

Determination of Carbon and Nitrogen Isotope Fractions in Tartaric Acid, Oxalic Acid, Glucose and Fructose

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Abstract

Tartaric acid, oxalic acid, glucose, and fructose are highly important compounds. A comprehensive study of these substances is fascinating from a scientific perspective. They are key components found in wine, vegetables, and fruits. Understanding the isotopic compositions in organic compounds is crucial for comprehending various biochemical processes and the nature of substances present in different natural products. Tartaric acid, oxalic acid, glucose, and fructose are widely distributed compounds, including in vegetables and fruits. Tartaric acid plays a significant role in determining the quality and taste properties of wine, while oxalic acid is also prevalent but holds great interest for further research, especially in terms of carbon isotopic composition. We can unveil the mechanisms of processes that were previously impossible to study. Glucose and fructose are the most common monosaccharides in the hexose group, and both are found in fruits, with sweeter fruits containing higher amounts of these substances. In addition to fruits, wheat, barley, rye, onions, garlic, lentils, peppers, dried fruits, beans, broccoli, cabbage, tomatoes, and other foods are also rich sources of fructose and glucose. To determine the mass fraction of the carbon-13 isotope in these compounds, it is important to study their changes during natural synthesis. These compounds can be modified with a carbon center. According to the existing isotopic analysis method, these compounds are converted into carbon oxide or dioxide [1]. At this point, the average carbon content in the given compound is determined, but information about isotope-modified centers is lost. Dilution may occur through the transfer of other carbon-containing organic compounds in the sample or by dilution with natural carbon or carbon dioxide during the transfer process. This article discusses the possibility of carbon-13 isotope propagation directly in these compounds, both completely

modified and modified with individual carbon centers. The literature provides information on determining carbon-13 substance in organic compounds, both with a general approach and for individual compounds [2] [3].

Keywords

Tartaric Acid, Oxalic Acid, Glucose, Fructose, Mass Spectrum, Ion Current, Intensity, Mass Line, Mass Number, Molecular and Fragment Ions, Carbon, Carbon Center

1. Introduction

The use of isotope-modified compounds significantly increases the area of their application. With their help, it is possible to conduct such studies that were impossible without the use of isotope-modified compounds. Their use depends to a significant extent on the existence of cheap and simple methods.

The mass spectrum of the compounds was recorded by an isotope mass spectrometer. This allowed us to determine the elemental composition of individual fragments, including their gross formulas, the origin of each carbon and the secondary processes that occur during the ionization of the compound by electron bombardment. It's important to note that, as with most organic compounds, the molecular peak is either not observed or has very low intensity. However, we can still determine the isotopic composition of carbon based on the intensity of various fragment ions in the mass spectrum. Additionally, special systems for introducing organic compounds were developed [4]-[10].

Tartaric acid is one of the substances of wine that determines the acidity of wine. Its synthesis can occur both naturally and artificially. When the acidity of the wine is not enough, they add tartaric acid specially obtained by artificial synthesis. Tartaric acid can be modified at both the carbon center of the carboxyl group and the hydroxyl carbon center, or with all four carbon centers simultaneously. This article shows the determination of the carbon-13 atomic fraction in each case.

Tartaric acid is the simplest dicarboxylic acid. It contains two carboxyl groups. These compounds are synthesized in plants and can also be synthesized artificially. It is included in the composition of many foods and is produced by oxidizing alcohol to carbohydrates. Carbon centers do not differ from each other.

The hexose group contains the most common monosaccharides, including glucose and fructose. Both fructose and glucose are found in fruits, with sweeter fruits containing higher amounts of these substances. Glucose and fructose are stereoisomers and have six heteroatoms in their molecules, with a cyclic structure. They are both polar compounds with five mobile hydrogens. In isotopic studies, the ionization by electron bombardment method was employed. It contains three different carbon centers: two carboxylic carbons, one hydroxyl, and one in the chain. It can be isotopically modified with carbon centers other than ertmannite, and also

completely isotopically modified with all carbon centers simultaneously.

To determine the distribution of stable carbon isotopes in this compound, we proposed equations to calculate the abundance of the carbon-13 isotope in both the entire molecule and in specific functional groups.

2. Experiments

With isotope-modified **tartaric acid**, it is possible to conduct such studies, without the use of which it was impossible to study these processes. To control the synthesis and further use of tartaric acid, it is necessary to develop a relatively simple method by which the atomic fraction of the carbon-13 isotope is determined. The atomic fraction of carbon isotopes in tartaric acid was determined by converting them to carbon oxide or dioxide. At this time, the conversion process is added to the determination of the atomic fraction of the carbon-13 isotope and the average value of the atomic fraction of the carbon-13 isotope is measured. Information about isotope-modified carbon centers is unclear if the sample contains carbon-containing organic compounds, dilution will occur, increasing measurement error. It is also possible to overlap the residual gases of the mass spectrometer on the peaks of ions with mass numbers $m/z = 28, 29$ or $m/z = 44, 45$. This article proposes a method through which the atomic fraction of the carbon-13 isotope is determined directly in tartaric acid, both in isotope-modified with all four centers and in tartaric acid modified with individual carbon centers. Since tartaric acid can be isotope-modified.

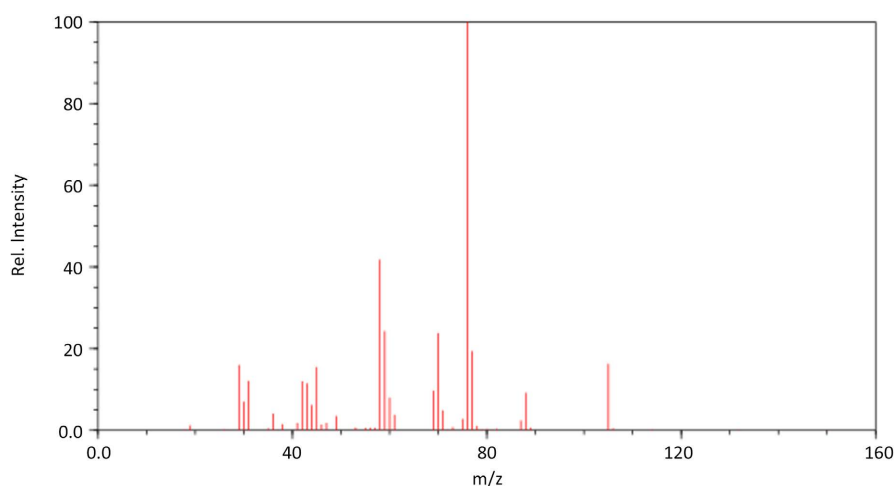


Figure 1. The mass spectrum of tartaric acid.

In the spectrum (**Figure 1**) of tartaric acid, we observe a peak of molecular ions with low intensity. The molecule contains six heteroatoms and the charge is mainly localized on them. Depending on which oxygen the charge is localized, different fragment ions are formed. If the charge is localized on the oxygen of the hydroxyl group, then hydrogen migrates from the neighboring hydroxyl group and water is eliminated. It is also possible to do the same for the second, even

the elimination of the water molecule, which is confirmed by the low-intensity peaks with mass numbers of $m/z = 132$ and $m/z = 114$. These fragments are unstable and undergo further fragmentation. When the charge is localized on the oxygen of the carbonyl group, this group is removed and quite intense ions with mass numbers $m/z = 105$ and 106 are formed. After the elimination of water, carbon dioxide is also removed and ions with $m/z = 88$ and 89 are formed. Further fragmentation, by removing hydrogen, produces a rather intense ion $m/z = 87$. The fragment ion $m/z = 105$ is formed after removing the carboxyl group from the molecular ion, which undergoes further fragmentation by removing "COH". By removing oxygen from the fragment with mass number $m/z = 88$, ions are formed, which are further fragmented by removing the hydrogen atom. This process is quite probable because the ion $m/z = 58$ is more intense than the initial fragment from which these ions are derived. Intense ions with mass numbers $m/z = 44$ and 45 will also be observed in the spectrum. Separation of carbon dioxide and the carboxyl group from the fragment with mass number $m/z = 132$ and fragment ions with mass number $m/z = 43$ will be observed. Also, intense peaks with mass numbers $m/z = 31$ and $m/z = 29, 30$ will be observed.

The analysis of the elemental content of each fragment and the origin of each carbon center from the spectrum indicates that isotopic analysis can be conducted using mass lines, with mass numbers of $m/z = 104, 105, 106$, as well as $m/z = 87, 88, 89$ and $m/z = 75, 76, 77$; $m/z = 69, 70, 71$ and $m/z = 58, 59, 60$. However, the use of the mass numbers $m/z = 29, 30, 31$ and $m/z = 41, 42, 43, 44, 45$ for isotopic analysis is not recommended, because fragmented ions of different elemental content can overlap with them.

A system of equations is used to determine the proportion of the carbon-13 isotope in tartaric acid, which has been modified with all carbon centers.

The atomic fraction of the carbon-13 isotope in fully modified tartaric acid is determined by calculating the mass lines $m/z = 104, 105$ and 106 and reducing the system of equations to a single equation

$$6I_{104}y^2 - (3I_{105} - 0.00666I_{104})y + (I_{106} - 0.00222I_{105} - 0.00817I_{104}) = 0 \quad (1)$$

where

$$y = X^{13}c/X^{12}c \quad (2)$$

The carbon-13 to carbon-12 isotopic ratio is calculated as the ratio of the atomic fraction of carbon-13 to carbon-12

$$Xc^{13}\% = \frac{y}{y+1} \cdot 100 \quad (3)$$

Further, the atomic fraction of the carbon-13 isotope in percentages is calculated in the same way as each of the equations using the formula (3).

When tartaric acid is isotope-modified with carbons attached to the hydroxyl group, then

$$I_{104}y^2 - (I_{105} - 0.002463I_{104})y + (I_{106} - 0.02463I_{105} - 0.00775I_{104}) = 0 \quad (4)$$

If tartaric acid is isotope-modified with a carboxylic carbon center, then the equation has the form

$$3I_{104}y^2 - (2I_{105} - 0.02686I_{104})y + (I_{106} - 0.01343I_{105} - 0.00803I_{104}) = 0 \quad (5)$$

It is also possible to use fragment ions with mass numbers $m/z = 87, 88, 89$. Carbon-13 isotopes with all carbon centers in isotope-modified tartaric acid are determined by the equation

$$6I_{87}y^2 - (3I_{88} - 0.005109I_{87})y + (I_{89} - 0.001707I_{88} - 0.00614I_{87}) = 0 \quad (6)$$

At the carbon center attached to the carbons of the hydroxyl group by the equation

$$3I_{87}y^2 - (2I_{88} - 0.02592I_{87})y + (I_{89} - 0.01291I_{88} - 0.00598I_{87}) = 0 \quad (7)$$

Even in the isotope modified with carboxyl carbon center

$$I_{87}y^2 - (I_{88} - 0.02411I_{87})y + (I_{89} - 0.02411I_{88} - 0.00557I_{87}) = 0 \quad (8)$$

Studies have shown that fragment ions with mass numbers $m/z = 75, 76$ and 77 contain both carboxyl and hydroxyl carbon. Therefore, the following equation is used to calculate the atomic fraction of the carbon-13 isotope in tartaric acid, which is equally isotope-modified with both centers.

$$3I_{75}y^2 - (2I_{76} - 0.00340I_{75})y + (I_{77} - 0.00170I_{76} - 0.00614I_{75}) = 0 \quad (9)$$

In isotope-modified tartaric acid with a carboxyl or hydroxyl group by equation

$$I_{75}y^2 - (I_{76} - 0.01291I_{75})y + (I_{77} - 0.01291I_{76} - 0.00599I_{75}) = 0 \quad (10)$$

Mass-spectrum analysis is required to determine the carbon-13 isotope-modified center. To calculate the atomic fraction of the carbon-13 isotope, if we use fragment ions with mass numbers $m/z = 69, 70, 71$, then we will have the following equations:

For fully modified tartaric acid

$$6I_{69}y^2 - (3I_{70} - 0.00267I_{69})y + (I_{71} - 0.00089I_{70} - 0.00409I_{69}) = 0 \quad (11)$$

For tartaric acid isotope modified with hydroxyl carbon center

$$3I_{69} - (2I_{70} - 0.02418I_{69})y + (I_{71} - 0.01209I_{70} - 0.00396I_{69}) = 0 \quad (12)$$

Even in tartaric acid isotope modified with carboxyl carbon center

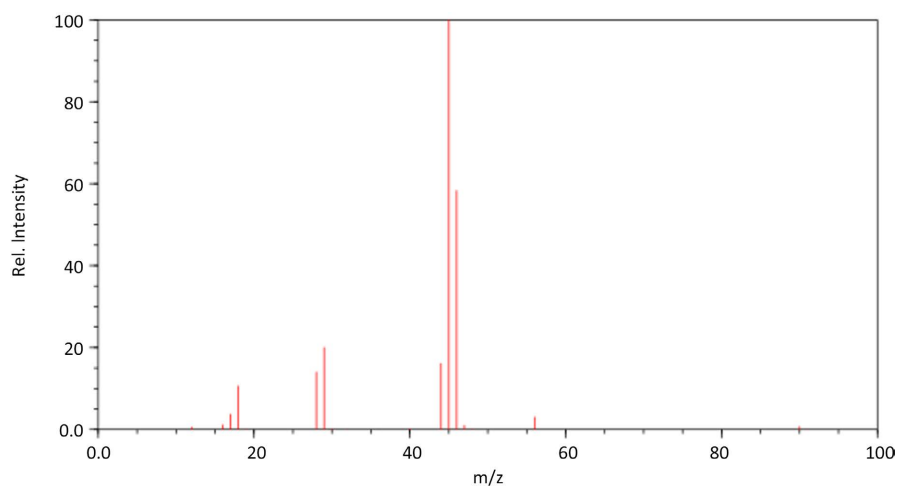
$$I_{69}y^2 - (I_{70} - 0.02345I_{69})y + (I_{71} - 0.02345I_{70} - 0.00398I_{69}) = 0 \quad (13)$$

As shown by the analyses in **Table 1**, the measurement results are consistent within the margin of error.

As in tartaric acid, **oxalic acid**, glucose and fructose, the atomic fraction of carbon-13 isotopes in oxalic acid was determined by converting them to carbon oxide or dioxide. To determine the presence of carbon-13 in oxalic acid, the mass spectrum (**Figure 2**) obtained from an isotope mass spectrometer was analyzed.

Table 1. Atomic fraction of carbon-13 isotope determined by equations.

	¹³ C %		
	Equation (1)	Equation (6)	Equation (9)
1	1.11	1.1	1.11
2	1.11	1.10	1.11
3	1.08	1.11	1.10
4	1.09	1.10	1.10
5	1.09	1.12	1.12
6	1.11	1.13	1.14
7	1.12	1.12	1.12
8	1.12	1.10	1.10
9	1.10	1.12	1.11
10	1.13	1.14	1.14
	1.11 ± 0.02	1.12 ± 0.02	1.12 ± 0.02

**Figure 2.** The mass spectrum of oxalic acid.

During electron bombardment, the molecular peak is not constant. The molecule contains four heteroatoms, with most of the charge localized on the oxygen atoms. In the excited molecule, hydrogen moves from one hydroxyl group to another, leading to the elimination of water. The resulting fragment is unstable and further breaks down by losing carbon oxide, resulting in a peak with a mass number of $m/z = 56, 57, 58$. The chain also breaks, causing one of the carboxyl groups to break off, forming a peak with mass numbers $m/z = 45, 46$, which is the highest peak in the spectrum. Additionally, intense peaks with mass lines $m/z = 44$ and $m/z = 46$ can be observed. In this case, hydrogen migration from one carboxyl group to another is also observed, resulting in fragment ions formed by subsequent carbon dioxide evolution or hydrogen migration. An intense peak with mass lines of $m/z = 28, 29$ is also present. Peaks of ions with low-intensity $m/z = 16, 17, 18$ are also observed in the spectrum. On the mass

line of $m/z = 29$, hydrogen ions migrating to carbon oxide are superimposed. Both carbon centers in the molecule containing the atom are equivalent and their isotopic content can be calculated using the mass lines $m/z = 56, 57, 58$. In this case, the system of equations will be reduced to the equation

$$3I_{56}y^2 - (2I_{57} - 0.00148I_{56})y + (I_{58} - 0.00074I_{57} - 0.00409I_{56}) = 0 \quad (14)$$

It is also possible to determine the carbon-13 isotopic fraction by the intensities of mass peaks with $m/z = 28, 29, 30$. In this case, the system of equations is reduced to the following equation

$$I_{28}y^2 - (I_{29} - 0.00052I_{28})y + (I_{30} - 0.00052I_{29} - 0.00204I_{28}) = 0 \quad (15)$$

The carbon-13 isotope can be detected by analyzing the peaks of ions with mass numbers $m/z = 44, 45, 46$, and 47 . In this scenario, three types of fragments need to be considered, each differing by the number of hydrogen atoms. The fragments and their isotopic backgrounds overlap, leading to a system of equations that can be simplified to a cubic equation

$$I_{44}y^3 - (I_{45} - 0.00104I_{44})y^2 + (I_{46} - 0.000104I_{45} - 0.00408I_{44})y - (I_{47} - 0.00109I_{46} - 0.00408I_{45}) = 0 \quad (16)$$

Table 2. Atomic fraction of carbon-13 isotope determined by equations.

	¹³ C %	
	Equation (14)	Equation (16)
1	1.10	1.11
2	1.09	1.11
3	1.10	1.13
4	1.09	1.13
5	1.09	1.14
6	1.11	1.13
7	1.13	1.13
8	1.12	1.09
9	1.09	1.12
10	1.10	1.12
	1.10 ± 0.02	1.12 ± 0.02

Based on **Table 2**, the results obtained with fragment masses of $m/z = 56, 57$, and 58 are consistent with the results obtained with ion currents of $m/z = 44, 45, 46$, and 47 . The table excludes the results calculated using **formula 15**, as superimposed background at $m/z = 28, 29, 30$ would compromise the accuracy of the results.

3. Glucose and Fructose

When molecules undergo electron bombardment, they experience significant fragmentation, resulting in spectra in **Figure 3** and **Figure 4**.

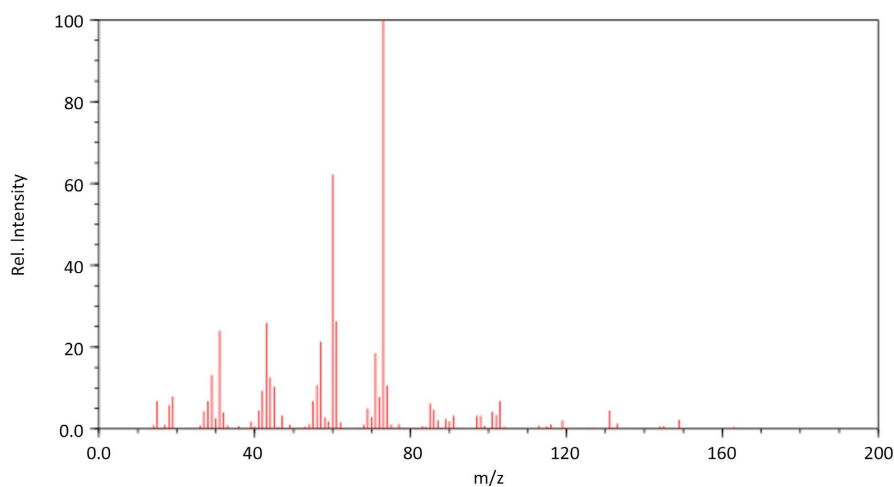


Figure 3. The mass spectrum of glucose.

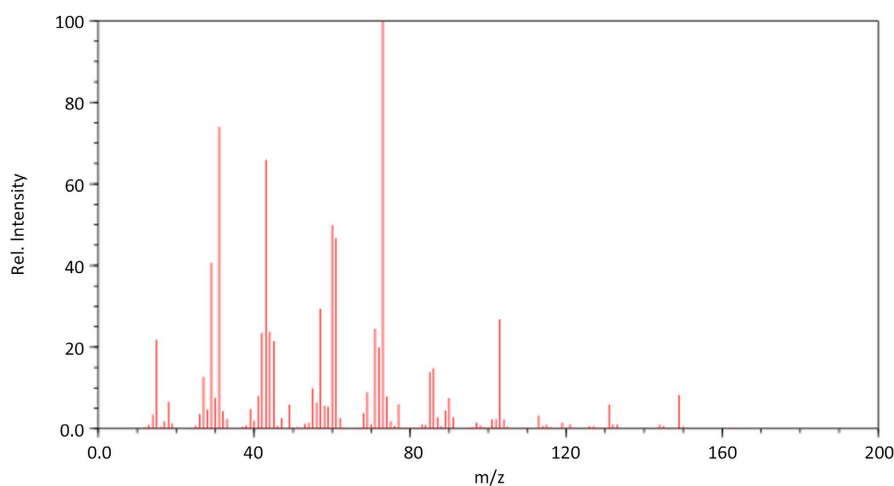


Figure 4. The mass spectrum of fructose.

Typically, at the energies used for isotopic measurements, the molecular peak is of negligible intensity. Our analysis of the spectrum revealed that it's not possible to determine the atomic fraction of the carbon-13 isotope with individual carbon centers through fragmented ions. However, it is possible to determine the atomic fraction of the carbon-13 isotope in the methyl groups only by the carbon centers of the chain. To determine the carbon isotope content, it's necessary to fix the molecular peak or use an isotope mass spectrometer using the phase ionization method, but such mass spectrometers are currently unavailable. In the future, creating isotope mass spectrometers for measuring the atomic fraction of element isotopes in unstable chemical compounds is desirable.

Experiments have shown that a molecular peak can be obtained when the energy of the electrons required for the collisions is in the range of 20 to 30 electron volts and titanium powder should be added to the sample in a 1:1 ratio. In these compounds, the positive charge is predominantly localized on oxygen atoms. It's relatively less likely that the charge is localized on the closed chain, so the most intense peak is at $m/z = 73$. Unlike the mass spectrum of glucose, in the

mass spectrum of fructose, ions with mass number $m/z = 74$ are formed intensively, but the gross formula of these two fragments differs from each other only by one hydrogen atom. Therefore, the proposed method of measuring carbon isotopes can be used for both glucose and fructose.

The fragment $m/z = 60$ is also very intense and the atomic fraction of carbon isotopes can be determined from it. However, in the latter two cases, three fragmentation processes need to be considered: dissociation of hydrogen from main fragment ions, fragment ions and migration of hydrogen to fragment ions. Similarly, these processes are considered with the intensities of fragment ions with mass numbers $m/z = 58, 59, 60, 61$ to calculate the atomic fraction of the carbon-13 isotope, reducing the formula for determining the atomic fraction of the carbon-13 isotope to a cubic equation.

For molecular peak ions, two processes need to be considered. In the glucose and fructose molecules, there are mostly mobile hydrogens, so the molecular ion easily loses hydrogen and forms an “M-1” ion radical. We only consider this process for the determination, which can be used to determine the presence of carbon isotopes in the closed chain or the methyl group. In this case, the equation will be quadratic.

Peaks with $m/z = 43, m/z = 31$ and $m/z = 15$ are also intense in the spectrum. However, these peaks are superimposed on both background and combustion compounds and the research shows that their use for isotopic analysis is not acceptable.

To calculate the atomic fraction of the carbon-13 isotope in isotope-modified glucose and fructose, we can use the intensities of peaks with mass numbers $m/z = 179, 180$ and 181 . This allows us to reduce the system of equations to a single equation

$$2I_{179}y^2 - (6I_{180} - 0.02400I_{179})y + (I_{181} - 0.004I_{180} - 0.01226I_{179}) = 0 \quad (17)$$

In glucose modified with chain carbon centers, the atomic fraction of the carbon-13 isotope is calculated using the following equation

$$10I_{179}y^2 - (5I_{180} - 0.07605I_{180})y + (I_{181} - 0.01521I_{180} - 0.01209I_{179}) = 0 \quad (18)$$

In isotope-modified glucose with a branched carbon center and fructose, the system of equations for limiting the atomic fraction of the carbon-13 isotope is reduced to a single equation

$$I_{179}y^2 - (I_{180} - 0.06002I_{179})y + (I_{180} - 0.06002I_{180} - 0.00890I_{179}) = 0 \quad (19)$$

The system of equations for determining the proportion of the carbon-13 isotope in the branched carbon centers can be simplified to a quadratic equation

$$3I_{179}y^2 - (2I_{180} - 0.09774I_{179})y + (I_{181} - 0.04882I_{180} - 0.01011I_{179}) = 0 \quad (20)$$

In the closed chain of fructose and glucose, there are four carbon atoms. The system of equations for calculating the fraction of the carbon-13 isotope in these carbon centers will be reduced to the following quadratic equation

$$10I_{179}y^2 - (4I_{180} - 0.10564I_{179})y + (I_{181} - 0.02641I_{180} - 0.01175I_{181}) = 0 \quad (21)$$

In glucose and fructose, all carbon atomic centers are equally modified, allowing for the determination of fragment ions with mass numbers $m/z = 71, 72, 73, 74$. The system of equations is then reduced to the following equation

$$10I_{71}y^3 - (I_{72} - 0.00888I_{71})y^2 + (3I_{73} - 0.00444I_{72} - 0.01227I_{71})y - (I_{74} - 0.00148I_{73} - 0.00409I_{72} - 0.00001I_{71}) = 0 \quad (22)$$

It is possible to calculate the intensities of peaks with mass numbers $m/z = 58, 59, 60, 61$ using the following equation

$$4I_{58}y^3 - (3I_{59} - 0.00399I_{58})y^2 + (2I_{60} - 0.000266I_{59} - 0.008189I_{58})y - (I_{61} - 0.00133I_{60} - 0.00409I_{59} - 0.00001I_{58}) = 0 \quad (23)$$

The results of the experiment are provided in **Table 3**.

Table 3. Atomic fraction of glucose determined by equations.

glucose	
Equation (22)	
1	1.13
2	1.11
3	1.12
4	1.11
5	1.13
6	1.11
7	1.11
8	1.09
9	1.08
10	1.09
1.12 ± 0.02	

The results of a similar experiment are provided in **Table 4**.

Table 4. The atomic fraction of fructose determined by equations.

fructose	
Equation (23)	
1	1.08
2	1.09
3	1.10
4	1.09
5	1.10
6	1.08
7	1.10
8	1.09

Continued

9	1.08
10	1.08
	1.10 ± 0.02

The measurement results are consistent within the margin of error.

4. Conclusions

Based on the information provided, the atomic fraction of the carbon-13 isotope in carbon-isotope-modified tartaric acid can be calculated using four different groups of fragment ions, allowing the result to be cross-checked four times.

When determining the atomic fraction of the carbon-13 isotope using the last two formulas, it's important to be aware of residual gases. The addition of these gases can cause errors in the measurement results. Therefore, it's crucial to maintain strict vacuum conditions or use equation (14) to determine the atomic fraction of the carbon-13 isotope. By cross-checking the results, we can identify any errors caused by waste gases.

Determining the atomic fraction of the carbon-13 isotope using molecular peak intensities is challenging due to their low intensities. As a result, the atomic fraction of the carbon-13 isotope with these mass lines is only determined within the concentration interval of (3 ÷ 97) % atom.

The results for all four considered compounds are mutually verifiable. This means the atomic fraction of carbon can be calculated using two or more different mass lines.

Conflicts of Interest

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

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