Ministry of Education and Science of Ukraine
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Potentiometric Sensors for the Determination of Vitamins in Pharmaceuticals, Food of Plant and Animal Origin

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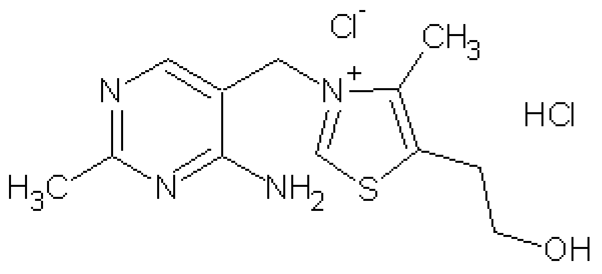
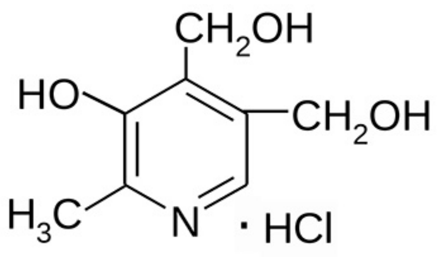
Purpose of the work: To develop sensitive, rapid and easy-to-perform potentiometric techniques for the quantitative determination of vitamins in objects with a complex matrix, in particular, in pharmaceuticals of various dosage forms (solutions for injections, tablet forms), food products of plant and animal origin.

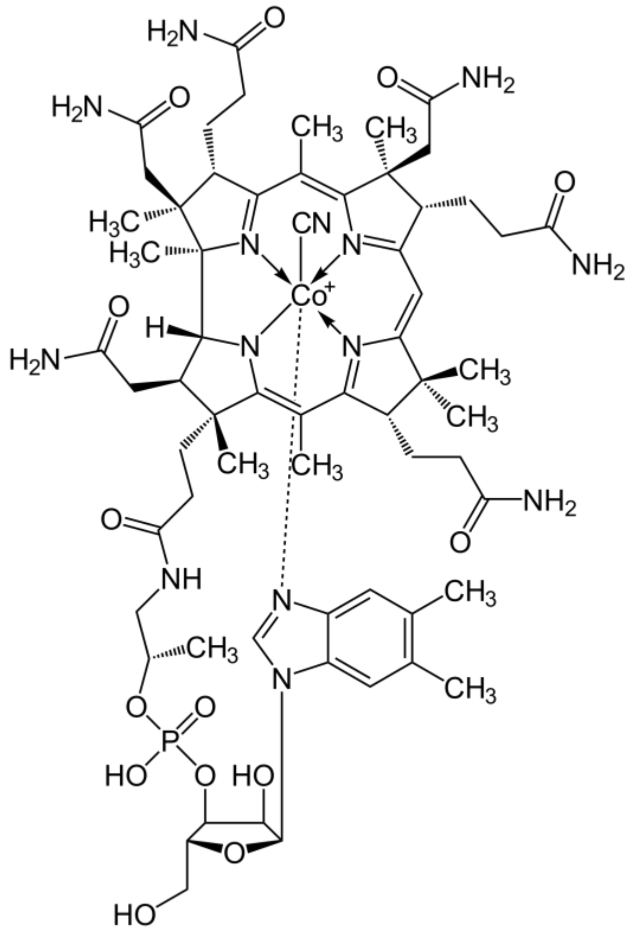
Structural formulas of vitamins



Thiamine hydrochloride



Pyridoxine hydrochloride



Cyanocobalamin

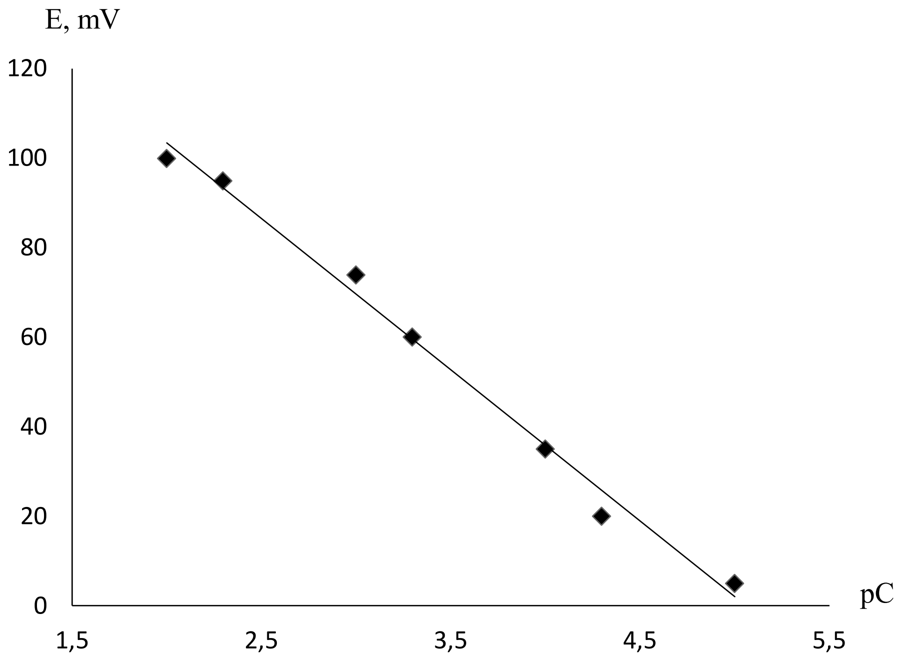


Fig.1 - Dependence of the potential of the sensor with EAS: MPA - B_1 on the concentration of vitamin B_1, internal solution of vitamin B_1 with a concentration of $C = 1 \cdot 10\text{-}4$ M, $R^2 = 0.989$.

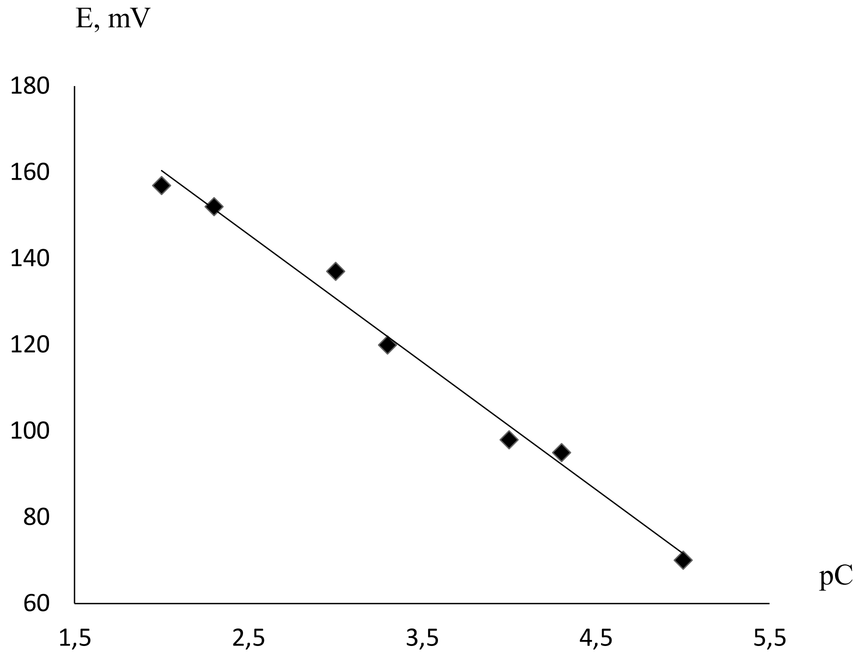


Fig. 2 - Dependence of the potential of a solid-state sensor on concentration vitamin B_1 with EAS: MPA- B_1, $R^2 = 0.988$.

Table 1 - Electrode-analytical characteristics of the designed sensors, which are reversible to vitamin B_1

Electrode type	EAS	pC	S, mV/pC	Time response, min	C_{min}, M
Membrane	MPA – B_1	2,0-5,3	31,7	3	$2,0 \cdot 10^{-5}$
Solid state	MPA – B_1	2,0-5,0	29,0	2	$3,0 \cdot 10^{-5}$

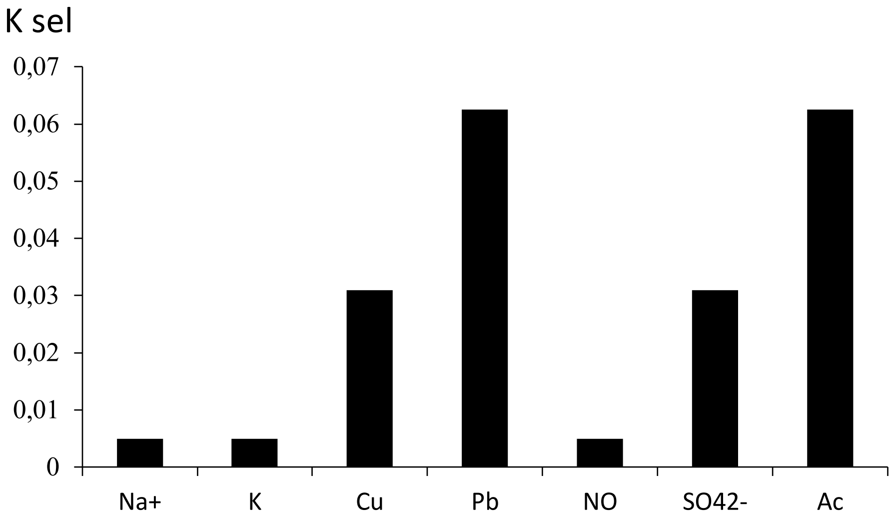


Figure: 3 - Selectivity coefficients of the membrane sensor with EAS: MPA - B_1, reversible to vitamin B_1

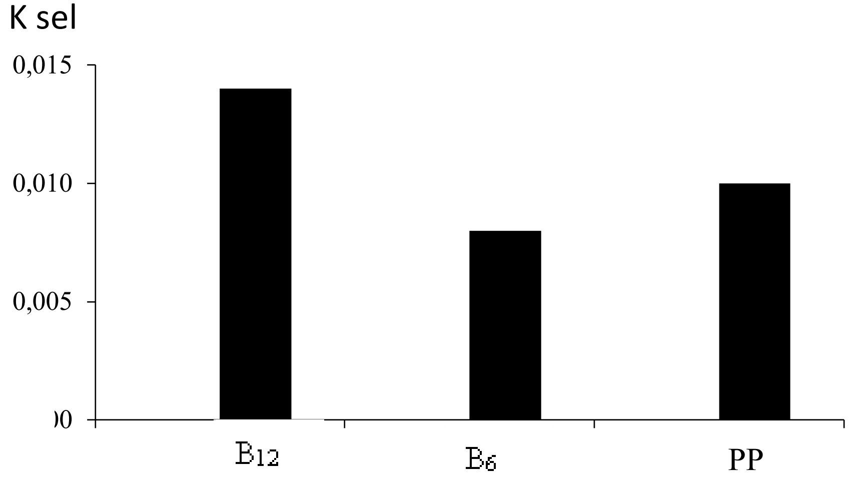


Figure: 4 - Selectivity coefficients of a membrane sensor with EAS: MPA - B_1, reversible to vitamin B_1

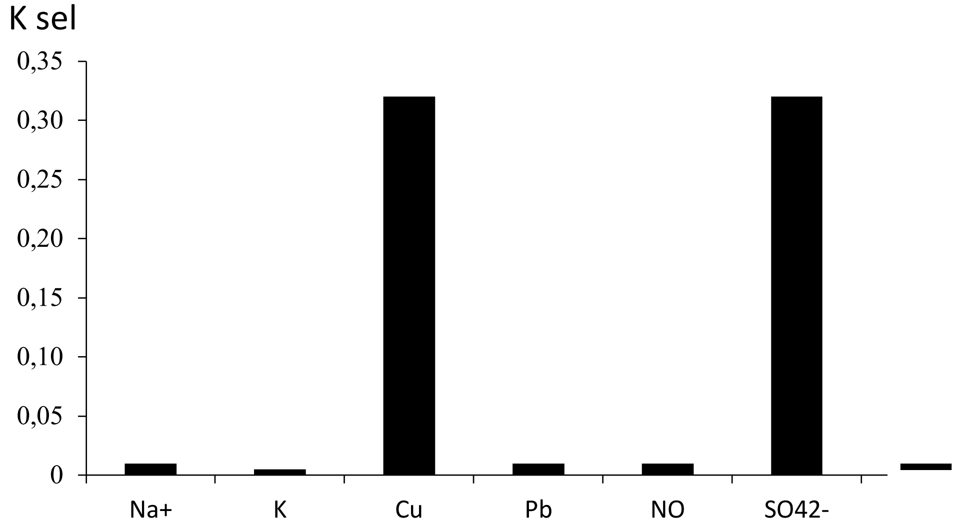


Figure: 5 - Selectivity coefficients of a solid-state sensor with EAS: MPA - B_1, reversible to vitamin B_1

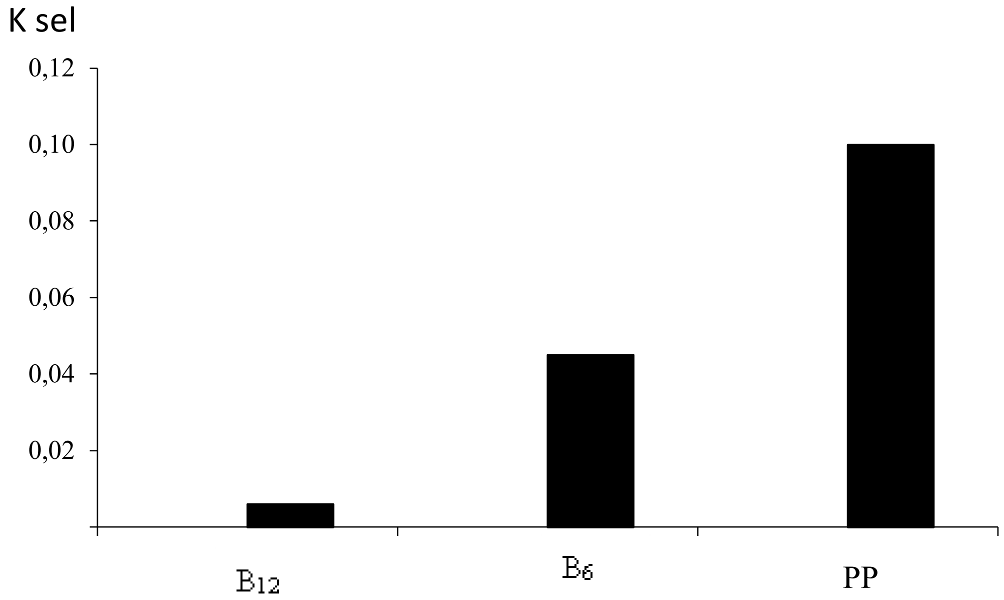


Figure: 6 - Selectivity coefficients of a solid-state sensor with EAS: MPA - B_1, reversible to vitamin B_1

Table 2 - Results of potentiometric determination of thiamine hydrochloride content in real objects by the method of calibration graph (P=0,95; n=3)

An object	**Found**		Declared
	Membrane MPA – B_1	Solid-state MPA – B_1	
Thiamine hydrochloride injection, mg / ml	(48,25±0,12)	(51,33±0,11)	50,00
Tablet form of vitamin B_1 "21-st Century", mg	(97,40±0,35)	(98,06±0,17)	100,00
Pine nut, mg / 100 g of product	(26,69±1,7)	(28,90±1,9)	33,82
Sesame, mg / 100 g of product	(0,74±0,13)	(0,99±0,16)	1,27
Walnut leaves, mg / 100 g of product	(12,15±0,55)	(12,63±0,44)	–

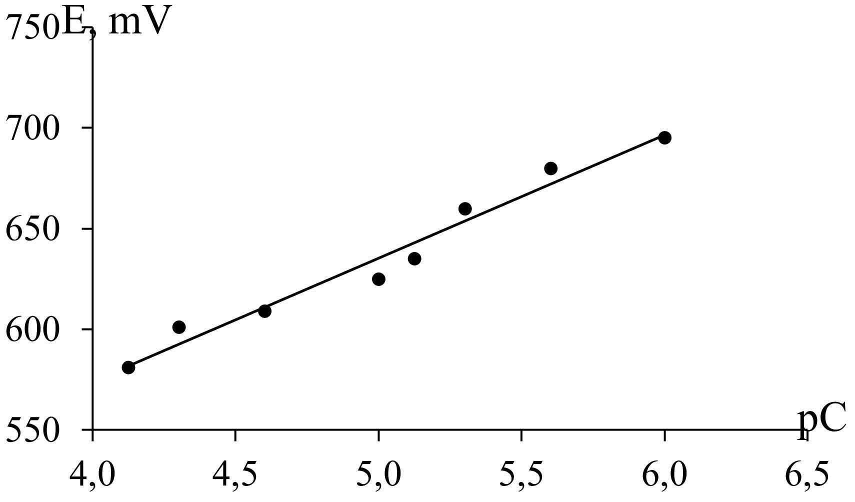


Fig. 7 - Dependence of the membrane sensor potential on the concentration of cyanocobalamin: EAS (B_{12}- MPA), $R^2 = 0{,}9705$

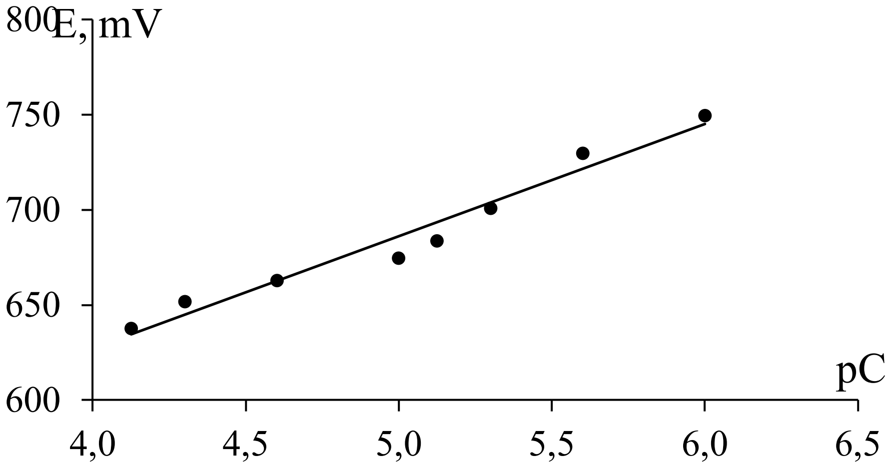


Figure: 8- Dependence of the potential of a solid-state sensor on the concentration of cyanocobalamin: EAS (B_{12}- MPA), $R^2 = 0{,}9658$

Table 3 - Electrode-analytical characteristics of the designed sensors, reversible to cyanocobalamin

Electrode type	EAS	pC	S, mV/pC	Time response, min	C_{min}, M
Membrane	B_{12}:MG =1:2	4,0-7,0	40	3	$3{,}2\cdot10^{-8}$
	B_{12}:MG =3:2	4,0-7,0	42	3	$3{,}2\cdot10^{-8}$
	residue MPA-B_{12}	4,0-6,0	60	3	$6{,}3\cdot10^{-8}$
Solid-state	residue MPA-B_{12}	4,0-6,0	57	2	$7{,}9\cdot10^{-9}$

Table 4 - Selectivity coefficients of sensors reversible to B_{12}

Electrode type		Membrane		Solid-state
EAS	Interfering ions	B_{12}:MG=1:2	B_{12}-MFA	B_{12}-MFA
K_{sel}	Na^+	$1{,}0\cdot10^{-2}$	$1{,}0\cdot10^{-3}$	$1{,}3\cdot10^{-3}$
	Pb^{2+}	$1{,}0\cdot10^{-1}$	–*	–*
	K^+	$1{,}0\cdot10^{-2}$	$2{,}0\cdot10^{-3}$	$2{,}5\cdot10^{-3}$
	Cu^{2+}	$1{,}0\cdot10^{-2}$	$1{,}0\cdot10^{-3}$	–*
	Cl^-	–*	$2{,}0\cdot10^{-3}$	$1{,}0\cdot10^{-3}$
	Ac-	$5{,}0\cdot10^{-2}$	–*	–*
	SO_4^{2-}	$1{,}0\cdot10^{-2}$	$3{,}0\cdot10^{-3}$	–*
	PO_4^{3-}	$1{,}0\cdot10^{-3}$	$1{,}0\cdot10^{-3}$	$1{,}0\cdot10^{-3}$
	NO_3^-	$1{,}0\cdot10^{-2}$	$1{,}2\cdot10^{-3}$	$0{,}9\cdot10^{-3}$
	Tartrate-	–*	–*	$1{,}3\cdot10^{-3}$
	Salicylate-	$1{,}0\cdot10^{-1}$	$1{,}0\cdot10^{-3}$	$1{,}0\cdot10^{-3}$

Note: * — interfere at the ratio 1:1.

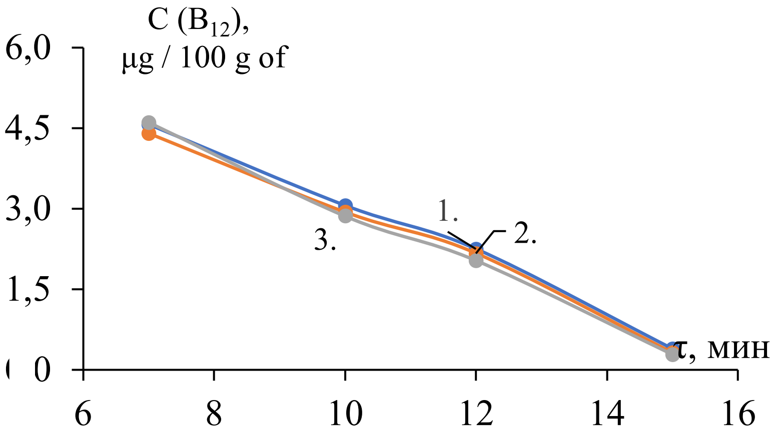


Figure: 9 - Dependence of the B_{12} content in acidic extracts of chicken egg yolk samples on the time of ultrasonic treatment. The B_{12} concentration was determined by the designed sensors: 1-membrane sensor with EAS: B_{12}-MG (1: 2); 2-membrane sensor with EAS: B_{12}-MPA; 3 - solid-state sensor with EAS: B_{12}-MPA

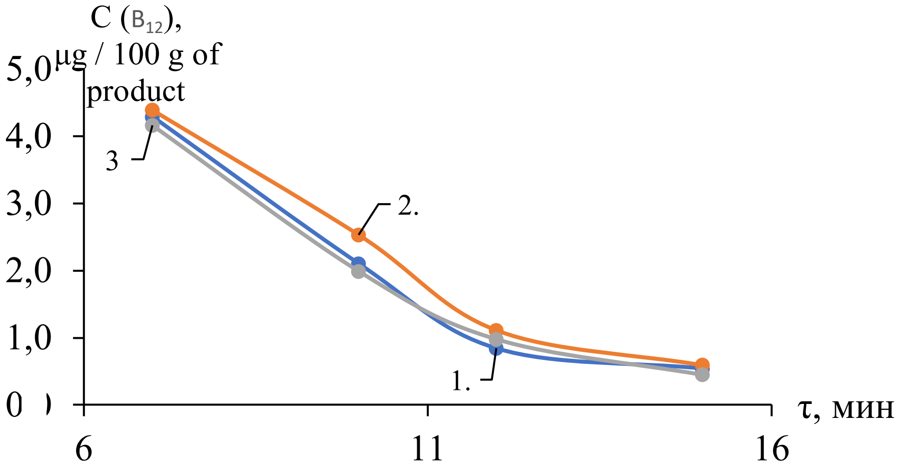


Figure: 10 - Dependence of the B_{12} content in acid extracts of salmon meat samples on the time of treatment with ultrasound action. The B_{12} concentration was determined by the designed sensors: 1 - membrane sensor with EAS: B_{12}-MG (1: 2); 2 - membrane sensor with EAS: B_{12}-MPA; 3 - solid-state sensor with EAS: B_{12}-MPA

Table 5 - Results of potentiometric determination of cyanocobalamin in real objects by the calibration graph method (P=0,95; n=3)

An object	Found			Declared
	Membrane B_{12} :MG=1:2	Membrane B_{12} -MPA	Solid-state B_{12} -MPA	
Injection "Cyanocobalamin", mg / ml	(0,49±0,12)	(0,54±0,11)	(0,53±0,11)	0,50
Sundown Naturals Vitamin B_{12} Tablet Form, mg	(1,48±0,31)	(1,47±0,33)	(1,53±0,32)	1,50
Tablet mixture of vitamins B_1-B_6-B_{12} "Neurobeks-Forte", mg	(0,30±0,07)	(0,34±0,07)	(0,29±0,07)	0,30
Chicken egg yolk, µg / 100 g of product	(4,35±1,02)	(4,24±0,96)	(4,45±1,00)	0,90*
Salmon meat, µg / 100 g of product	(4,14±0,93)	(4,24±0,96)	(3,95±0,93)	7,00*
Note: * - literature data				

Conclusion: a complex of potentiometric techniques for the determination of B vitamins in pharmaceutical preparations, including vitamin mixtures, samples of food products of plant and animal origin, has been developed. The techniques are distinguished by their rapidity, sufficient selectivity and sensitivity.