APPLICATION OF THE IMPEDANCE METHOD FOR DETERMINATION OF MONOSODIUM GLUTAMATE IN FOOD PRODUCTS

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Abstract. The article presents the results of studying how impedance analysis can be used for determination of monosodium glutamate in order to identify food fraud. We have suggested that the parameters of complex conductivity (admittance) of a two-terminal circuit could allow detecting monosodium glutamate (E 621), an additive used in the food industry to enrich the taste. The method involves passing current of different frequencies through solid foodstuffs and a cell with liquid foodstuffs, measuring the electrical conductivity, and determining and analysing the frequency dependence of admittance. The active G component and the reactive B component of the admittance have been measured at different frequencies, from 100 Hz to 100 kHz. For the experiment, food samples were prepared in accordance with the Codex Alimentarius recommendations for the dosage of the food additive E 621: orange juice with monosodium glutamate added in the amount of 0.3%, and mashed potatoes with glutamate added in the amount of 1%, of the total weight of the products. The temperature of the tested products was 22 ± 0.2°C. The results of the studies have shown the dependences of the admittance components on the frequency for the control samples of juice and mashed potatoes and for the samples with monosodium glutamate added. The dependence of the active component and the reactive component of the foodstuff admittance have been established, with monosodium glutamate (added in the above-specified proportion) and without it. The difference is in how the dependences change in their nature. The monosodium glutamate curves both in juice and in mashed potatoes are similar. The samples containing monosodium glutamate have far higher values of the active and reactive admittance component than the control samples do, with a distinct peak of the reactive component characteristic. Therefore, impedance analysis is a possible method to detect quickly the flavour enhancer monosodium glutamate in foods of different consistency and thus identify food fraud.

Key words: impedance analysis, food fraud, monosodium glutamate (MSG).
determine the physicochemical characteristics of food and thus assess its quality and safety. The impedance method has a number of advantages: it is fast, non-destructive, inexpensive, and easy to apply. Its potential of developing a tool for detecting adulterated products online offers a good alternative to traditional methods and techniques.

Therefore, it is extremely important to improve metrological support and study how impedance analysis can be applied to detect monosodium glutamate in foodstuffs that may be an object of food fraud.

**Analysis of recent research and publications**

The impedance method has recently become widespread as an effective analytical method to determine the physicochemical characteristics of food and thus assess its quality and safety.

The method was first used in 1894 by W. Nernst to measure the dielectric constant of different types of electrolytes [1].

Now impedance analysis is used in a wide range of industries [2,3]; microbiology [4-15], analysis of the human body composition [16-28], characterisation and quality assessment of various foodstuffs and water [29-50], studying corrosion of metals [51-54], coatings, and the state of surfaces [55-59]. Using the method of impedance analysis, one can measure the state of charge of batteries and fuel cells [60-65], detect cancer cells [66-67], study the quality of petroleum products [68-69] and soils [70].

Impedance analysis as a method to control quality and safety is considered in a number of noteworthy works. Using it, A. Aleynikov et al., O. Shchebentovska, Ye. Pokhodylo et al. determined meat freshness [29-31,33], M. Chaten et al. studied the manufacturing process of meat products [37], A. Bauchot, A. Chowdhury, F. Harker, and S. Forbes assessed the quality of fruits and berries [35,38,39,48,49], A. Fuentes et al. identified fresh fish [40], M. Grossi et al. determined the parameters of milk, ice cream, and olive oil safety [41-47]. All researchers agree that the method of impedance analysis is fast, non-destructive, inexpensive and easy to apply.

In the middle of the 20th century, there was practice of adding monosodium glutamate only to low-quality products, minced meat to be re-frozen, frozen meat that had lost its original quality and characteristics. Products that contain the highest amounts of monosodium glutamate added are those made from legumes, fish, vegetables, and poultry, as well as tinned food, soups, concentrates, condiments, sausages, and fast food products.

Now food manufacturers, consumers, government regulators, and other people concerned face significant challenges of preventing food fraud and developing fast and effective methods with appropriate metrological support to detect adulterated products and thus increase economic benefits.

Food adulteration involves a set of actions aimed at deliberately substituting, altering, or falsifying food or individual ingredients, packaging and labelling, and providing false or misleading information about a product to obtain economically motivated benefits [71]. Among the methods of food adulteration, the most used are: dilution (mixing an expensive liquid ingredient with a cheaper liquid ingredient), substitution (replacing an expensive ingredient or part of a product with a cheaper ingredient or part of a product), concealing information about the low quality of food or ingredients, incorrect labelling (placing wrong information on the package to obtain economic benefits), unauthorised changes in the recipe (adding unknown and unidentified ingredients to food to improve its quality characteristics), counterfeiting (copying a certain brand, packaging, recipe, method of production, etc. to obtain economic profit). Almost all of these methods of food fraud involve introducing certain additives to preserve or improve the organoleptic characteristics of food products (taste, smell, texture, or colour). One of the most common types of food additives that can enhance the taste of food is monosodium glutamate.

Monosodium glutamate is a permitted food additive in the EU, USA, and Ukraine, but it is often used to disguise dilution, substitution, unauthorised changes to the recipe. There are cases of food fraud with sodium glutamate that are qualified as concealment of information and incorrect labelling, when the label either does not indicate the food additive in the product, or describes the product as “glutamate-free,” though laboratory testing identifies glutamates.

The chemical name of monosodium glutamate (E 621) is monosodium L-glutamate, its chemical formula is \( \text{C}_6\text{H}_{12}\text{NaNO}_2\cdot\text{H}_2\text{O}. \) its physical state is a white crystalline substance, well-soluble in water and practically insoluble in ethanol and ether. The structural formula is presented in Fig. 1.

Monosodium glutamate is a low-toxic substance. In the body, glutamates act as neurotransmitters in the nervous system. They stimulate amino acid receptors in the brain, are an important potential source of energy, and are the substances that can cause the umami taste, thus being flavour enhancers.

![Fig. 1. Structural formula of monosodium L-glutamate](image)

That is why when diluting a product, or using raw materials of lower quality, etc., which leads to loss or weakening of the taste, monosodium glutamate is used.

Modern research has not unequivocally established whether glutamate has any dangerous effects on the human body [72].

Glutamates are absorbed in the intestine and are metabolised on its walls. There are studies that show an
increase in the kidney and spleen mass in rats that received the maximum dose of monosodium glutamate. In some cases, excessive consumption of glutamate is accompanied by an increase in the blood pressure and insulin levels, and by headaches. Some studies suggest that monosodium glutamate can cause obesity and metabolic disorders.

An adult’s daily intake of sodium glutamate is 30 mg/kg body weight. Consuming more than 42.9 mg/kg body weight of glutamate a day is highly probable to result in such symptomatic effects as facial or neck redness, heart palpitations, and headache. 85.8 mg/kg body weight a day causes headaches, 150 mg/kg increases the blood pressure, and more than 143 mg/kg results in high insulin levels in the blood [72]. Besides, there are 45 food groups (of 67) where the use of glutamates is allowed: meat, fish, poultry, vegetable products, legumes, sauces, cooked sausages, tinned food, semi-finished products, salads, spices. Glutamates are prohibited in fruit juices and nectars, gluten-free pasta, foods for infants and young children, butter, rice, and honey.

When using monosodium glutamate in food formulations, manufacturers must indicate on the labelling either the name of the food additive or the code E 621 with an explanation of the composition of the additive. If the manufacturer states on the packaging “glutamate-free,” their absence must be documented, and there must be reports that the food has been tested in a specially accredited laboratory.

At present, Germany, France, Austria, and the United Kingdom have normative and technical documentation regulating how to apply the impedance method to food products. In Germany, there is a current standard DIN 10115:1999, which contains general requirements for the use of impedance method to identify microorganisms, DIN 10120:2018 to determine Salmonella by the impedance method, and DIN 10122:2018 to determine the number of aerobic mesophilic microorganisms in food. In France, the current standard AFNOR NF V08-106:2010 describes the general principles of applying the impedance method in food microbiology, and AFNOR NF V08-105:2010 deals with quantifying E. coli in living molluscs. All standardised methods involving impedance analysis of food only apply to microbiological research.

There is a way to determine monosodium glutamate in food using liquid chromatography methods producing phenylthiohydantoins of amino acids [73] and involving acid hydrolysis of samples, modification of amino acids with phenylisothiocyanate solution, column chromatography, and ultraviolet detection. There is another method [74] of quantifying monosodium glutamate in foods, which is based on registering the light absorption capacity of MSG, strengthened with 1% solution of ninhydrin with postchromatographic derivatisation. The biosensor method of determining L-glutamate [75] in liquid condiments is based on using L-glutamate oxidase in combination with hydrogen peroxide. Monosodium glutamate can also be detected by thin-layer chromatography, in particular by the method of thin layer chromatography with luminescent detection [76].

The disadvantage of all these methods is the impossibility of rapid and selective detection of monosodium glutamate. All these methods are complex and time-consuming, they require high-precision measuring equipment and instruments.

The purpose of the research was to study the feasibility of using impedance analysis and to develop a method of operational control to obtain certain information about the presence of monosodium glutamate in food. According to the purpose, the following objectives were set:

- to analyse ways of food adulteration and methods of detecting food fraud;
- to investigate how practical it is to use impedance analysis to determine the content of the monosodium glutamate additive in food;
- to analyse the quantitative values of the active and reactive components of the admittance by the changes in the curves of their dependence on the frequency, when using the impedance analysis to detect monosodium glutamate;
- to establish the differences in the graphical characteristics of the change in the active and reactive components of the admittance when using the impedance method to identify the presence of monosodium glutamate in food.

Research materials and methods

Samples of orange juice and mashed potatoes, with and without additives, were the research objects. Orange juice with 20% of distilled water added and mashed potatoes became the reference (basic) samples. In the experimental (controlled) samples, considering the Codex Alimentarius recommendations on the amount of the food additive E 621 in vegetable juices, monosodium glutamate was added to 80% orange juice in an amount of 0.3% by weight of the juice, and to the mashed potatoes, in an amount of 1% by weight of the product. The temperature of the products under study was 22±0.2°C.

To control the safety of food products by detecting glutamates in their composition, we used the impedance method of controlling the product quality [29]. The method of immittance quality control of non-electrical products is based on measurements of the parameters of the two-terminal circuits used to feed the objects controlled in an AC circuit. The quality of the product is controlled by comparing the vectors presenting the admittances or impedances of the reference and controlled samples on the complex plane. Let us consider the vectors of admittances. A graphical interpretation of the admittance vectors is shown in Fig. 2.
Fig. 2. Graphical interpretation of the components of admittance

\[ Y_0 - \text{admittance of the basic sample; } \]
\[ Y_s - \text{admittance of the controlled object; } \]
\[ B_0 - \text{reactive component of the basic sample; } \]
\[ B_s - \text{reactive component of the controlled object; } \]
\[ G_0 - \text{active component of the basic sample; } \]
\[ G_s - \text{active component of the controlled object; } \]
\[ \varphi_0, \varphi_s - \text{phase angles of the controlled object and the basic sample. } \]

In Fig. 2, the vector \( Y_0 \) represents the admittance of the basic sample, and the vector \( Y_s \) shows the admittance of the controlled object at one fixed frequency of the test signal. At other frequencies, the vectors will differ in other parameters.

The parameters for comparing the vectors can be the modulus of admittance and the phase angle, or the active and reactive components of the admittance of the controlled and reference samples. According to the measurement results, the ratio of the corresponding measured parameters of the samples is analysed.

In our study, the active and reactive components of the admittance of the objects compared were taken as the informative electrical parameters of the objects of control.

So, the measured parameters of the reference sample have been compared with those of the sample with the modified composition. Besides, it has been evaluated how the active and reactive components of admittance change at fixed frequencies of the defined frequency range of the fixed-level sinusoidal test signal.

This method allows determining the relative quality and safety of products. For the immittance control, it is the ratio between the reactive and active components of the conductivity of the test object and the reference sample without their equivalent circuits, namely:

\[
\begin{align*}
B_{01} & \quad B_{s1} & \quad B_{02} & \quad B_{s2} & \quad \ldots & \quad B_n & \quad B_{sn} \\
G_{01} & \quad G_{s1} & \quad G_{02} & \quad G_{s2} & \quad \ldots & \quad G_n & \quad G_{sn}
\end{align*}
\]

(1)

where \( B_{s1}, B_{s2}, B_{s3}, \ldots, B_n \) are reactive components of admittance at certain frequencies; \( G_{s1}, G_{s2}, G_{s3}, \ldots, G_n \) are active components of admittance at certain frequencies.

Admittance components can be measured indirectly or directly. Indirectly, the components (active and reactive) of the immittance of the objects compared can be measured with non-purpose-made measuring instruments using the existing methods [34]. This requires different kinds of measurements of the necessary informative parameters, and the procedure is time-consuming. To measure the admittance components directly, it is necessary to use special-purpose measuring instruments: multifrequency meters of immittance parameters in the mode of measuring the active and reactive admittance components.

The results of measuring the active and reactive components of admittance at certain frequencies can be shown as graphical dependences between the reference sample and the food product with monosodium glutamate added.

It is only possible to compare the results of measuring the admittance components of the samples, and to make conclusions about the feasibility of using the method for detection of monosodium glutamate, if the following conditions are met:

- the primary transducer used is the same;
- the level of the test sinusoidal signal is the same;
- the primary transducer is connected according to the same scheme;
- the measurement conditions are the same.

During the studies of the electrical parameters of the objects controlled, the admittance components were determined in the frequency range of the test sinusoidal signal with a constant amplitude. The components were measured with an immittance meter at individual frequencies in the range of 100Hz – 100kHz. It has been determined how the admittance parameters (active and reactive components) change with the frequency in a given range, with the object controlled, and with the system “electrode – object.”

As a result, the values of the parameters of the reference food product sample have been compared with those of the sample with the modified composition, and it has been assessed how the active and reactive admittance components change at fixed frequencies within the defined frequency range of a fixed-level sinusoidal test signal.

**Results of the research and their discussion**

Juices, as the most expensive soft drinks, are most often counterfeited. A drink can be adulterated by introduction of additives, which are not provided by the recipe, dilution with water, replacement of one type of drink with another. Adulteration can be widely used both in the course of production and at the stage of selling. The most common falsification of juices is diluting a natural drink with water. When 10–20% of
If water is added to juices, it is impossible to feel the difference organoleptically, and only when up to 50% of it is added, the watery taste appears. So that the watery taste is not felt, various food additives are introduced: sugar substitutes, flavour enhancers, acidity regulators, etc. In accordance with the requirements of international standards, it is forbidden to add flavour enhancers to fruit juices and nectars.

The Codex Alimentarius standards and regulations of the International Association of Juices and Nectars (AIJN) present international approaches to identifying juices, which should be taken into account when studying and developing the methods of determining the quality and authenticity of juices.

Orange juice samples with 20% of distilled water added were used for the experiment. Taking into account the Codex Alimentarius recommendations on the dosage of the food additive E 621 for vegetable juices, monosodium glutamate was added in an amount of 0.3% by weight of the juice into the 80% orange juice. The temperature of the test samples was 22±0.2°C, pH 3.5.

Glutamates are mainly used in the production of snacks and so-called “fast food.” Examples of such food products on the market are potato chips and dry food concentrates. Mashed potatoes were taken as a sample, since potatoes are a component of a great many food concentrates. In accordance with the Codex Alimentarius recommendations on the dosage of E 621 for this group of food products, monosodium glutamate was added into the sample in an amount of 1% by weight of the product. The temperature of the products under study was 22±0.2°C.

The active and reactive admittance components of the food samples were measured with an immittance meter in the mode of measuring the active and reactive components at fixed frequencies in the range 100 Hz – 100 kHz.

The measurement results have allowed obtaining the graphical dependences between the admittance components and the frequency for the controlled and basic samples of juice (Fig. 3) and mashed potatoes (Fig. 4).

Analysis of the dependences of the admittance components for the samples of orange juice and mashed potatoes (Fig. 3, Fig. 4) has shown that the nature of the curves describing them is similar. However, there are significant differences in the absolute values between the controlled (2, 4) and basic (1, 3) samples. The curves for the reactive components of the controlled samples (the ones containing the additive) at frequencies of the lower frequency range (100–1000 Hz) have clearly expressed extreme values (maximum values). Also, the values of the reactive components of both the controlled and the basic samples at frequencies in the higher frequency range (over 20 kHz) become negative (change their polarity). The negative values of the reactive component for the samples with monosodium glutamate added, with an increase in the frequency, are much larger than the values of the basic sample.

The curves that characterise the dependence of the active admittance components on the frequency of the controlled sample, in comparison with similar curves for the reference sample, increase rapidly as the frequency increases. At higher frequencies in this range, the change in values is insignificant. Accordingly, in the frequency range 10–50 kHz, the value of the active admittance component of the juice sample containing monosodium glutamate increases by 2–2.3 times. For the samples of mashed potatoes, these values increase 4 times.

The curves that characterise the dependence of the reactive admittance components on the frequency of the products controlled, in comparison with similar curves for the basic sample, increase rapidly as the frequencies increase. Similarly, the values of the reactive component increase 4 times for juice (frequency 500 Hz), and 8 times for mashed potatoes.

The results of the study have shown that the active and reactive components of the controlled object containing monosodium glutamate differs significantly from the reference sample without monosodium glutamate. Based on this, one can choose the identification criteria by which the presence of monosodium glutamate can be determined. Taking into
account the obtained experimental data on the dependences of the active and reactive admittance components of the juice and mashed potato samples on the frequency, it should be noted that to identify the presence of glutamate in these products, it is necessary to measure the active admittance component of the controlled sample at higher frequencies, and the reactive component at lower frequencies in the range 500 Hz – 50 kHz. Besides, an identification criterion can also be the presence of an extreme value of the reactive component in a certain frequency range.

Such identification features can be based upon to develop a method of identification of monosodium glutamate in food products.

Fig. 4. Dependence of the active (a) and reactive (b) components of admittance on the frequency for mashed potatoes: No. 3 – reference (basic) sample of mashed potatoes, No. 4 – sample of mashed potatoes with monosodium glutamate added

1. The experimental studies of orange juice and mashed potato samples with and without food additives have shown that impedance analysis can be used for process monitoring to obtain information about the presence of monosodium glutamate in food products.

Analysis of the obtained dependences of the active and reactive components on the test signal frequency has indicated ways to identify products with monosodium glutamate. The presence of monosodium glutamate (flavour enhancer) in foods can be determined:

- by changes in the amplitude values of the active admittance component of the controlled sample at a fixed frequency of a certain frequency range;
- by changes in the amplitude values of the reactive admittance component of the controlled sample at a fixed frequency of a certain frequency range;
- by the nature of the change of the curves depending on the defined frequency ranges.

2. At each frequency from 500Hz to 100kHz, the values of the active admittance component of the food samples containing monosodium glutamate are significantly higher than the values of the active components in the same frequency range for the samples with no food additive. This difference can be an identifier for qualitative determination of the presence of monosodium glutamate in food if the measuring conditions are the same.

3. At each frequency from 500Hz to 100kHz, the values of the reactive admittance component of the samples with monosodium glutamate are significantly higher than the values of the active components in the same frequency range for the samples with no food additive. This difference can be an identifier for qualitative determination of the presence of monosodium glutamate in food if the measuring conditions are the same.

4. By the nature of the changes of the curves, their dependence on the frequency reflects a pronounced extreme value for foods that contain a food additive. That is, for a glutamate-containing product, the reactive admittance component increases, with increasing frequency, to a certain value, and then decreases again. For a food sample that does not contain this flavour enhancer, the reactive admittance component only increases in the same frequency range. This difference in the graphical characteristics allows detecting monosodium glutamate in foods in a limited frequency range.

5. The suggested method of identifying the monosodium glutamate additive in foodstuffs allows quickly detecting food products adulterated by dilution, use of raw materials of lower quality, etc., which leads to loss or weakening of the taste and is compensated by introducing the E 621 food additive.

6. The ratio between the components allows determining the dose of the additive in the product if there are samples with different amounts of additives.

References:


Нова робота науковців відкриває нові шляхи екологічної безпеки і продуктивності в сфері харчової промисловості. Використання імпедансного аналізу (EIS) для оцінювання колірної складової (адмітансу) двополюсних систем в перспективних продуктах є ефективним інструментом для забезпечення безпеки харчових продуктів.

Харчові добавки, в яких переважають глутамат натрію, використовуються для підсилення смаку різної консистенції продуктів. У статті представлено результати досліджень з використанням імпедансного аналізу для виявлення глутамату натрію з метою виявлення фальсифікації харчових продуктів, які містять глутамат натрію в кількості 2 ± 0,2 до маси продукту. Результати показали, що глутамат натрію визначається в харчових продуктах з високою достовірністю.

Підсумок

- Встановлено, що глутамат натрію в сировині має значні варіації в залежності від ступеня та часу приготування.
- Порівняння показали, що глутамат натрію в овочевих продуктах має інші властивості, які не дозволяють враховувати його безпосереднім скористання.
- Ультразвукова релаксація має високу точність та проєктує експериментальні умови для ідентифікації глутамату натрію в харчових продуктах.

Ключові слова: глутамат натрію, фальсифікація харчових продуктів, глутамат натрію.


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