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Natalia Lutsenko[1], Maria Mironyak[1], Jurij Panchenko[2] and Volodymyr Tkach

IONOMETRIC DETERMINATION OF TANNINS IN INDUSTRIAL PRODUCTION

[1]Ukrainian State University of Chemical Technology, Dnipropetrovsk, Ukraine;TkachVI@ukr.net
[2]Lviv Polytechnic National University, 12 S.Bandery St., 79016 Lviv, Ukraine

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Abstract. The interaction of organic cationic complex particle tannin-Ba^{2+} with heteropolyanion of Keggin structure $PMo_{12}O_{40}^{3-}$ was investigated with the help of spectrophotometric method. These slightly soluble associates were used as electrode active substances (EAS) in plasticized polyvinyl chloride (PVC) membranes of ion-selective electrodes (ISE), sensitive to organic cationic complex particle tannin-Ba^{2+}. Based on the experimental data, a new method of tannin determination in industrial products and oak bark extract by direct potentiometry with the help of ISE was developed.

Keywords*:* electrode active substance, heteropolyanion, ion-selective electrode, direct potentiometry, spectrophotometric research, tannin.

1. Introduction

Tannin belongs to the group of polyphenolic compounds of natural origin, containing a large number of hydroxyl groups (–OH). Its molar mass ranges from 500 to 3000 g/mol. Tannins show tanning properties and have characteristic astringent and sour taste. Tanning action is based on their properties to form stable compounds with proteins, polysaccharides and other biopolymers. In nature tannins are present in the bark and fruits (sometimes in the seeds, roots, tubers) of a large number of plants. The maximum concentration of tannin (20–60 %) was found in an oak, chestnut, acacia, spruce, eucalyptus, chinese camellias (tea), cocoa, persimmons. Tannins create an astringent taste, which is characteristic of fruits and leaves of many plants. Tannic acid protects the plants against different pathogenic bacteria and the consumption of food by insects and animals [1].

In food industry tannin is used to color food products. Coloration properties of the substance food additive E181 (tannin) are especially prized by manufacturers of beverages (mainly wine) and confectionery products – mostly pastries and sweets. Tannin gives an additional light-yellow color and slightly tart flavor to processed food [2].

In medicine and cosmetics beneficial properties of tannin are primarily related to its antibacterial and anti-inflammatory properties. Tannin is able to actively inhibit the reproduction of pathogenic organisms. Astringent, disinfectant, strengthening and wound healing action are basic properties of tannin. Also tannin can be used as a light dye while manufacturing “hand made” soap [3].

In industry tannins are used for tanning leather and fur, preparation of ink, etching of textile fibers [4].

Hydrolyzed and condensed tannins are distinguished by chemical structure. The base of hydrolyzed tannins is esters of gallic acid or related to it digallic and threegallic acids with polyhydric alcohols. Condensed tannins are derivatives of flavonoids, mainly 3,4-flavandiol or 3-flavanol dimers.

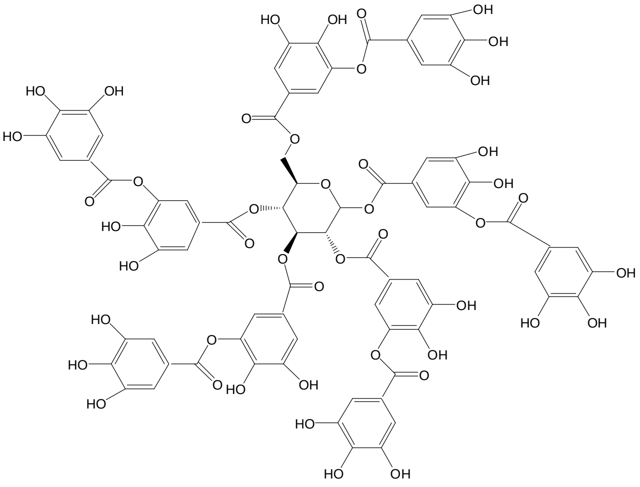
The main sources of tannins are nut-galls, bark of oak, acacia, chestnut, *etc*. The resulting product is a powder of light-yellow color, has a faint specific odor and pungent taste. The powder is dissolved in water, alcohol and glycerol [5].

Classical methods of determining the content of tannins are gravimetric (weight) and titrimetric methods.

Gravimetric method (using skin (ankle) powder) has been adopted as a standard in skin and tanning-extraction industry to evaluate natural tanning materials. This method characterizes the basic properties of tannins but it differs by bulkiness and overestimated results (the additional adsorption occurs over skin powder of polysaccharides and phenolic compounds) [6].

Titrimetric methods of determining tannins include titration with a solution of potassium(VII) manganate [7-8], 2,2',2'',2'''-(ethane-1,2-diyldinitrilo)tetracetic acid

[9-10] and gelatin [11]. These methods are expressive and simple in handling, but have some disadvantages: visual establishing of the equivalence point depends on the human factor; low sensitivity.



Structure of tannin

There is a method of coulometric titration of tannin with coulometric titrant (hypoiodite ions that are formed during disproportionation of electrogenerated iodine in alkaline medium) [12-13]. The method is distinguished by high sensitivity and accuracy, but complicated in handling.

Spectrophotometric methods of determining tannins are based on the ability of tannins to form colored chemical compounds with iron-tartaric reagent in the presence of phosphate buffer [14], Folin- Ciocalteu reagent [15-16], Folyna-Denis reagent [17-18] and other substances. One of the reagents is added to the studied sample of plant material. The absorbance is measured by a spectrophotometer after coloring. Percentage of tannins is determined from the calibration curve using the tannin solutions series.

Conductometric method for determination of tannin is also known [19-20]. The disadvantages of this method are the use of toxic solvents (isobutyl alcohol) and the use of the color reaction with Fe(III). The product of this reaction is the substance unstable in time.

Hence, the urgent analytical problem is the development of alternative methods of tannins quantitative determination in the industrial products, allowing to identify compounds in cosmetics and pharmaceutical dosage forms in the presence of auxiliary components without their prior separation.

The usage of electrochemical methods of analysis, including direct potentiometry is an alternative to existing methods as far as it provides an opportunity to develop new expressive and simple ways for quantitative determination of tannin content in cosmetics and medical forms that will differ by sufficient analytical and metrological parameters (the expressiveness and sensitivity), simplicity and low cost equipment.

A new method of quantitative determination of tannin content in cosmetics by direct potentiometry using ion-selective electrode sensitive to the complex organic cationic tannin- Ba^{2+} was developed in this work. Heteropolyanions (HPA) of Keggin structure as counterions for electrode active substances and for ion-selective electrodes were used [21-22].

2. Experimental

UV absorption spectra were registered on a SF-46 spectrophotometer within the range $\lambda = 200–350$ nm in quartz cuvettes ($l = 1$ cm). Distilled water was used as a solvent in all cases. UV spectra of these substances were recorded relatively to the solvent (distilled water).

Plasticized membranes were synthesized for ion-selective electrodes by the standard method [21, 22].

Electrode characteristics were obtained using the electrochemical cell:

Ag	Ag Cl, KCl	Test solution	Membrane	Solution of the test substance $C = 1.0 \cdot 10^{-4}$ M	KCl, AgCl	Ag

Galvanic cell consists of a membranous ion-selective electrode (inner solution – solution of the test substance $C = 1.0 \cdot 10^{-4}$ M; inner electrode – wire Ag/AgCl in KCl) and silver chloride electrode EVL-1M31 with KCl solution. An electromotive force (EMF) was measured using an ionomer I-130.

pH was measured by the universal ionomer 150 MI with the electrode ESC 10601/4.

Following reagents were used:

1. Tannin.

Tannin solution with the concentration $C = 1.0 \cdot 10^{-2}$ mol/l was prepared as it is further shown. A sample of dry tannin (1.7010 g) was dissolved in 100.0 ml of distilled water at the temperature of 293 K. Further solutions were prepared by diluting the previous one.

2. MPA (12-molybdophosphoric acid) $H_3PMo_{12}O_{40} \cdot 26H_2O$.

The solution with the concentration $C = 1.0 \cdot 10^{-2}$ mol/l was prepared as follows. 2.2940 g of the sample were dissolved in 100.0 ml of distilled water at the temperature of 343–353 K. Further solutions were prepared by diluting the previous one.

3. WPA (12-wolframophosphoric acid) $H_3PW_{12}O_{40} \cdot 31H_2O$.

The solution with the concentration $C = 1.0 \cdot 10^{-2}$ mol/l was prepared in the following way. 3.4382 g of the sample were dissolved in 100.0 ml of distilled water at the temperature of 343–353 K. Further solutions were prepared by diluting the previous one.

4. Ba $(NO_3)_2$ (barium nitrate).

The solution with the concentration $C = 1.0 \cdot 10^{-2}$ mol/l was prepared as follows. 2.6100 g of the sample were dissolved in 100.0 ml of distilled water at the temperature of 293 K.

To produce membranes ISE the following reagents were used:

– PVC (polyvinyl chloride), grade C-70 – membrane matrix.

– CH (cyclohexanone) – solvent matrix.

Esters of phthalic acid were used as solvents of plasticized membrane:

– Dibutyl phthalate (DBP);

– Dioctyl phthalate (DOP).

The associates of organic cationic complex particle tannin-Ba^{2+} with 12-molybdophosphoric and 12-wolframophosphoric acids were used as electrode active substances.

3. Results and Discussion

To investigate the influence of solution pH on the properties of tannin the absorption spectra in the UV region of the spectrum of tannin solutions at its own pH = 5 (Fig. 1) and more acidic and more alkaline solutions (Fig. 2) were recorded.

Table 1 shows the results of spectroscopic studies of aqueous solutions of tannin, depending on the solution acidity.

According to experimental data the absorption bands of tannin aqueous solution (270–280 nm) are stored by changing the acidity of the solution, but their intensity decreases with decreasing pH or increasing the acidity relative eigenvalue solution. At higher pH as to its own (pH = 5) absorption bands are shifted by 15–20 nm towards visible light.

The interaction of the organic cationic complex particle tannin-Ba^{2+} with 12-molybdophosphoric heteropolyacid was investigated with the help of spectrophotometric method (Fig. 3). The study was conducted at tannin solution own pH (pH = 5), since the absorption band at a given pH solution corresponds to the published data on tannin (Tan) [13].

Table 2 shows the results of spectroscopic studies of tannin aqueous solution, MPA and associate of Tan-Ba^{2+}-MPA.

The absorption bands of aqueous solutions of ionic associates Tan-Ba^{2+}-MPA retain the absorbtion bands typical of the starting material. It indicates immutability of the chromophore in the reaction system and confirms the associative nature of the interaction.

Since the associate retains the absorption band at $\lambda_{max} = 300$ nm, which is characteristic of MPA, the ratio of the reacting components in the reaction is determined by saturation at a given wavelength.

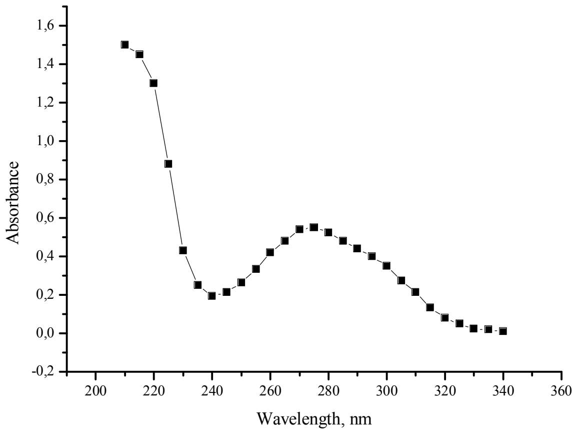


Fig. 1. UV absorption spectra of tannin aqueous solution at pH = 5 (own acidity of the solution) $l = 1$ cm, $C = 1.0 \cdot 10^{-5}$mol/l, solvent, comparison solution –distilled water

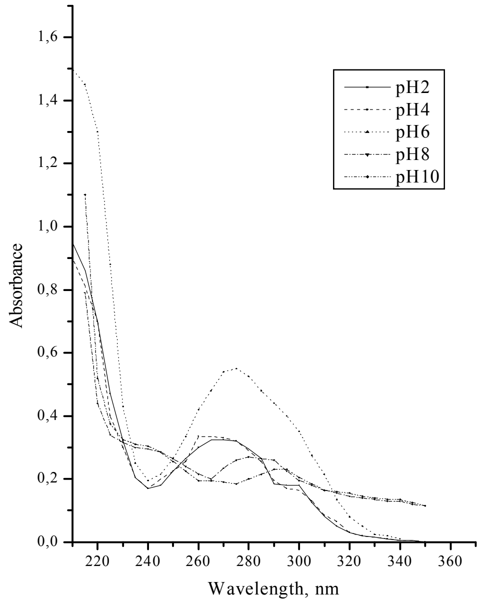


Fig. 2. UV absorption spectra of tannin aqueous solution at different pH $l = 1$ cm, $C = 1.0 \cdot 10^{-5}$mol/l, solvent, comparison solution –distilled water

Table 1

UV absorption spectra of aqueous solutions of tannin, depending on pH

pH	λ_{max}, nm	Characteristic	$\varepsilon_{conditional.}$
2	210	Absorption band of medium strength	95000
	270	Weak absorption band	32500
	295	Shoulder (290–300)	18000
4	210	Absorption band of medium strength	90000
	270	Weak absorption band	33000
	295	Shoulder (290–300)	17000
5	210	Iintense absorption band	150000
	275	Absorption band of medium strength	56000
6	210	Intense absorption band	150000
	275	Absorption band of medium strength	55000
8	220	Absorption band of medium strength	90000
	235	Shoulder (230–240)	30000
	280	Weak absorption band	27000
10	220	Absorption band of medium strength	110000
	235	Shoulder (230–240)	31000
	295	Weak absorption band	23000

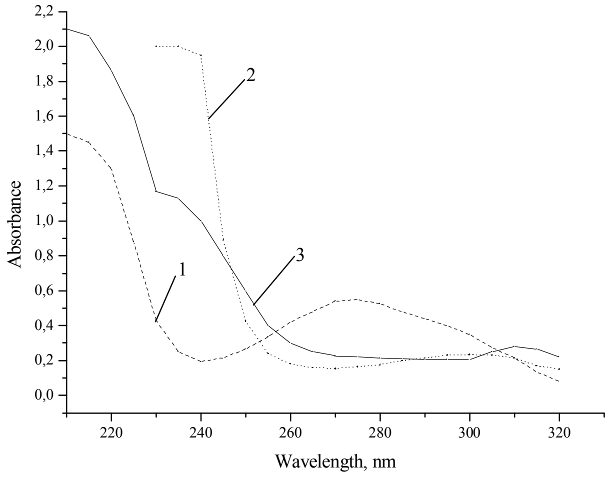


Fig. 3. UV-absorption spectrum of tannin aqueous solution (Tan) (1), an aqueous solution of 12-molybdophosphate acid (MPA) (3) and their association with Ba^{2+} (2). $C_{MPA} = 1.0 \cdot 10^{-5}$ mol/l, $C_{Tan} = 1.0 \cdot 10^{-5}$ mol/l, $C_{associate} = 1.0 \cdot 10^{-5}$ mol/l, solvent and comparison solution – distilled water; $l = 1$ cm, pH = 5

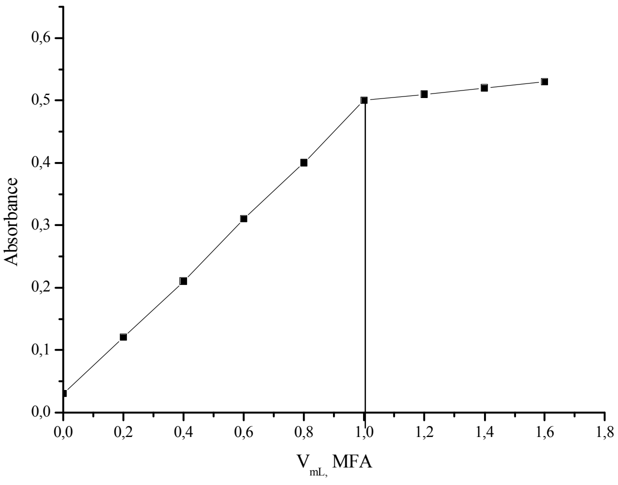


Fig. 4. Dependence of Tan-Ba^{2+}-MPA system absorbance on MPA concentration. $V_{Tan} = 1.5$ ml, $C_{MPA} = 1.0 \cdot 10^{-4}$ mol/l, $C_{Tan} = 1.0 \cdot 10^{-4}$ mol/l, $\lambda = 300$ nm, $l = 1$ cm

Table 2

UV absorption spectra of aqueous solutions of tannin , MPA and their associate

Compound	λ_{max}, nm	Features of UV spectra	$\varepsilon_{conditional.}$
$H_3PMo_{12}O_{40}$	210	Intense absorption band	210000
	235	Shoulder	113000
	310	Weak absorption band	28000
Tannin	210	Intense absorption band	150000
	275	Absorption band of medium strength	56000
Tannin associate with MPA	235	Intense absorption band	200000
	300	Weak absorption band	23500

The compositon of the complex formed with HPA was determined by UV spectroscopy. To determine the associate composition the method of molar ratios is considered to be very informative. To establish the possible composition of tannin-Ba^{2+}-HPA associate the direct saturation of the aqueous solution of the system (tannin-Ba^{2+}) with a concentration of $1.0\cdot10^{-4}$ mol/l is performed by MPA standard solution with a concentration of $1.0\cdot10^{-4}$ M.

Methods of solutions preparation are as follows. In 9 volumetric flasks with the volume of 25.0 ml we add 1.5 ml of $1.0\cdot10^{-4}$ M aqueous solution of tannin and 0.5 ml of barium nitrate with a concentration of $1.0\cdot10^{-2}$ mol/l. Then we saturate them by MPA aqueous solution (0.2; 0.4; 0.6; 0.8; 1.0; 1.2, 1.4, 1.6 ml) with a concentration of $1.0\cdot10^{-4}$ mol/l at pH = 5.0. The volume is adjusted to the mark by distilled water and the optical density of the resulting solution at $\lambda = 300$ nm is determined.

The curve of saturation was built and the reacting components ratio was determined (Fig. 4).

According to experimental data (Fig. 4) the ratio of the reacting components of the (Tan-Ba):MPA complex is 3:2 and the complex compound structure $(Tan\text{-}Ba)_3(PMo_{12}O_{40})_2$ is formed.

$$[Tan\text{-}Ba]^{2+} + [PMo_{12}O_{40}]^{3-} = (Tan\text{-}Ba)_3(PMo_{12}O_{40})_2$$

These associates were used as an electrode active matter in the plasticized membrane ion-selective electrodes sensitive to tannin.

ISE with plasticized PVC membranes were developed, where ionic associates $(Tan\text{-}Ba)_3(PMo_{12}O_{40})_2$ and $(Tan\text{-}Ba)_3(PW_{12}O_{40})_2$ were used as the electrode active substances.

The influence of different factors on the characteristics of developed ISE (the slope of the electrode function and range of linearity) was investigated:

– pH test solution;

– the nature of the solvent-plasticizer membrane;

– the nature of electrode active substance;

– electrode active substances quantitative content in the membrane.

The main characteristics of the developed ion-selective electrode of EAS based on complex organic cationic particles tannin-Ba^{2+} and heteropolyanion 12-molybdophosphoric heteropolyacid according to the nature of the membrane solvent-plasticizer and pH are shown in Table 3.

According to experimental data, the best electrode characteristics are observed in the range of pH = 3–5 and DBP as a solvent (linearity $C = 1.0\cdot10^{-5}$ M).

Table 3

Dependence of ISE electrode characteristics on solution pH for membrane with $PMo^{VI}_{12}O_{40}^{3-}$ heteropolyanion

pH	Solvent	S, mV	Range of linearity, mol/l	C_{min}, mol/l
2	DBP	35.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$7.0\cdot10^{-6}$
	DOP	43.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$9.0\cdot10^{-6}$
3	DBP	30.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$5.0\cdot10^{-6}$
	DOP	35.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
4	DBP	31.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$5.0\cdot10^{-6}$
	DOP	34.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
5	DBP	30.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$5.0\cdot10^{-6}$
	DOP	27.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-4}$	$5.0\cdot10^{-5}$
6	DBP	28.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$3.0\cdot10^{-6}$
	DOP	25.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-3}$	$5.0\cdot10^{-4}$
8	DBP	40.0 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$8.0\cdot10^{-6}$
	DOP	22.0 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-3}$	$4.0\cdot10^{-4}$
10	DBP	41.0 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$9.0\cdot10^{-6}$
	DOP	21.0 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-3}$	$5.0\cdot10^{-4}$

Table 4

Dependence of ISE electrode characteristics on solution pH for membrane with WPA

pH	Solvent	S, mV	Range of linearity, mol/l	C_{min}, mol/l
2	DBP	31.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
4		31.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
5		32.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
6		35.0 ± 1.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-5}$	$3.0\cdot10^{-5}$
8		40.0 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-4}$	$5.0\cdot10^{-5}$
10		42.5 ± 2.0	$1.0\cdot10^{-2}$–$1.0\cdot10^{-4}$	$5.0\cdot10^{-5}$

Table 5

Electrode characteristics developed by ISE

The solvent	Content of EAS in the membrane	*S*, mV	Range of linearity, mol/l	C_{min}, mol/l
DBP	0.005	30.0 ± 1.0	$1.0 \cdot 10^{-2}$–$1.0 \cdot 10^{-5}$	$5.0 \cdot 10^{-6}$
	0.010	30.5 ± 1.0		
	0.020	31.0 ± 1.0		
DOP	0.005	27.0 ± 1.0	$1.0 \cdot 10^{-2}$–$1.0 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$
	0.010	27.5 ± 1.0		
	0.020	27.3 ± 1.0		

Table 4 shows the main characteristics of electrodes for membrane-based EAS 12-wolframophosphoric acid.

It is observed from experimental data (Table 4) that ISE membrane-based 12-molybdophosphoric acid has better characteristics, so in further studies we use the membrane with EAS-based MPA.

Table 5 shows the results of determining the effect of quantitative content electrode active substances in the membrane on the characteristics of ISE (EAS-$(Tan\text{-}Ba)_3(PMo_{12}O_{40})_2$). The studies were conducted at pH = 5.

As we can see from the experimental data content of EAS does not significantly affect the characteristics of the membrane ISE.

The results of instrumental studies of the reaction of heteropolyanion $PMo_{12}O_{40}^{3-}$ with organic cationic complex particle tannin-Ba^{2+} are used in the development of quantitative determination methods of tannin.

Validation of the developed method ionometric tannin determination was performed on the solution of tannin substances by "introduced-found" Table 6.

Table 6

Results of tannin content determination in the solution of tannin substances (*n* = 5, *P* = 0.95)

Introduction, mg	Found, $x \pm \delta$, g	Sr
17.00	17.00±0.31	0.22

The aqueous extract of oak bark with the greatest tannin content was selected as a solution to be tested for verifying the developed method.

Ionometric determination of tannin in the extract of oak bark was performed according to the following procedure. The exact weight of oak bark (10.0 g) was transferred to a heat resistant flask, 100.0 ml of distilled water was added and extracted in a water bath for 30–35 min at 363–368 K. The obtained extract was filtered and transferred to a volumetric flask of 100.0 ml and adjusted to the mark by water. The obtained solution was diluted if necessary by distilled water and placed in the electrochemical cell with the system of electrodes. ISE is indicator electrode, silver chloride electrode is sensitive to organic cationic particles tannin-Ba^{2+} and reference one. We measured the electromotive force in the solution and determined the quantitative tannin content by the calibration curve with ionomer (Fig. 5).

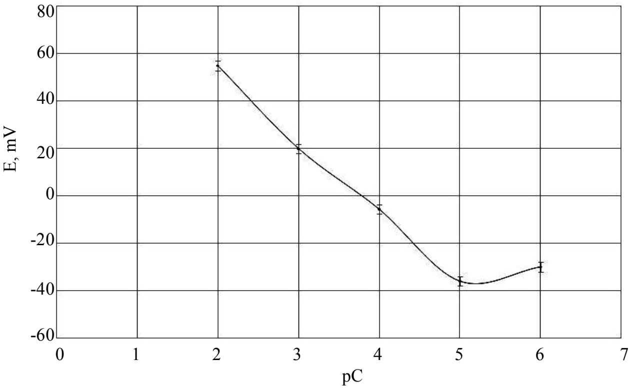


Fig. 5. Graphical dependence of the ion-selective electrode potential on the logarithm of tannin concentration *E* = *f*(*pC*). The cathode (indicator electrode) – developed ion-selective electrode; the anode (reference electrode) – silver chloride electrode; pH = 5.0

The correctness of the results of direct potentiometric determination of tannin in the extract of oak bark was evaluated using the method of supplements. To do this, the aliquot volume 1.0 ml of the extract obtained from the oak bark was transferred to a volumetric flask of 100.0 ml and adjusted to the mark by distilled water. 0.5 ml of standard solution with tannin concentration of 0.001 mol/l were added to 25.0 ml of the resulting solution and the electromotive force is measured after each supplement.

The use of the developed ion-selective electrode with EAS based on complex organic cationic particles tannin-Ba^{2+} and heteropolyanion 12-molybdophosphoric heteropolyacid in the analysis of cosmetic products was investigated.

Since tannin is used as a component of cosmetics the ionometric method was developed for determining tannin in the lotion using the developed ion-selective electrode and the silver chloride electrode as the reference electrode.

Ionometric determination of tannin in the lotion for rinsing the oral cavity was performed by the following procedure. The aliquot of 1.0 ml of lotion transferred to a volumetric flask of 100.0 ml and the volume adjusted to the mark with distilled water. The obtained solution was placed in the electrochemical cell with a system of electrodes. The cathode (indicator electrode) developed ion-selective electrode and the anode (reference electrode)– silver chloride electrode. The electromotive force measured in solution by ionomer and tannin quantitative content was determined by calibration curve (Fig. 5).

The correctness of the results of direct potentiometric determination of tannin in the lotion was evaluated by the additives method. For this purpose, aliquots lotion of 1.0 ml volume was taken, transferred to a volumetric flask of 100.0 ml and adjusted to the mark by distilled water. 0.3 ml of standard solution with tannin concentration of 0.001 mol/l was added to 25.0 ml of the resulting solution and the electromotive force was measured after each supplement.

We compared the results obtained by the designed method with the results obtained according to the known procedures (spectrophotometric method [24] and titration with a solution of potassium(VII) manganate [6]).

Table 7 shows the results of the quantitative determination of tannins in water extract of oak bark and cosmetic products.

The experimental data show the relative error of the potentiometric single determination of the amount of tannins is ± 2.45 % (*P* = 0.95). The latter indicates that the developed method is more accurate than titration with a solution of potassium(VII) manganate and no worse than the spectrophotometric method. Metrological characteristics of the methods coincide with theoretical data [6, 25].

Examining correct determination of tannin content in oak bark extract and cosmetic products was performed by the additives method. The results are shown in Table 8.

Experimental data confirm the correctness of the results of direct potentiometric determination of tannin content in the extract of oak bark and industrial products, as well as lack of the systematic error.

4. Conclusions

On the basis of comprehensive studies the reaction of interaction of the organic cationic complex particle tannin-Ba^{2+} with heteropolyanion of Keggin structure $PMo_{12}O_{40}^{3-}$ and $PW_{12}O_{40}^{3-}$ a new method of tannin content determination in substance, oak bark extract and cosmetic products was developed with the best analytical and metrological parameters.

1. The reaction of interaction of the organic cationic complex particle tannin-Ba^{2+} with heteropolyanion of Keggin structure $PMo_{12}O_{40}^{3-}$ by the spectrophotometric method was investigated. Composition and bond character of the obtained slightly soluble associates were determined.

Table 7

Results of tannin content determination in oak bark extract and cosmetic products (*n* = 5, *P* = 0.95)

Method	Sample	The theoretical tannin content, %	Found tannin, %	Sr	*E*, %
Ionometric	Oak bark extract	8.0–40.0	15.48 ± 0.38	0.02	2.45
	Lotion	-	2.25 ± 0.05	0.01	2.22
Titration with a solution of potassium(VII) manganate	Oak bark extract	8.0–40.0	18.17 ± 0.95	0.03	5.08
	Lotion	-	3.12 ± 0.13	0.02	4.17
Spectrophotometric	Oak bark extract	8.0–40.0	15.90 ± 0.40	0.02	2.52
	Lotion	-	2.39 ± 0.07	0.01	2.93

Table 8

Validation of tannin content ionometric determination in oak bark extract and cosmetic products (*n* = 5, *P* = 0.95)

Sample	Content in aliquot volume, g	Additive, mg	$x \pm \delta$, mg	Sr
Oak bark extract	0.330	–	0.334 ± 0.011	0.028
		0.330	0.662 ± 0.017	0.022
		0.660	0.996 ± 0.014	0.011
Lotion	0.220	–	0.220 ± 0.007	0.030
		0.220	0.442 ± 0.007	0.012
		0.440	0.663 ± 0.011	0.010

2. We synthesized the slightly soluble associates of the constant composition with the associative character of the bond of the organic cationic complex particle tannin-Ba^{2+} with heteropolyanion of Keggin structure $PMo_{12}O_{40}^{3-}$ and $PW_{12}O_{40}^{3-}$ which were used as electrode active substances in ISE membranes sensitive to organic cationic complex particle tannin-Ba^{2+}.

3. ISE sensitive to organic cationic complex particle tannin-Ba^{2+} were developed. They have satisfactory electrode characteristics and are recommended for quantitative determination of tannin content in the industrial products by a direct potentiometry.

4. The technique of determining tannin in oak bark extract and cosmetic products by direct potentiometry was developed. The technique was tested on real objects of industrial production and complies with all the requirements of modern analysis. It is simple, quick, safe, available and has the sufficient accuracy, sensitivity and selectivity. Experimental data confirm the results of ionometric determination of tannin content in industrial output and lack of error.

Developed method can be used for quantitative determination of tannin content in cosmetic products (lotions, deodorants).

List of abbreviations

PVC – polyvinyl chloride
ISE – ion-selective electrode
HPA – heteropolyanion
MPA – 12-molybdophosphoric acid
WPA – 12-wolframophosphoric acid
Tan – tannin
EAS – electrode active substance

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ЙОНОМЕТРИЧНЕ ВИЗНАЧЕННЯ ТАНІНУ У ПРОМИСЛОВІЙ ПРОДУКЦІЇ

Анотація. *Досліджено реакцію взаємодії катіонної комплексної частки танін-*Ba^{2+} *з гетерополіаніоном структури Кеггіна* $PMo_{12}O_{40}^{3-}$ *спектрофотометричним методом. Отримані малорозчинні асоціати використано як електродноактивні речовини в пластифікованих полівінілхлоридних мембранах йон-селективних електродів (ІСЕ), оборотних до органічної комплексної катіонної частки танін-*Ba^{2+}*. На основі отриманих експериментальних даних розроблено нову методику визначення таніну у промисловій продукції і екстракті кори дуба методом прямої потенціометрії з використанням розроблених ІСЕ.*

Ключові слова: *електродноактивна речовина, гетерополіаніон, йон-селективний електрод, пряма потенціометрія, спектрофотометричне дослідження, танін.*