

Electrochemical Method for Determination of Cyclamate using 12-Molybdophosphoric Acid

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Procedure for quantitative determination of the Cyclamate (E-952) by a direct ionometric method with ion-selective electrode (ISE) has been developed. The electrode is reversibly selective to the product of Cyclamate decomposition – cationic complex of cyclohexene sulfamic acid with barium ions. Electrochemical sensor with Polyvinylchloride membrane having an ionic associate of cyclohexene sulfamic acid with barium ions and 12-molybdophosphoric acid as ion exchanger is proposed. It has been experimentally studied the influence of membrane composition and preparation procedure on electroanalytical characteristics of electrode, such as: electrode function, slope, linearity range, pH. The possibility of quantitative determination of the cyclamate in the food additive E-952 and other industrial products using the developed ISE is demonstrated. The method meets all the requirements of modern analysis - simple, safe and inexpensive, sufficient precise, sensitive and selective. Sensor response time doesn't exceed 50 s, and long membrane life (35-55 days) allows to perform analysis without replacement of the membrane. By means of sensor it is possible to determine Cyclamate in solutions containing 10^{-5} – 10^{-2} mol/l with relative standard deviation less than 2.3%. ($\bar{x} - \mu$) 100% / $\mu < RSD$.

eywords: cyclamate; ion-selective electrode (ISE); 12 -molybdophosphoric acid; ionometry; sensor membranes

Електрохімічний метод визначення Цикламати з використанням 12 - молібдофосфорної кислоти

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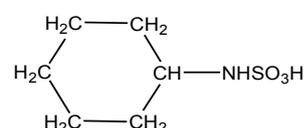
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Опрацьована методика здійснення кількісного визначення Цикламати (E-952) методом прямої іонометрії за допомогою йон-селективного електроду (ISE), котрий оборотний до продукту Цикламати – катіонного комплексу циклогексенсульфамінової кислоти з барій йонами. Запропонована ПВХ мембрана з йонним асоціатом циклогексенсульфамінової кислоти з йонами барію та 12-молібдофосфорною кислотою. Експериментально вивчений вплив різних факторів на характеристики електроду. Показана можливість здійснення кількісного визначення цикламати в харчовій добавці E-952 та інших промислових виробках з використанням розробленого електроду. Спосіб відповідає усім вимогам сучасного аналізу - простий, безпечний та недорогий, достатньою точний, чутливий та вибірковий. Час відгуку датчика не перевищує 50 с та тривалість життя мембрани (35-55 днів) дозволяє проводити визначення без заміни. Тривалість сенсорної відповіді не перевищує 50 с і мембранне життя (35-55 днів) дозволило провести визначення без заміни. За допомогою сенсора можна визначити цикламати у розчинах з концентрацією 10^{-5} – 10^{-2} моль/л. $RSD < 2.3\%$. ($\bar{x} - \mu$) 100% / $\mu < RSD$.

Ключові слова: Цикламати; йон-селективний електрод (ISE); 12-молібдофосфорна кислота; іонометрія; сенсорні мембрани

Cyclamate - low-calorie sweetener [1, 2] is sweeter than sucrose 30 times. Used in food and beverages and the manufacture of diabetic products. Unlike other sweeteners it can be used in the manufacture of food products, requiring additional heat treatment due to resistance to light, temperature and acidity. The

structural formula of sweetener cyclamate (cyclohexylamine - N - sulfonic acid) is as follows:



There are many methods for quantitative determination of cyclamate: colorimetry using pikryl chloride [3], chromatographic [4-9], spectrophotometric [10, 11] with the formation of N,N-dychlorocyclohexylamine, indirect spectrophotometric determination of cyclamate by its degradation products [12] capillary isotachopheresis [13] and others. Chromatographic methods of analysis based on the separation of cyclamate mixture of sweeteners and food additives, followed by determination of individual components using a UV detector and spectrophotometric determination sweetener based on his previous destruction to N,N-dychlorocyclohexylamine. Then carry out specific reactions resulting product with various reagents - resulting in formation of colored complexes that determine photometrically. However, existing methods are complex performance multistage sample preparation and toxic reagents used in the analysis. Thus, the development of alternative methods for the quantitative determination of cyclamate in substance and industrial production is relevant analytical problem. Newly analytical methods shall have a sufficiently metrological parameters and allow cyclamate determine the presence of auxiliary components without their prior separation. The authors of the paper presented by the technique of cyclamate determination by direct potentiometry using ion selective electrodes (ICE), working to product degradation cyclamate.

Experimental part

Cyclamate substance food additive (E-952) production Foodchem International Corporation, China. The content of the basic substance according to the quality certificate was: Sodium cyclamate $C_6H_{12}NNaO_3S$ (E-952), 99.52% in terms of dry matter. Low-calorie sweetener «Cologran» in the form of tablets, which are a part of: sodium cyclamate 40 mg, sodium saccharin 4 mg and excipients such as lactose, acidity regulator and others produced by ONG (Germany).

Liquid sweetener «Milford» produced by ONG (Germany) 200 ml of: sodium cyclamate 24 g and saccharin 2.4 g. Additional components: water, fructose, sorbic acid. Heteropoly acid (HPA) $H_3PMo_{12}O_{40}$, cyclohexanone (CH), grade "p.a" as a solvent-matrix, dibutyl phthalate (DBP) as a plasticizer, dioctylphthalate (DOP), tricresyl phosphate (TCP) puriss p.a., polyvinyl chloride (PVC), grade C-70 puriss p.a. and other reagents grade "p.a"

IR and UV spectra were taken on a spectrophotometer M-80 and M-40 (Carl Zeiss Jena, Germany), respectively. Measurements of electromotive force carried out on the digital ionomer I-130 (Gomelskiy ZIP, Belarus).

Plastifying PVC membrane for ICE synthesized by a known method [16]. As the previously used electrode-active component (EAC) soluble in water ($2 \cdot 10^{-6}$ g/l) and soluble in solvents, plasticizers membrane (10-12 g/l)

deposit product structure interaction heteropoly anions Keggin's and cationic complex with barium particles.

For the synthesis of membrane ion-selective electrode are 0.4500 g of polyvinyl chloride and mix it with 4.5 ml of cyclohexanone (solvent PVC) at 35-40°C and with continuous stirring using a magnetic stirrer. Separately, 1.1 ml of membrane solvent-plasticizer (DBP) was added 0.01 g EAC and stirred to a homogeneous state. The resulting solution mixed with heated after complete dissolution mixing it transferred into a Petri dish with a diameter of 55 mm and kept in a fume hood until complete evaporation of the solvent (cyclohexanone). The result is a homogeneous elastic film containing components in mass %: EAC - 0.62; dibutyl phthalate (DBP) - 71.42; PVC - 27.96. By the same method plasticized membranes were synthesized using as solvent - dioctylphthalate plasticizer (DOP) and tricresyl phosphate (TCP). Before using ISE soaked in solutions of cationic complex with barium particles formed destruction cyclamate, with a concentration corresponding to mid-range content detectable substance. For electrode performance using an electrochemical range (chain): $Ag|AgCl, KCl (sat.) |$ solution substance (10^{-4} M) | membrane ISE || sample solution | $KCl (sat.), AgCl|Ag$.

Due to the impossibility of obtaining the necessary associates through direct deposition anion sweetener typical analytical reagents, such as heteropolyanions Keggin's structure was investigated reaction of complete and partial decomposition cyclamate in an acidic environment. As we know from published data [12], the process is complete destruction of cyclamate by the following reaction (Fig. 1):

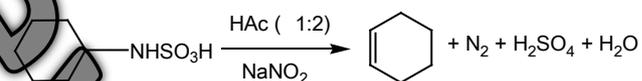


Fig. 1. The scheme complete destruction of chemical cyclamate.

The reaction occurs in a strongly acid medium (pH 1-2) in the presence of 0.1 M solution of sodium nitrite. In the reaction of free nitrogen is released and produced cyclohexene and sulfate ion. However, as seen from the reaction equation, with the resulting products only barium sulfate can be used as an electrode-active substance (EAC) for the synthesis of PVC film membranes ISE, which could indirectly determine cyclamate products for the destruction of the latter. The analysis of scientific data [14, 15] indicates that administration of barium sulfate phase in PVC membrane electrode film is difficult due to its low solubility in typical solvents by ionometry. Therefore, in this case, the use of solvent-plasticizer esters of phthalic acid are not, and specific organic reagents such as potassium tetrakis(4-chlorophenyl) borate, derivatives of bis-(1,2,3,6 - tetrahydrobenzo) - crown ethers. al., which reduces the availability of this method. In addition, techniques developed using

a similar ISE have low sensitivity (10^{-3} M), which limits their use. Therefore, the authors proposed to carry out a partial chemical destruction cyclamate, followed by precipitation EAC, which is the scheme shown in Fig. 2.

Partial chemical destruction cyclamate spend on softer terms, compared with the full destruction. So, to create an acidic environment using acetic acid concentration of 1:10, in contrast to the complete destruction of the chemical, which used acetic acid concentration of 1: 2. This acidity of the medium after the destruction of pH 4-5. Under such conditions the degradation product is cyclohexensulfamide cyclamate, which is further treated with barium salt, resulting in a cationic complex with barium share that the interaction with an excess of 12-molybdophosphoric heteropoly acid forms a soluble compound with lithium-associative nature of the interaction macroions. Methods of UV and IR spectroscopy was confirmed speculation that a weakly acidic medium partial degradation product cyclamate in the presence of doubly charged metal ions in solution exists in the form of stable cationic complex

particle that is able to form soluble ionic associates with heteropoly anion $\text{PMo}_{12}\text{O}_{40}^{3-}$. As the ion metal was used Ba^{2+} , however, given the ability to form chelate complexes with product partial destruction cyclamate, promising also be used cations Mg^{2+} and Ca^{2+} [17]. The resulting sparingly soluble compounds meet the requirements imposed on the electrode-active agents (of sustainability, low water solubility, high solubility in organic solvents) and thus can be used as an EAC for the development of ion-selective electrodes, working to product degradation cyclamate. It was established that the dependence of electromotive force vs the logarithm of the concentration of cationic complex part OC in the concentration range $1 \cdot 10^{-5}$ - $1 \cdot 10^{-2}$ mol/L and linear expressed by the equation:

$$E = a + b \lg C$$

It was the influence of various factors on the characteristics of the developed electrode:

- pH test solution;
- nature of the solvent-plasticizer for the membrane;
- EAC content in the membrane.

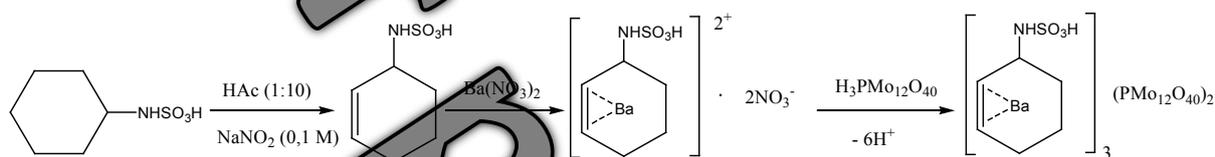


Fig. 2. Scheme of partial chemical destruction cyclamate, followed by precipitation of the formed product to EAC.

The effect of pH test solution on the electrode function slope and linearity range of concentrations shown in the Table 1. Analysis of the experimental data showed that the optimum electrode characteristics ISE achieved with the contents of EAC homogeneous

membrane at 0.01 g, which coincides with the optimum pH of the developed electrodes (pH = 5), and used as a solvent-plasticizer esters phthalic acid - dibutyl- and dioctylphthalate.

Table 1. Dependence ISE electrode characteristics of pH.

Characteristics electrode	pH								
	3	4	5	6	7	8	9	10	
S, mV/pC	10 ± 1	12 ± 1	29 ± 2	25 ± 1	30 ± 2	24 ± 2	31 ± 3	26 ± 2	
Interval linearity mol/l	$1 \cdot 10^{-2}$								
	$-1 \cdot 10^{-3}$	$-1 \cdot 10^{-4}$	$-1 \cdot 10^{-5}$	$-1 \cdot 10^{-5}$	$-1 \cdot 10^{-5}$	$-1 \cdot 10^{-5}$	$-1 \cdot 10^{-4}$	$-1 \cdot 10^{-4}$	$-1 \cdot 10^{-4}$
LOD, mol/l	$1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	

Main characteristics electrode developed by ISE with membranes based product partial destruction sweetener depending on various factors listed in the Table 2.

The response time for the resulting electrode is 40-50 s at concentrations of 10^{-6} - 10^{-4} mol/l is reduced to 10-20 s at concentrations of 10^{-3} - 10^{-2} mol/l. Experimentally determined that the optimal time soaking electrode in a solution with a concentration

that meets mid-range content of the substance, is 7-10 minutes. The slope of the calibration curve (option b) close to the theoretical and twocharged cation is 27-29 mV/pC. Statistical analysis of the data by least squares showed a high enough accuracy. Table 3 shows the calibration curve parameters a and b , the variance Sa^2 and Sb^2 constants a and b , the correlation coefficient r , which characterizes the proximity investigated dependence to functional.

Table 2. The influence of various factors on the characteristics of the resulting electrode.

Plasticizer	EAC content in the membrane, g	S, mV/pC	Interval linearity, mol/l	LOD, mol/l	Life time, days
DBP	m=0.005	27±2	10 ⁻² –10 ⁻⁵	10 ⁻⁵	50
	m=0.01	29±2	10 ⁻² –10 ⁻⁵	10 ⁻⁵	55
	m=0.02	20±2	10 ⁻² –10 ⁻⁵	10 ⁻⁵	50
DOP	m=0.005	24±1	10 ⁻² –10 ⁻⁵	10 ⁻⁵	35
	m=0.01	28±3	10 ⁻² –10 ⁻⁵	10 ⁻⁵	30
	m=0.02	18±2	10 ⁻² –10 ⁻⁵	10 ⁻⁵	35
TCP	m=0.005	31±3	10 ⁻² –10 ⁻⁵	10 ⁻⁵	35
	m=0.01	30±3	10 ⁻² –10 ⁻⁵	10 ⁻⁵	40
	m=0.02	21±3	10 ⁻² –10 ⁻⁵	10 ⁻⁵	34

Table 3. Results of regression analysis calibration curve for the determination of cyclamate ISE through its degradation product in an appropriate range of linearity.

Mass EAC, g	Solvent	a±Δa	b±Δb	S _a ²	S _b ²	r
0.01	DBP	268±8	31±2	3.68	0.34	0.995
	DOP	267±3	33±1	3.09	0.32	0.999
	TCP	261±4	30±1	2.96	0.27	0.999

Potentiometer ICE selectivity ratios determined by mixed solutions [18] and calculated using the formula:

$$K_{i/j}^{\text{pot}} = a_i/a_j.$$

ISE selectivity was determined for the product partial chemical destruction cyclamate relatively cations Na⁺, K⁺, Ca²⁺, Ba²⁺ and relatively sweeteners saccharin, acesulfame potassium and aspartame. Selectivity ratios relative to the organic components of the mixture are shown in Table 4.

Table 4. Potentiometer selectivity ratios K_{i/j} ISE, working to product degradation cyclamate (i - ordainable cation, j - preventing cation)

Interfering ion	K _{i/j}	Excess interfering ion
K ⁺	0.0016	625
Na ⁺	0.0017	588
NH ₄ ⁺	0.0015	667
Ba ²⁺	0.0016	625
Ca ²⁺	0.0019	526
Mg ²⁺	0.002	500
Saccharinate	0.024	40
Acesulfamate	0.24	4
Aspartame	0.26	4

Based on the experimental data, we can conclude that lists organic and inorganic cations have a significant impact on preventing electrode ISE function.

It was investigated by the use ion-selective electrode developed and worked out procedures for potentiometric determination of cyclamate product

through its partial destruction in substance food additive E-952 and other industrial products:

Methods of direct potentiometric determination of cyclamate product through its partial destruction in substance food additive E-952.

To construct the calibration curve developed ISE, cyclamate sample weighing 0.0895 grams quantitatively transferred to a volumetric flask 50.0 ml, add 10 ml of acetic acid (1:10) and made up to mark with distilled water. From the resulting solution 15.0 ml aliquot taken away and transferred to a volumetric flask of 25.0 ml, there is made in 5.0 ml of sodium nitrite solution 0.01M and barium nitrate. Then, the resulting solution is mixed thoroughly and then use it to prepare a series of model solutions with concentrations between 1·10⁻²–1·10⁻⁵ mol/L, containing cationic complex with barium compound. Each solution is transferred to a series of electrochemical cell system of electrodes: indicator - ISE working with the product partial chemical destruction cyclamate, silver chloride - electrode. With potentiometer-ionometer measure electromotive force of each of the solutions. According to the data we plot the dependence E = f(pC). Similarly prepared solution of unknown concentration sweetener, carry it to the electrochemical cell and measure the electromotive force of the sample solution. For the calibration curve (Figure 3) are integrated concentration of cationic compounds, which then transfer the content cyclamate. The research were conducted on model solutions (Table 5), which make it possible to state that the results of potentiometric determination of cyclamate product through its partial destruction is reproducible for n = 7, P = 0.95 (RSD = 0.02). Recovery was 6.98 ± 0.15 (δ = -0.29%).

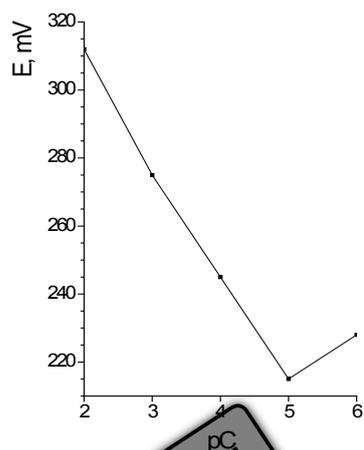


Fig. 3. Potential changes of ion-selective electrode vs logarithm molar concentration of cationic complex of cyclamate product with barium particles, pH = 5.0.

Table 5. The results of analysis of cyclamate in model solutions of pure substance by the proposed ionometric method ($n = 7$, $P = 0.95$)

Taken cyclamate, mg	Founded cyclamate, $(\bar{X} \pm \Delta \bar{X})$, mg	RSD, %	δ , %
7.0	6.98 ± 0.15	2.0	0.3

Note: $\delta = (\bar{X} - \mu) \cdot 100\% / \mu$

Table 6. The results of analysis of cyclamate in «Cologran» Sweetener by potentiometric method ($n = 7$, $P = 0.95$).

The analyte	Content cyclamate in aliquots, mg	Added, mg	Founded cyclamate, $(\bar{X} \pm \Delta \bar{X})$, mg	RSD, %	δ , %
Sweetener «Cologran»	9.60	0	9.64 ± 0.15	1.7	+0.4
		1.00	10.61 ± 0.17	1.7	+0.1
		2.00	11.63 ± 0.12	1.6	+0.3

Note: $\delta = (\bar{X} - \mu) \cdot 100\% / \mu$

The experimental data (Table 6) showed no bias and thus determine the correctness of the results of cyclamate sweetener in «Cologran» by potentiometric method.

Procedure for the determination of cyclamate in «Milford Suss» sweetener.

An aliquot of the sweetener containing sodium citrate and sodium saccharinate is transferred to a volumetric flask of 25.0 ml. In flask add 5.0 ml of acetic acid (1:10) and dilute the flask to the mark with water. With selected pipette 15.0 ml of the resulting solution and transferred into a volumetric flask of 25.0 ml, there is added in 5.0 ml of sodium nitrite and barium nitrate (0.01 mol/l). The resulting solution is thoroughly

Method for determining sodium cyclamate product through its destruction in the dining sweeteners «Cologran».

The exact weight pills pounded powder equal to the average weight of the tablet, quantitatively transferred to a volumetric flask of 25 ml. In a flask made 5.0 ml of acetic acid (1:10) and dilute to the mark with water. From the resulting solution selected aliquot of 15.0 ml, transferred to a volumetric flask of 25.0 ml, there is added in 5.0 ml of sodium nitrite and barium nitrate (0.01 mol/l). The resulting mixture of solutions is mixed thoroughly, then select aliquot of 10.0 ml, transfer it to a beaker and medium acidity adjusted diluted NaOH solution to pH 5.0. Made solution containing cationic complex with barium compound is transferred to the electrochemical cell and measure the electromotive force system. The concentration of cyclamate are on the calibration curve (Figure 3). The results of analysis of cyclamate are shown on Table 6.

The correctness of the results of direct potentiometric determination of cyclamate sweeteners in its degradation by product is estimated by the method of additives (Table 6). To 25.0 ml aliquot sample solution is added 1.0 or 2.0 ml of standard solution with a concentration of 1.0 mg/ml after each additive measure the electrode potential.

mixed, then 10.0 ml aliquot taken away, carry it in a beaker and medium acidity adjusted diluted NaOH solution to pH 5.0. Made solution containing cationic complex with barium compound is transferred to the electrochemical cell and measure the electromotive force system. The concentration of cyclamate find the equation pre-constructed calibration curve (Figure 3).

The accuracy of the results of direct potentiometric determination of sodium cyclamate sweeteners through of its degradation product is estimated by additives method (Table 7). To 25.0 ml aliquot sample solution is added 1.0 or 2.0 ml of standard solution with a concentration of 1.0 mg/ml after each additive measure the electrode potential.

Table 7. The results of potentiometric analysis of cyclamate in «Milford Suss» sweetener for dining ($n = 7$, $P = 0.95$) by additives method.

Sample	Content cyclamate, mg	Added, mg	Founded cyclamate, ($\bar{X} \pm \Delta \bar{X}$), mg	RSD, %	δ , %
«Milford Suss»	9.60	-	9.63±0.16	1.8	+0.3
		1.00	10.71±0.17	1.7	+1.0
		2.00	11.74±0.17	1.6	+1.2

Note: $\delta = (\bar{X} - \mu) \cdot 100\% / \mu$

Conclusion

The method for the direct potentiometric determination of cyclamate using of ion-selective electrode based on the chelate complexes with partial degradation product of cyclamate, which has a high sensitivity, selectivity and ease of implementation

has been developed. In determining the content of the basic substance in Cyclamate substance food additive (E 952) and in samples of industrial products containing Cyclamate, RSD is less than 2.3%. ($\bar{X} - \mu$) 100%/ μ <RSD.

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