

Full Paper

Potentiometric Sensor for the Determination of Povidone-Iodine

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Abstract- The triiodide-selective sensor with a PVC membrane containing ion pair of methyl violet triiodide as electro-active substance was developed. The operating pH range of the triiodide sensor is 2–12. The linearity ranges of triiodide sensor function are 9×10^{-6} – 1×10^{-1} M, the sensor super Nernstian slope are 76 mV/decade. The efficiency of the use of sensor for povidone-iodine determination was shown by potentiometric titration methods.

Keywords- Ionic associates, Triiodide sensor, Potentiometric titration, Povidone-iodine determination

1. INTRODUCTION

The successful application of potentiometry as an analysis method is related in the recent years to the development and practical use of ion-selective electrodes with plasticized polymer membranes. Due to relative simplicity of the principles of the creation of these electrodes and the availability of the manufacturing technology, the realization of fundamentally new opportunities requires more theoretical research both on the nature of the

selectivity of the electrode membrane and the determination of the composition and properties of ion associates that these membranes are composed of. A challenge of the determination of important chemical-analytical properties of the developed sensor samples is of interest. Due to their versatility, the potentiometric sensors of this kind occupy the leading place among electrochemical sensors for the analysis of various objects, and the field of their application constantly widens [1]. The development of scientific approaches in this direction is far from completion. The main challenges are caused by the absence of a theory that would forecast the structure of an ionophore for the creation of a sensor with pre-set electroanalytical properties. A substantial role in this challenge may be played by the determination of the interrelation of physico-chemical properties of the electrode-active component (EAC) (formation, association, distribution constants, thermal behavior etc.) and electroanalytical characteristics of the sensor membranes based on these components.

2. EXPERIMENTAL SECTION

2.1. Reagents and solutions

All chemicals were of analytical-reagent grade. Twice-distilled water was used to prepare all solution and in all experiments. Dibutylphthalate (DBP), dioctylphthalate (DOP), dinonylphthalate (DNP), dibutylsebacate (DBS), tricresylphosphate (TCP), cyclohexanone (CHN), high molecular weight polyvinylchloride (PVC) were obtained from Sigma-Aldrich. Methyl violet (MV) was purchased from Merck.

Standard thiosulfate solution, 1×10^{-1} M, prepared from $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and standardized with potassium iodate solution.

Standard iodine (triiodide) solution, 1×10^{-1} M, prepared from 40 g KI and 12.7 g of I_2 , dissolved in 500 ml of twice-distilled water and standardized with thiosulfate solution. Working solutions were prepared by dilution of the corresponding standard solutions. Triiodide solutions used for the sensor characterization and analytical determinations (1×10^{-8} – 1×10^{-1} M) were prepared daily from the stock solution, diluting the required volume with 0.2 M KI and using 50 mL volumetric flasks.

The stock solution of the basic dye Methyl violet (Fig. 1) with a concentration of 1×10^{-2} M was prepared by dissolving an accurately weighed portion of dye, which was recrystallized from methanol, in twice-distilled water.

The ionic strength of the solutions was adjusted with 0.2 M KI solution. The pH value of solutions was maintained with the use of a buffer mixture (0.04 M CH_3COOH , H_3BO_3 , H_3PO_4 , and a 0.2 M NaOH solution) and controlled potentiometry with a glass electrode.

2.2. Preparation of ion-pair and membrane for sensor

The ion-pair was prepared by mixing 1×10^{-2} M solutions of Methyl violet and triiodide in a ratio of 1:1. The resulting solution was settled for 2 h, and the sediment of ion-pair was filtered out (quantitative rapid filter paper). This residue was treated with 50 mL of cold distilled water. The filter paper containing the precipitate was then dried for 24 h at room temperature. These IPs (low solubility in water and good solubility in membrane plasticizers, along with ion-exchange properties) were used as an electrode-active material for preparing membranes of triiodide sensor.

The generally accepted technique of plasticized membrane: the consists of thorough mixing of the electrode-active substance with PVC dissolved in cyclohexanone or tetrahydrofuran followed by the evaporation of the solvent in a glass ring. We weighed 0.1 g PVC and the respective amount of isolated IP (such that its concentration in the membrane was 5–25 mass%), then mixed the materials thoroughly for homogenizing. The degree of materials homogeneity was estimated from photomicrographs obtained with a LEICA VMHT Auto microhardness tester. Afterwards, 0.1 mL of a plasticizer (DBP, DBS, DOP, DNP or TCP) and 0.5 mL of solvent (cyclohexanone or tetrahydrofuran) were added. The resulting solution was transferred into a previously polished glass form 1.7 cm in diameter, glued to the glass substrate, and dried in air for 1–2 days.

The films obtained after evaporation of the solvent were cut using a rubber cork cutter into disks of 0.5–1.0 cm diameter. These were then glued to the end of the PVC tube with 10% PVC solution in cyclohexanone. The tube was filled with the concentrated standard triiodide solution (1×10^{-2} M), and a copper wire was immersed into it. The sensor was then used for the investigation.

2.3. Apparatus

All EMF measurements were carried out with the following cell assembly. An I-160 M and AI-123 model pH-mV meter with an EVL-1MZ silver-silver chloride reference electrode was used for the measurements of potential difference at 25.0 ± 1.0 °C.

The electronic absorption spectra of solution were measured on an SF-2000 spectrophotometer (LOMO, RUSSIA) over a range of 450–750 nm.

The IR spectra were measured on an AVATAR 330 FT-IR instrument (Thermo Nicolet).

The thermal studies (TG, DTG and DTA) were carried out on an apparatus for complex dynamic thermal analysis–MOM derivatograph (Hungary) under the following conditions: temperature range 20–900 °C, heating rate 5 K/min, sample weight 36 mg, static air medium, channel sensitivities: DTA–150 mV, TG–50 mV.

2.4. Procedure of real samples analysis

The content of povidone-iodine in pharmaceutical preparations "Jox" and "Betadyne" was determined.

The determination of povidone-iodine in "Jox" formulation was performed as follows: a 2–5 ml aliquot of the preparation was taken, then 0.2 M KI solution and 2 ml 2 M H₂SO₄ solution were added. The triiodide sensor and Ag/AgCl reference electrode were immersed into the solution which was then titrated with 1×10^{-3} M Na₂S₂O₃ solution.

"Betadyne" preparation comes as suppositories. The determination of povidone-iodine was performed as follows: the suppositories were placed in a heat-resistant beaker, added 20 ml bidistilled water and heated to the dissolution of the preparation. After the solution cooled, we added 0.2 M KI solution and 2 ml 2 M H₂SO₄ solution, immersed the triiodide sensor and the reference electrode, and then titrated with 1×10^{-3} M Na₂S₂O₃ solution.

3. RESULTS AND DISCUSSION

The association constant was calculated for the ion pair (IP) of methyl violet triiodide MV⁺I₃⁻, numerically expressed as log K_{as}=3.56.

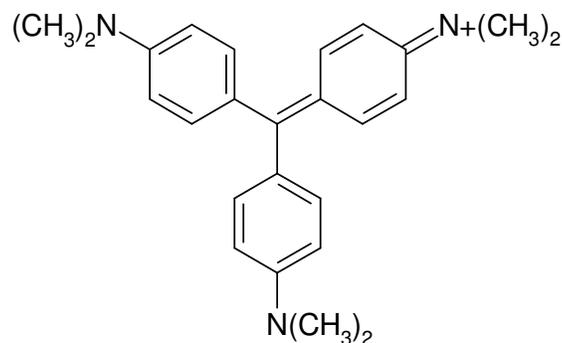


Fig. 1. The chemical structure of Methyl violet

The increase of triiodide content at the constant dye concentration leads to the decrease of intensity and the bathochromic shift of the absorption band of the basic dye.

Such a character of the spectral lines indicates the formation of IP in the aqueous phase [2]. Absorption spectra of the aqueous solutions of IP and the dye are presented in (Fig. 2).

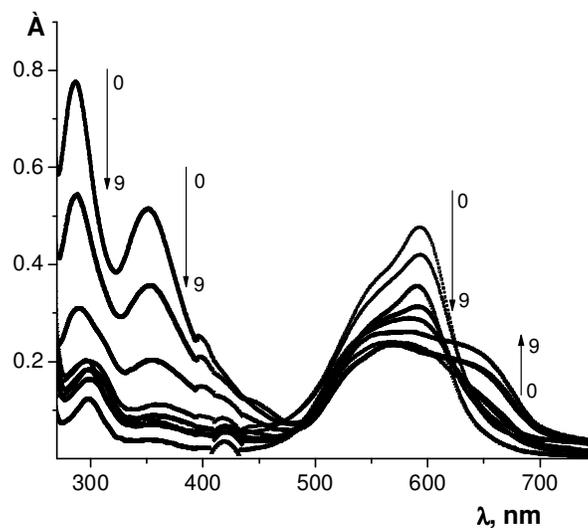


Fig. 2. Absorption spectra of the triiodide-ion – MV system, 1×10^{-5} M MV. Triiodide-ion concentrations, M: 1 – 1×10^{-5} , 2 – 1×10^{-6} , 3 – 2×10^{-6} , 4 – 3×10^{-6} , 5 – 4×10^{-6} , 6 – 5×10^{-6} , 7 – 6×10^{-6} , 8 – 7×10^{-6} , 9 – 8×10^{-6} .

Using sufficiently dilute reagent solutions and maintaining acidity at the level where single-charged species dominate, the formation of the IP of basic dye methyl violet and triiodide follows the reaction:



The association constant then equals:

$$K_{as} = \frac{[MV^+ \cdot I_3^-]}{(C_{I_3^-} - [MV^+ \cdot I_3^-]) \cdot (C_{MV} - [MV^+ \cdot I_3^-])} \tag{2}$$

where $[MV^+ \cdot I_3^-]$ is the equilibrium concentration of the IP. It is easily determined from the spectral data:

$$[MV^+ \cdot I_3^-] = \frac{\epsilon_{MV} \cdot C_{MV} \cdot l - A}{(\epsilon_{MV} - \epsilon_{as}) \cdot l} \tag{3}$$

where A is the optical density at the maximum of the absorption band of MV cation, ϵ_{MV} and ϵ_{as} are the respective molar absorption coefficients of the dye cation and the associate.

IR spectroscopy of the methyl violet–triiodide IP was performed. Determined values of the vibration frequencies in the IR spectrum of the synthesized IP (Fig. 3) were compared to those of the dye spectrum and the tabulated data [3,4].

IR spectra of MV feature a strong band at $3500\text{--}3100\text{ cm}^{-1}$ with a maximum at 3480 cm^{-1} that corresponds to symmetrical and asymmetric vibrations of amine group $\nu(\text{N-H})$. A band at 1400 cm^{-1} , 1390 cm^{-1} , 1170 cm^{-1} feature three strong and medium peaks that correspond to valence vibrations $\nu(\text{C-N})$ which agrees with the tabulated absorption in the range of $\nu(\text{C-N}) = 1280\text{--}1180\text{ cm}^{-1}$.

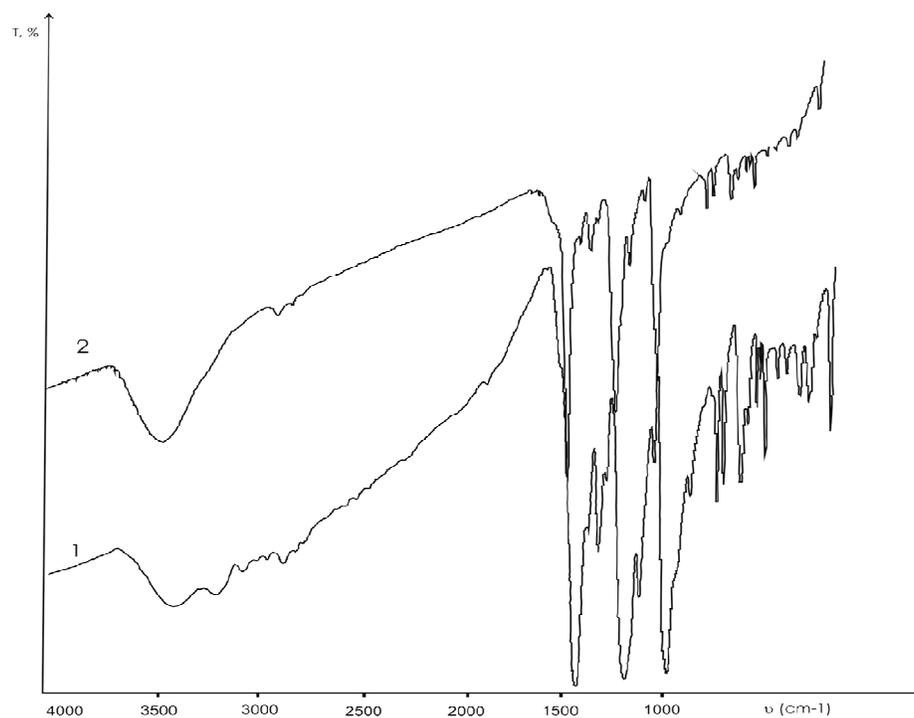


Fig. 3. IR spectra of MV (1) and ion-pair (2)

Thermal behavior of obtained IP was investigated by differential thermal analysis that would show the thermal stability and the character of the decomposition of the complexes [5–9].

The thermolysis of MV^+I_3^- IP undergoes three stages that fit a theoretical interpretation. The thermogram is shown in (Fig. 4), and its computation is presented in Table 1.

Thermal decomposition starts above $170\text{ }^\circ\text{C}$ and is accompanied by the loss of mass and the discharge of the decomposition products. This is followed by carbonization and combustion of the IP which is shown at the thermogram by large exothermal effects at 485

and 530 °C and a significant loss of mass. A large amount of amorphous carbon remained as black plaque at the walls of the crucible in which the thermolysis reaction took place.

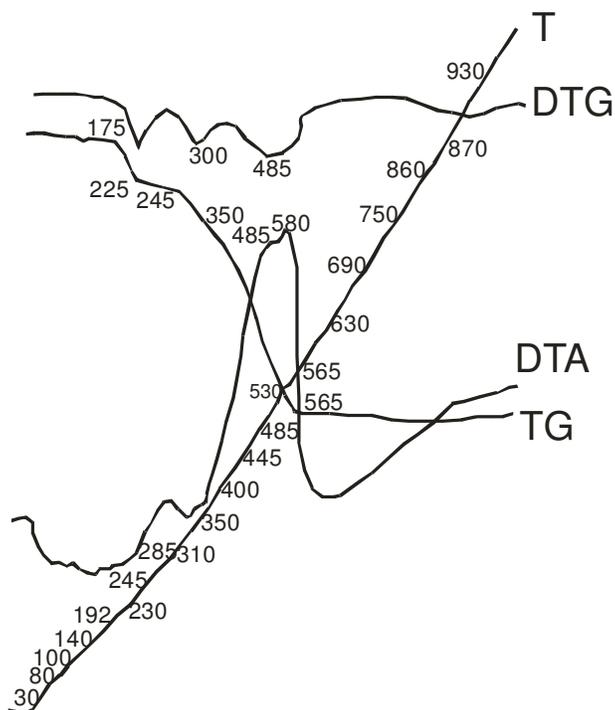


Fig. 4. Simultaneous TG, DTA and DTG curves of the IP $MV^+I_3^-$ in air

It is considered that the ionic permeability of the membrane electrodes is defined by the nature of the EAS and the membrane plasticizer-solvent, and the matrix plays the role of an inert structure-forming element. Therefore the optimization of the electroanalytical characteristics of the developed sensor centered on the investigation of the effects of the membrane composition (EAS content), pH of medium, nature and content of the plasticizer solvent, response time etc.

We have discovered that the best electroanalytical properties are exhibited by the sensors with membranes plasticized by DNP, DOP, DBP and TCP, with the electrode function slope close or equal to the theoretical value of Nernstian function for the single-charged ions (Table 2). The super Nernstian slope has been obtained (76 mV/decade) because possible of the conjugate ion exchange and red-ox processes ($I_3^- + 2e^- = 3 I^-$) will resume in the membrane phase.

DBS-plasticized sensors show somewhat poorer characteristics. The study of the effect of EAS content in the membrane showed that the electrode function slope is steady in the range of 7–15% of EAS (Table 2). Certain small changes were noted in the detection limit values

which are $n \times 10^{-4}$ – $n \times 10^{-5}$ M triiodide. The study of the effect of the plasticizer content proved that the optimal amount is 55–65% of the plasticizer (Table 2).

Table 1. Data of DTA curve of the ion associate $MV^+I_3^-$ and decomposition products

Ion associate	Temperature range, °C	t_{max} , °C	Loss of mass, %		Decomposition products
			Experimental	Decomposition products	
$C_{24}H_{28}N_3^+ I_3^-$ $MV^+I_3^-$	170 – 285	205 endo	16.36	16.67	3NH ₃ + CH ₄ + 2C ₂ H ₄ (12C + 3H + 3I)
	285 – 350	310 exo	10.91		
	350 – 800	485 exo 530 exo	61.36	71.41	
Total loss of mass			88.63	88.08	7C

The effect of the background electrolyte concentration was also investigated. Its increase, in principle, does not affect the electrode characteristics of the system. Generally, the nature and concentration of the background electrolyte are very important in the measurement of the electrode potential. The anion must not compete with the potential-defining anion for the place in the membrane [10].

We also determined the mean time necessary for the membrane electrode potential to reach the value within ± 2 mV of the final equilibrium value. The sensor response time is 2–3 s for the triiodide concentration in the range of 10^{-4} – 10^{-1} M and 5–6 s for the 10^{-6} – 10^{-5} M I_3^- solutions (Fig. 5). Upon reaching the equilibrium, the value of the potential remains constant.

The sensor lifetime is mainly determined by the frequency of its use and averages 10 months from the manufacture date.

The effect of pH on main electroanalytical characteristics of the triiodide sensors was investigated. This factor has the greatest effect on the operation of most all electrodes, due to the chemical processes involving the membrane components, e.g. the triiodide-determining substance, and H_3O^+ or OH^- ions. The acidity of the medium affects also the state of IP and other membrane components. The parallel protolytical processes at the membrane–solution interface are quite complex in description. Generally, the operating range of the sensors is determined by the components of the IP.

The study of the dependence of electrochemical properties of triiodide sensors for the investigated system ($MV^+I_3^-$) on pH showed that the slope of the calibration curves retains constant value in a wide pH range of 2–12 (Fig. 6).

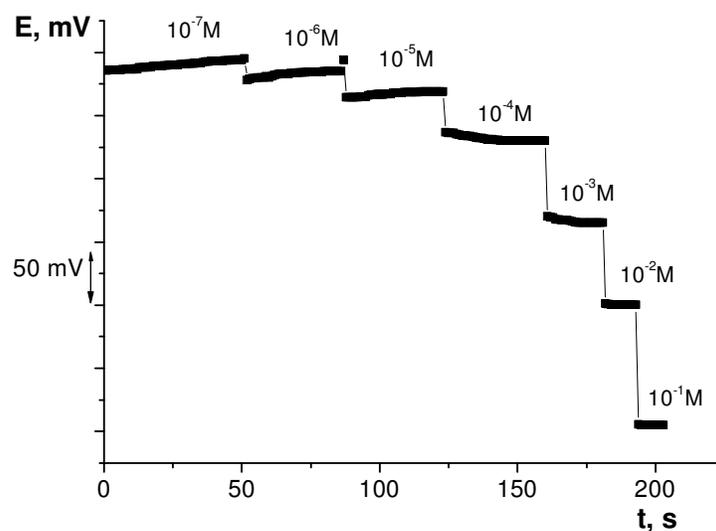


Fig. 5. Sensor response time for various triiodide concentrations

Table 2. Effect of EAS content, plasticizer content and plasticizer nature on main electroanalytical characteristics of the developed sensors

EAS content, %	Plasticizer, content, %	Slope, mVpC^{-1}	Linearity range, M	Low detection limit, M
5		66 ± 1	$1 \times 10^{-4} - 1 \times 10^{-1}$	3.6×10^{-5}
7		52 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	2.4×10^{-6}
9		62 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	7.5×10^{-6}
10	DNP, 65	73 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	6.9×10^{-6}
12		63 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	1.2×10^{-6}
15		62 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	3.5×10^{-6}
	DBS, 65	41 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	1.9×10^{-6}
10	DNP, 65	73 ± 1	$9 \times 10^{-6} - 1 \times 10^{-1}$	1.5×10^{-6}
	DBP, 65	50 ± 1	$9 \times 10^{-5} - 1 \times 10^{-1}$	6.1×10^{-5}
	TCP, 65	60 ± 1	$9 \times 10^{-6} - 1 \times 10^{-1}$	2.8×10^{-6}
	DOP, 65	50 ± 1	$9 \times 10^{-5} - 1 \times 10^{-1}$	6.5×10^{-5}
	DNP, 35	50 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	4.6×10^{-6}
	DNP, 45	53 ± 1	$9 \times 10^{-6} - 1 \times 10^{-1}$	5.2×10^{-6}
10	DNP, 55	76 ± 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	4.1×10^{-6}
	DNP, 65	73 ± 1	$9 \times 10^{-6} - 1 \times 10^{-1}$	1.5×10^{-6}

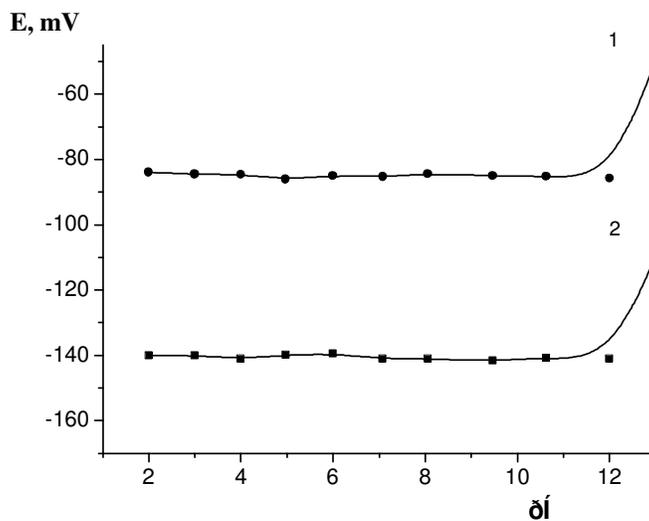


Fig. 6. The effect of the solution pH on the electrode potential of triiodide: pC=3 (1), pC=4 (2)

One of the important questions that still have no explanation theory is selectivity. It is known that the potentiometric selectivity of this kind of electrodes is quite complex and depends on the extraction selectivity of the solvent and on specific bonds of the active centers and counterions.

It was established that the selectivity has practically no dependence on the nature and amount of the plasticizer of the membrane of the triiodide sensors. The selectivity was mostly the same for all investigated membranes. The developed sensors are selective towards Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Na^+ , K^+ , tartrate-, citrate-, benzoate-, salicylate-, oxalate-, phthalate-ions, glucose, glycine, histidine, and aspirin.

3.1. Analytical application

The content of povidone-iodine in pharmaceutical preparations "Jox" and "Betadyne" was determined.

The determination of povidone-iodine in "Jox" formulation was performed as follows: a 2–5 mL aliquot of the preparation was taken, then 0.2 M KI solution and 2 ml 2 M H_2SO_4 solution were added. The triiodide sensor and Ag/AgCl reference electrode were immersed into the solution which was then titrated with 1×10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ solution.

"Betadyne" preparation comes as suppositories. The determination of povidone-iodine was performed as follows: the suppositories were placed in a heat-resistant beaker, added 20 mL bidistilled water and heated to the dissolution of the preparation. After the solution cooled, we added 0.2 M KI solution and 2 ml 2 M H_2SO_4 solution, immersed the triiodide

sensor and the reference electrode, and then titrated with 1×10^{-3} M $\text{Na}_2\text{S}_2\text{O}_3$ solution. The results are given in Table 3.

Based on obtained results, we developed a new sensitive, selective, simple technique of the potentiometric determination of povidone-iodine that was approved in its determination in pharmaceuticals. One can see in Table 3 that $F^*_{\text{tabl}}=9.55>F$; $t^*_{\text{tabl}}=4.3020>t$, confirming that the developed technique has good metrological characteristics and provides a possibility of the determination of povidone-iodine in complex pharmaceutical preparations.

Table 3. Results of the determination of povidone-iodine in pharmaceuticals (n=3; P=0.95)

Name, manufacturer	Stated content	Potentiometric titration with triiodide sensor					Comparison method		
		\bar{X}	ΔX	S^2	t	F	\bar{X}	ΔX	S^2
"Jox", Czech industries	Teva 4.25g in 50 mL	4.13	0.1	0.0016	3.5712	9.12	3.88	0.3	0.0146
"Betadyne" Alkaloid AD-Skopje	200 mg	198.7	0.2	0.0049	4.0195	8.26	197.2	0.5	0.0405

4. CONCLUSIONS

The triiodide-selective sensor with a PVC membrane containing ion pair of methyl violet triiodide was developed. The operating pH range of the triiodide sensor is 2–12. The linearity ranges of triiodide sensor function are 9×10^{-6} – 1×10^{-1} M. Obtained electroanalytical characteristics of the sensors indicate their efficient application as indicator electrodes, for instance, in the potentiometric determination of povidone-iodine in pharmaceuticals.

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