}{1 + \frac{I_{120}}{I_{121} - 0.06856I_{120}}} \cdot 100\% \quad (44)$$

$$X^{12}C\% = \frac{\frac{I_{120}}{I_{121} - 0.06856I_{120}}}{1 + \frac{I_{120}}{I_{121} - 0.06856I_{120}}} \cdot 100\% \quad (45)$$

and

$$X^{13}C\% = \frac{1}{1 + \frac{I_{92}}{I_{93} - 0.05735I_{92}}} \cdot 100\% \quad (46)$$

$$X^{12}C\% = \frac{1 + \frac{I_{92}}{I_{93} - 0.05735I_{92}}}{1 + \frac{I_{92}}{I_{93} - 0.05735I_{92}}} \cdot 100\% \quad (47)$$

The measurement was conducted on the 2-Hydroxybenzoic acid isotopically modified by the carboxylic center; according to the certificate data, the fraction of the isotope carbon-13 was 44.4% at.

The atomic fraction of the isotope carbon-13 has been determined by the formulas (42), (44) and (46); the obtained results were respectively 44.3%, 44.6%, and 44.2%.

Such accuracy is acceptable for certification; the method is self-checking and it has been adopted as the standard method for the determination of atomic fractions of carbon isotopes in 2-Hydroxybenzoic acid.

3. Conclusions

The given methods meet the requirements of the isotope analysis and are successfully used for the determination of the atomic fraction of isotopic carbon in urea, benzophenone, benzoic acid, 2-Hydroxybenzoic acid and Nitrobenzene isotopically modified by carbon.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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