Chemistry, Technology and Application of Substances

Vol. 5, No. 2, 2022

T. I. Savchuk[1] , S. I. Korolchuk[1], Zh. O. Kormosh[1], O. M. Yurchenko[1], Yu. V. Panchenko[2]

[1] Lesya Ukrainka Volyn National University,
Department of Chemistry and Technology,
[2] Lviv Polytechnic National University,
Department of Organic Chemistry
Savchuk.Tanja@vnu.edu.ua;
yurii.v.panchenko@lpnu.ua

POTENTIOMETRIC DETERMINATION OF PEROXO COMPOUNDS IN MAYONNAISE

https://doi.org/10.23939/ctas2022.02.149

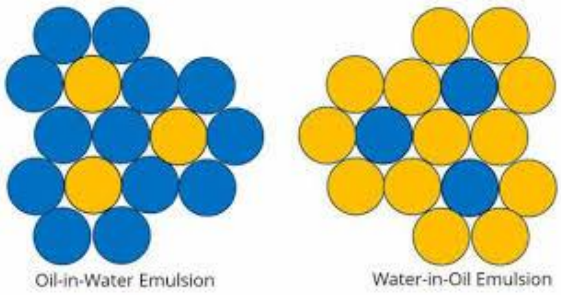
I_3-sensitive sensor was developed, where the ionic acetate of the neutral red triiodide was used as the electrodoactive substance. The main electroanalytical characteristics of the sensor have been studied. It is established that the operating interval of the pH of the chain is 2–12. The interval of linearity of the electrode function is 9×10^{-5} – 1×10^{-1} mol/l, the slope is 51–59 mV/pC. The selectivity of the triiodide sensor by the "individual-solutions" method has been studied. The method of potentiometric titration allows to determine peroxo compounds and peroxide number in mayonnaise in the presence of tartrate, citrate, benzoate, salicylate, oxalate, phthalate ions, glucose, glycine, histidine, aspirin.

Key words: I_3-sensitive sensor; neutral red; ionic acetate; electrode function; density; peroxocompounds; peroxide number; potentiometric titration.

Introduction

Mayonnaise is the most popular ready-to-use sauce. In the concept of healthy nutrition policy, the priority is to eliminate micronutrient deficiencies in the population, and specialized foods and dietary supplements are among the most important tools for optimizing nutrition and public health.

The modern market offers consumers a wide range of mayonnaise of different composition, which is sometimes difficult to navigate. In addition, there is a significant amount of counterfeit products on the market, which do not correspond to the original mayonnaise in terms of quality. The most common falsification of sauces in terms of fat content and egg product content [1–4, 13]. Along with the current trend of creating mayonnaise products with functional ingredients, there is an increase in tempoes and types of falsification of mayonnaise, which are common in the market. One of the methods of falsification of mayonnaise is the replacement of high-calorie product with less caloric, with the appropriate substitution of vegetable oil for water, thickeners, flavors and condiments [16].



Qualitative falsification of mayonnaise can be carried out in the following ways: violation of production technology; violation of the prescription composition; introduction of extraneous additives; introduction of high doses of preservatives and antioxidants. When falsifying the quality of the sauce, namely – violation of the recipe of production, add high doses of preservatives and flavors, emulsifiers and stabilizers when replacing vegetable oil with water.

The second way to falsify mayonnaise, which is quite common, is to replace such a basic ingredient as high-quality oil with low-quality oil, not the first freshness. Such qualitative falsification is established only by laboratory tests during the determination of physicochemical parameters. In addition, vegetable oil is one of the components of the cost of mayonnaise, so in most cases, low-calorie sauces should have a lower price [5–7].

Despite the fact that in mayonnaise and so enter the recipe water in the amount of 24–50 %, and in some species up to 55 %, some manufacturers also add water, and various emulsifiers and stabilizers, bringing the water content to 35–60 %.

This type of falsification of mayonnaise can occur by replacing high-quality vegetable oils – sunflower, corn, olive low-quality – soybean, peanut and even rapeseed.

Chemically, mayonnaise is an oil-in-water emulsion. Therefore, the main raw materials in the production of mayonnaise – oil and water. Emulsifiers and stabilizers are used to increase the stability of the emulsion. So, the main components of mayonnaise: water; oil; egg products; sugar, salt; starches; xanthan gum; acids (lactic, acetic, alcohol vinegar); dyes (Beta-carotene); rubbed mustard; antioxidants (EDTA); preservatives (potassium sorbate). During storage, the quality of mayonnaise depends significantly on the fatty components that are the main components. If fatty components are oxidized, the biological value and organoleptic characteristics deteriorate: "taste" and "smell" may also reduce the rate of "emulsion stability" of mayonnaise [5–15].

Therefore, there is a need to control the number of peroxo compounds, in particular, the peroxide number. An urgent task is to develop a method for determining peroxo compounds, which would have advantages among the proposed methods.

The purpose of the study is to develop a new method for determining peroxo compounds in mayonnaise.

Materials and methods of research

To develop a triiodide sensor, it was necessary to synthesize the ionic association of neutral red with triiodide. The synthesis was performed as follows. A portion of the bean was dissolved in a 100 ml flask, added alcohol and brought to the mark with distilled water. To 100 ml of KI_3 solution was added in small portions on a glass rod. They were left for one day to defend themselves. The precipitate was separated on a Schott filter, after which it was dried at room temperature in the air for three days. Membrane synthesis was performed according to the following method [11]. Powdered polyvinyl chloride (PVC) and an electroactive substance (EAP) were weighed on electron analytical scales. The plasticizers were thoroughly mixed and added: dibutyl phthalate (DBP), dioctyl phthalate (DOP), dinonyl phthalate (DNP), dibutyl sebacenate (DBS) and tricrezyl phosphate (TCP). Cyclohexanone (CGN) was added to the formed mixture and mixed. The clothes were moved to a glass ring attached to the glass; dried for 8 days. Disks with a diameter of 0.5–1.0 cm were cut out of the films with a rubber stopper and glued to the end of a polyvinyl chloride tube with a 10 % PVC solution in cyclohexane. The degree of homogenization of the membranes was assessed using microphotographs obtained on a metallographic microscope "LEICAVMHTAUTO".

An ionometer – I-160 M (measurement error ±0.1 mV) was used to measure the values of the electrode potential; the potential of the electrodes was determined relative to the argentum chloride electrode ECP-10103.

The scheme of the electrochemical cell for measuring the electrode potential is as follows: Ag, AgCl/KCI (sat.). Researched solution/membrane/ internal settlement.

The developed sensor was used for potentiometric determination of peroxo compounds in mayonnaise "European" manufacturer Torchin.

Research results and their discussion

The influence of the nature of the plasticizer on the main electroanalytical characteristics in the system was studied. As plasticizers used: tricrezyl phosphate – TCP, dibutyl sebacenate – DBS, dioctyl phthalate – DOP, dinonyl phthalate – DNP, dibutyl phthalate – DBP [17, 18]. The plasticizer content was 45 % for the triiodide sensor, and the ionic strength of the solutions was maintained at 0.2 mol/l with a solution of CI, respectively, at pH = 7.

The study of the electrochemical properties of the developed sensors by the nature of the plasticizer shows that the best plasticizer for the triiodide sensor is TCP. Since the slope of the electrode function corresponds to the theoretical values of the Nernst function, and the detection limit reaches $n \times 10^{-5}$ mol/l,

which is an order of magnitude higher than the sensors plasticized by other plasticizers (Table 1).

Slightly worse electrochemical characteristics for sensors using DBS plasticizer, the steepness of the electrode function does not reach the theoretical value of the Nernst function for single-charged ions and the lower detection limit $n \cdot 10^{-3}$ mol/l. It is established that the nature of the plasticizer affects the steepness and to some extent the limit of detection of triiodide sensors, which is important when choosing the optimal conditions for the studied sensors. The loss of elasticity and limitation of the life of the sensors on the line is due to the fact that the solvent content in the membrane is reduced and the structure is disturbed. To determine the optimal content of electroactive substance (EAP) in the membrane changed the content of EAP: 5 %, 7 %, 9 %, 12 %, 15 %, and as a plasticizer used TCP with a content of 45 %. The results of studies of the influence of electrode characteristics are summarized in Table 2. It is established that the EAR content does not significantly affect the steepness and the limit of detection of triiodide sensors. The steepness at all EAR contents ranges from 54 to 59 mV/pC, the detection limit varies from $n\ 10^{-5}$ mol/l, electrodoctive substance content 9 % and 15 % corresponds to the theoretical value of the Nernst function for single-charged ions.

Table 1

Influence of plasticizer nature on electroanalytical characteristics of developed sensors

Plasticizer content, %	Steepness of the electrode function, mV/pC	Linearity interval of the electrode function, mol/l	Detection limit, mol/l
tricrezyl phosphate (TCP), 45	59 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$6.3 \cdot 10^{-5}$
dioctyl phthalate (DOP), 45	57 ± 1	$1 \cdot 10^{-4} – 1 \cdot 10^{-1}$	$3.8 \cdot 10^{-4}$
dinonyl phthalate (DNP), 45	59 ± 1	$1 \cdot 10^{-4} – 1 \cdot 10^{-1}$	$6.9 \cdot 10^{-4}$
dibutyl phthalate (DBP), 45	50 ± 1	$1 \cdot 10^{-4} – 1 \cdot 10^{-1}$	$2.5 \cdot 10^{-4}$
dibutyl sebacenate (DBS), 45	51 ± 1	$1 \cdot 10^{-3} – 1 \cdot 10^{-1}$	$3.9 \cdot 10^{-3}$

Table 2

Influence of electrodoctive substance content on electroanalytical characteristics of developed sensors

EAR content, %	Steepness of the electrode function, mV/pC	Linearity interval of the electrode function, mol/l	Detection limit, mol/l
5	59 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$6.3 \cdot 10^{-5}$
7	57 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$5.8 \cdot 10^{-5}$
9	56 ± 1	$1 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$6.9 \cdot 10^{-5}$
10	59 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$6.3 \cdot 10^{-5}$
12	54 ± 1	$1 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$1.9 \cdot 10^{-5}$
15	56 ± 1	$1 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$3.9 \cdot 10^{-3}$

The influence of various factors on the electroanalytical properties of the developed sensors was studied: pH, response time, potential drift, etc.

It is established that the working interval of the electrode is pH 2–12 for the triiodide sensor (Fig. 1) corresponds to the dominant in aqueous solution single-charge anionic form I_3^-.

Potential drift does not exceed 2–4 mV/pC. Stable values of electrode potentials are set for 3–8 seconds. The synthesized membranes retain their characteristics from 4 to 10 months.

It was found that the selectivity does not depend on the nature of the anion that is part of the ionic associate and on the nature and amount of plasticizer that is part of the membrane of triiodide sensors. The selectivity is approximately the same for all membranes studied. The developed sensors are selective for Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, Na^+, K^+, tartrate, citrate-, benzoate-, salicylate-, oxalate-, phtha-

late-ions, glucose, glycine, histidine, aspirin. The selectivity coefficients are given in (Table 3).

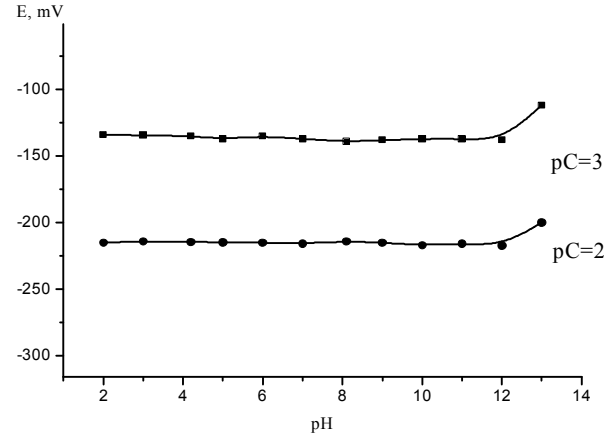


Fig. 1. Graphical dependence of the electrochemical characteristics of the electrode on the pH of the solution

The obtained electroanalytical characteristics of the sensors testify to their effective application for the analysis of various oxidants and reducing agents as an indicator electrode, for example, for potentiometric determination of peroxo compounds in mayonnaise.

The possibility of using the developed method of potentiometric titration for the analysis of food products, namely mayonnaise for the content of peroxo compounds and peroxide number is established.The object of analysis was selected mayonnaise "European" manufacturer Torchin. A solution of KI diluted (1: 4) with sulfuric acid was added to the appropriate portion of mayonnaise. The I_3 selective sensor and reference electrode were immersed in the resulting solution and titrated with $1 \cdot 10^{-2}$ mol/l $Na_2S_2O_3$ solution. Verification of the correctness of the obtained results of the peroxide number by the method of additives is given in Table 4.

Table 3

Coefficients of selectivity of the developed sensors

Ion, compound	lgK
Cl^-	< –4
Br^-	< –4
I^-	< –4
ClO_3^-	interferes
IO_3^-	interferes
$C_6H_5COO^-$	< –4
ClO_4^-	< –4
$B_4O_7^{2-}$	< –4
SCN^-	< –4
NO_3^-	< –4
$C_6H_4(OH)COOH$	< –4

Table 4

Results of determination of peroxo compounds in mayonnaise (n = 5; P = 0,95)

Weight of mayonnaise, mg	Additive, dibenzoyl peroxide, mg	Peroxide value, mmol/kg	S_r
1140	70	6.6 ± 0.6	0.1
1140	80	7.3 ± 0.7	0.2

The advantage of the developed method over the iodometric method recommended by DSTU No. 4570: 2006 [12] is that it does not require the use of organic solvents for pre-separation of fats.

Conclusions

It is shown that the synthesized ionic associates of neutral red triiodide can be used as electrodoactive substances for sensors. The operating conditions of the developed sensors were studied: the influence of the pH of the solution, the nature of the plasticizer, the content of the plasticizer, the content of the electroactive substance, the response time, the lifetime of the sensor. The issue of selectivity of the developed sensors is studied. Based on the obtained results, a new sensitive and selective, easy-to-implement method of potentiometric determination of peroxo compounds was developed, which was tested in their determination in mayonnaise.

References

1. *DSTU 4487-2005 National Standardization. Mayonnaise* [Valid from 2005-11-25]. Kyiv, 2005. 17 p.

2. *Regional Standardization. Mayonnaise. CODEX STAN 168-1989* [Текст]. 16 p. (Regional European Standard).

3. *National Standardization. Mayonnaise. PS:3947-1997* [Тект]. Pakistan standard specification.

4. *National Standardization. Mayonnaise. GSO 05/DS 1316/2002* [Тект]. Standardization organization for G.C.C (GSO). 7 p.

5. *Commercial item description "mayonnaise, salad dressing, and tartar sauce". A-A-20140D.* [Тект]. – The U. S. Department of Agriculture (USDA).

6. Chaban, N. (2012). Ukraine has begun developing a new standard for mayonnaise and mayonnaise sauces. *Oil and fat complex, 2*(37), 52.

7. DSTU 7525:2014. Voda pytna. Vymohy ta metody kontroliuvannia yakosti [Valid from 2014-10-25]. Kyiv, 2011. 13 p.

8. DSTU 4492. Oliia soniashnykova. Tekhnichni umovy [Valid from 2017-06-27]. Kyiv, 2017. 44 p.

9. Mirzanajafi-Zanjani, M., Yousefi, M., Ehsani, A. (2019). Challenges and approaches for production of a healthy and functional mayonnaise sauce. *Food Sci Nutr., 7*(8), 2471–2484. DOI: 10.1002/fsn3.1132.

10. Anamaria, M. (2019). The influence of different factors on the quality of mayonnaise. *Analele Universităţii din Oradea, Fascicula: Ecotoxicologie, Zootehnie şi Tehnologii de Industrie Alimentară, 18* (A), 75–83. DOI: 10.1007/s10068-016-0248-7.

11. Narayana, B., Pasha, C., Cherian, T., Mathew, M. (2006). Spectrophotometric method for the determination of iodate using methylene blue as chromogenic reagent. *Bull. Chem. Soc. Ethiop., 20*(1),143–147. DOI: 10.4314/ bcse.v20i1.21153.

12. *DSTU No. 4570:2006. Zhyry roslynni ta olii. Metod vyznachennia peroksydnoho chysla* [Valid from 2007-01-1]. Kyiv, 2007. 9 p.

13. Depree, J. , Savage, G. (2001). Physical and flavor stability of mayonnaise. *Trends in Food Science & Technology, 12*, 157–163. DOI: 10.12691/jfnr-3-3-2.

14. Kucherepa, N., Shemet, V., Drahonyuk, M., Chuyko, I. (2012). Methods for determining the physical and oxidative stability of mayonnaise. *Scientific Bulletin Lesya Ukrainka Volyn National University*, *17*, 123–127.

15. Saleba, L. (2018). Research of quality indicators of mayonnaise. *Bulletin of KhNTU*, *64*(1), 134–139.

16.Hetrysha, O., Nemirich, O., Valyako, O. (2015). Aspects of domestic and foreign normative documents on mayonnaise. *Scientific works of OnAFT*, *42*(2), 262–265.

17. Kormosh, Zh., Savchuk, T. (2012). New potentiometric sensor for the determination of iodine species. *Material science for the determination of iodine species*, *32*, 2286–2291. DOI: 10.1016/ j.msec.2012.06.016.

18. Kormosh, Zh., Savchuk, T., Korolchuk, S., Basel, Ya. (2013). Sensor for determination of food additive E-917. *Scientific Bulletin Lesya Ukrainka Volyn National University*, *23* (272), 17–20.

Т. І. Савчук[1], С. І. Корольчук[1], Ж. О. Кормош[1],
О. М. Юрченко[1], Ю. В. Панченко[2]
[1] Волинський національний університет імені Лесі Українки,
кафедра хімії та технологій,
[2] Національний університет "Львівська політехніка",
кафедра органічної хімії

ПОТЕНЦІОМЕТРИЧНЕ ВИЗНАЧЕННЯ ПЕРОКСОСПОЛУК У МАЙОНЕЗІ

Розроблено I_3^--чутливий сенсор із використанням як електродоактивної речовини йонного асоціату трийодиду нейтрального червоного. Досліджено основні електроаналітичні характеристики сенсора. Встановлено, що робочий інтервал pH сенсора – 2–12. Інтервал лінійності електродної функції становить $9\cdot10^{-5}$–$1\cdot10^{-1}$ моль/л, крутизна 51–59 мВ/pC. Досліджено селективність трийодидного сенсора методом "окремих розчинів". Розроблена методика потенціометричного титрування дає змогу визначати пероксосполуки та пероксидне число у майонезі в присутності тартрат-, цитрат-, бензоат-, саліцилат-, оксалат-, фталат-іонів, глюкози, гліцину, гістидину, аспірину.

Ключові слова: I_3^--чутливий сенсор; нейтральний червоний; йонний асоціат; електродна функція; крутизна; пероксосполуки; пероксидне число; потенціометричне титрування.