



SPECTROPHOTOMETRIC INVESTIGATIONS OF THE INTERACTION REACTIONS OF GUANIDINE COMPOUNDS WITH HETEROPOLYACIDS OF KEGGIN STRUCTURE

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ABSTRACT

The influence of the acidity of the solution on the properties of salts of polyhexamethylene guanidine was studied by the UV-spectroscopic method in this work. The studied guanidine compounds cannot participate in chemical reactions in an equivalent ratio due to the complex structure of the molecule under certain conditions. Therefore, the influence of the solution acidity and type of destruction on the properties of hexamethylenediamine salts, which are the products of chemical destruction of polyhexamethylene guanidine salts, was studied. The possibility of a reaction between the organic cations of the studied guanidine compounds and the anions of the 12-molybdophosphate heteropoly acid of the Keggin structure was investigated and the nature of the bond in the obtained compounds was determined. The composition of the complexes and the ratio of components in the reactions of polyhexamethylene guanidine, hexamethylene diamine and 12-molybdophosphate heteropoly acid were determined by the saturation method. The results of these studies can be used to develop methods for the determination of salts of polyhexamethylene guanidine and hexamethylenediamine in various industrial facilities using the ionometric method using potentiometric sensors sensitive to polyhexamethylene guanidine and hexamethylene diamine.

Keywords: hexamethylene diamine, heteropolyanion, 12-molybdophosphate heteropolyacid, polyhexamethylene guanidine, spectrophotometry, surfactants.

1. INTRODUCTION

Polyhexamethylene guanidine salts are high molecular weight surfactants of the cationic type. A comparative analysis of chemical compounds of various groups (chlorine-containing, peroxide, aldehydes, ketones, phenols, quaternary ammonium compounds, and surfactants) showed that the surfactants (cationic and ampholytic) are the most promising disinfectants. The advantages of cationic surfactant-based products are stability, safety and low toxicity.

The presence of polar guanidine groups in the molecule gives high antimicrobial efficacy to the salts of polyhexamethylene guanidine, and non-polar polyethylene units promote the adsorption of molecules on cell membranes. Polyhexamethylene guanidine salts are widely used as biocidal substances for various purposes: purification of drinking water, wastewater, swimming pool water, a component of medicines and cosmetics, industrial materials with prolonged antiseptic properties [1-8].

At the same time, polyhexamethylene guanidine salts are normally biodegradable substances. There are enzyme systems in a living organism that can cause their degradation, preventing the accumulation of the drug. When released into natural water bodies, these substances are able to be effectively sorbed by various components of water pollution with an anionic nature (colloidal particles, oil products, anionic surfactants, dye molecules). Salts of polyhexamethylene guanidine pass into the bottom layer,

where, under the action of activated sludge, their biodegradation processes are significantly accelerated [9].

The general formula of salts of polyhexamethylene guanidine (PHMG) is presented in Figure-1.

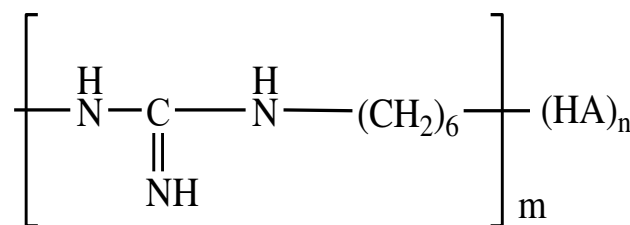


Figure-1. Polyhexamethylene guanidine salts structural formula.

Ratio $m/n = 1 - 2$, $m = 10 - 100$ monomer units.

The molecules of polyhexamethylene guanidine salts can take both expanded and folded conformation in the form of micro clubs in solutions due to the large mass and length of the polymer chains, depending on various conditions [10]. Moreover, not all reaction centers of guanidine groups can take part in intermolecular interactions, therefore, in addition to solutions of polyhexamethylene guanidine salts, solutions of its degradation products (hexamethylenediamine salts) were also investigated. Hexamethylene diamine salts are formed



during the destruction of polyhexamethylene guanidine salts when boiling alkaline or acid solutions [1].

The spectrophotometric methods are most often used to determine the content of various salts of polyhexamethylene guanidine [11-16]. Electrochemical (amperometric titration [17], inverse voltammetry [18], capillary electrophoresis [19]), titrimetric [20] and fluorimetric methods [21] are also used to determine these compounds in various industrial facilities. Ionometric methods using sensors sensitive to polyhexamethylene guanidine cations (PHMG) and its destruction product (hexamethylene diamine) can be an alternative solution.

The anion of 12-molybdophosphate heteropoly acid was chosen as the counterion for the possible formation of ionic associates since previous researches showed the high reactivity of the Keggin heteropolyanions with respect to nitrogen-containing organic substances with the formation of compounds with the ion-associative nature of the bonds between the organic cation and heteropolyanion [22-32].

The influence of the acidity of the solutions on the properties of polyhexamethylene guanidine salts and the interaction reactions of polyhexamethylene guanidine and hexamethylene diamine with the heteropolyanion of 12-molybdophosphate acid was researched spectrophotometrically in the UV spectral area (200-330 nm). Distilled water was used as a solvent and a comparison solution.

2. MATERIALS AND DEVICES

Spectrophotometric studies carried out with the spectrophotometer SF-46 (UV- spectra).

The following reagents are used in the work:

- 12-molybdophosphate acid, $H_3PMo_{12}O_{40} \cdot 26H_2O$ (analytically pure);
- polyhexamethylene guanidine phosphate $C_{252}N_{108}H_{594}O_{72}$ (pure grade);
- sodium hydroxide (analytically pure);
- chloride acid (conc.) (analytically pure).

3. EXPERIMENTAL PART

The UV spectra of aqueous solutions of polyhexamethylene guanidine salts are characterized by two absorption bands (Figure-2):

- a medium-intensity band with an absorption maximum at 210 - 220 nm corresponds to the chromophore group - NH_2 and the band appears due to the presence of a free pair of electrons in the Nitrogen atom ($n \rightarrow \sigma^*$ transition);
- a low-intensity band in the range 260 - 270 nm corresponds to the presence of the $C = N$ group in the molecule due to $\pi \rightarrow \pi^*$ transitions.

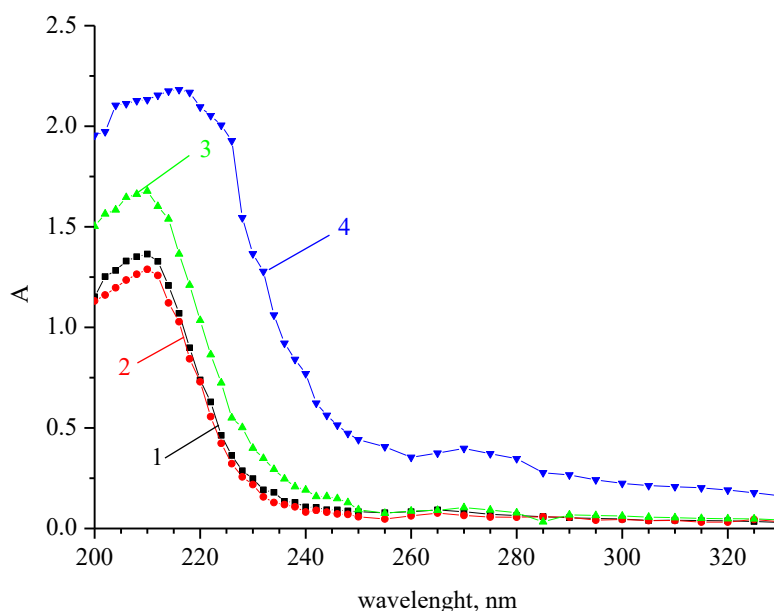


Figure-2. UV absorption spectrum of PHMG at pH = 3.0 (1), pH = 5.0 (2), pH = 7.0 (3), pH = 9.0 (4).

The aqueous solutions of PHMG salts should have absorption maxima at 210-220 nm and 268 nm according to published data [1]. The spectral characteristic at pH = 9.0 has the greatest correspondence with the

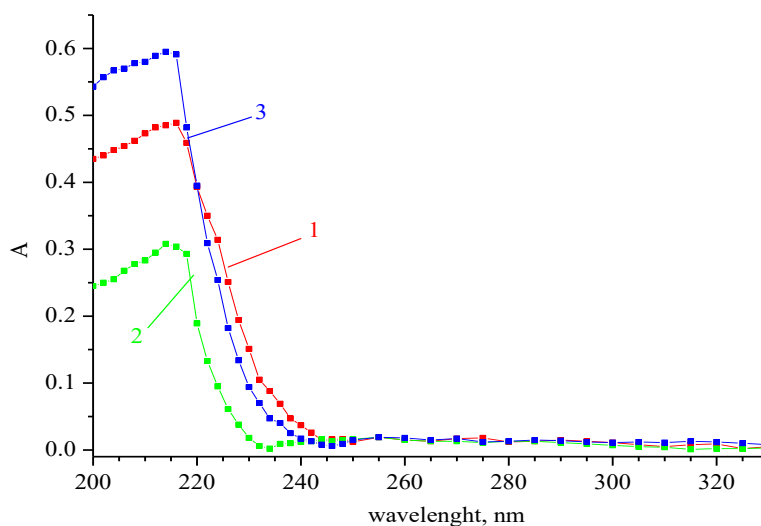
published data. The absorption bands of other solutions are shifted due to changes in the acidity of the medium (Table-1).

**Table-1.** The spectral characteristics of polyhexamethyleneguanidine depending on pH.

pH of the solution	wavelength, nm	$E_{exp.}, l \cdot mol^{-1} \cdot cm^{-1}$
3.0	210	136400
	265	9200
5.0	210	128800
	265	7700
7.0	210	167800
	270	10400
9.0	215	218200
	270	39800

The influence of pH during destruction on the properties of the obtained solutions of hexamethylenediamine salts was also investigated (Figure-3). Since ionic associates with a 12-molybdophosphate heteropolyacid cannot be obtained in strongly alkaline

solutions due to the destruction of the heteropolyacid anion and the formation of a molybdenum oxide precipitate, a solution obtained by alkaline degradation followed by adjusting the acidity to pH = 2.0 was also investigated.

**Figure-3.** UV absorption spectrum of HMDA depending on the obtaining conditions: destruction at pH = 2 (1) and pH = 12 (2), destruction at pH = 12 with adjustment to pH = 2 (3).

The UV spectra of aqueous solutions of hexamethylenediamine salts, regardless of the type of destruction, are characterized by a medium-intensity absorption band with an absorption maximum at 212-216 nm, which corresponds to the -NH₂ chromophore group and the n → σ* transition in the Nitrogen atom (Table-2). The highest intensity of this band is observed for hexamethylenediamine obtained by the method of acid destruction, as well as alkaline destruction with further conversion of pH to an acidic medium.

Table-2. The spectral characteristics of hexamethylenediamine.

Type of destruction	wavelength, nm	$E_{exp.}, l \cdot mol^{-1} \cdot cm^{-1}$
pH 2	216	2960
pH 12	214	1870
pH 12 - pH 2	212	3570

Figures 4-6 show the absorption spectra of polyhexamethylene guanidine salts, hexamethylenediamine, 12-molybdophosphate heteropolyacids, and its ionic associates.

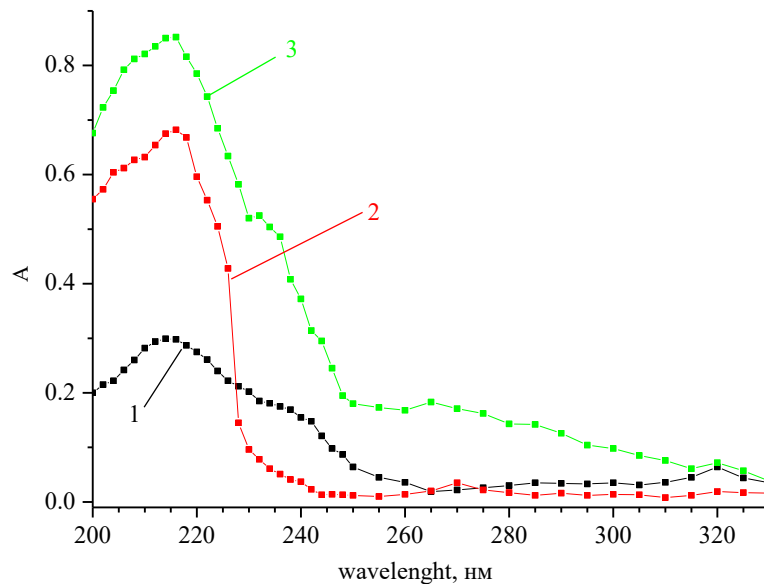


Figure-4. The UV absorption spectrum of the MPhA(1), PHMG (2), associate PHMG-MphA (3).

The spectra of 12-molybdophosphate heteropoly acid are characterized by three absorption bands:

- the intense absorption band with a maximum at 215 nm corresponds to the presence of O = Me groups and appears due to electron transfer from

orbitals localized on Oxygen atoms to the metal atom of the final bonds [22];

- a medium-intensity band with an absorption maximum at 235 nm and a weak-intensity band at 320 nm correspond to charge transfers along O - Me - O bridges.

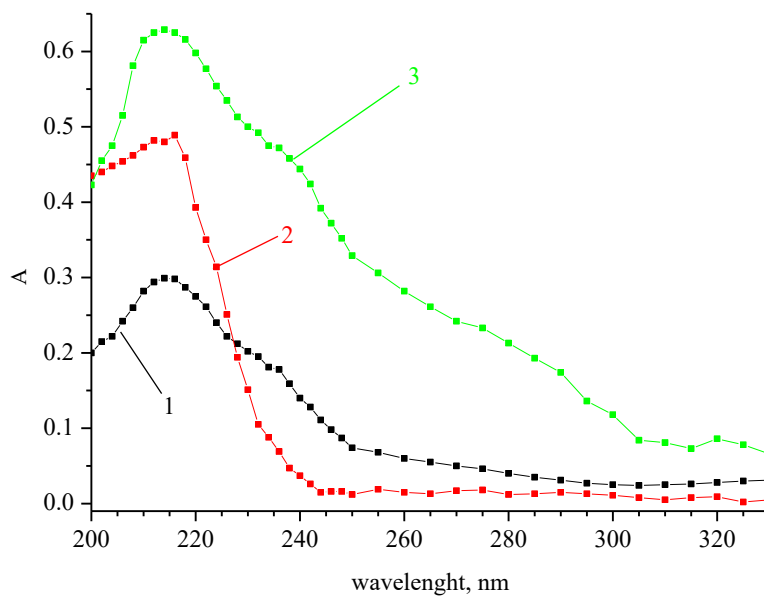


Figure-5. The UV absorption spectrum of the MPhA (1), HMDA(2) (acid destruction PHMG), associate HMDA-MPhA (3).

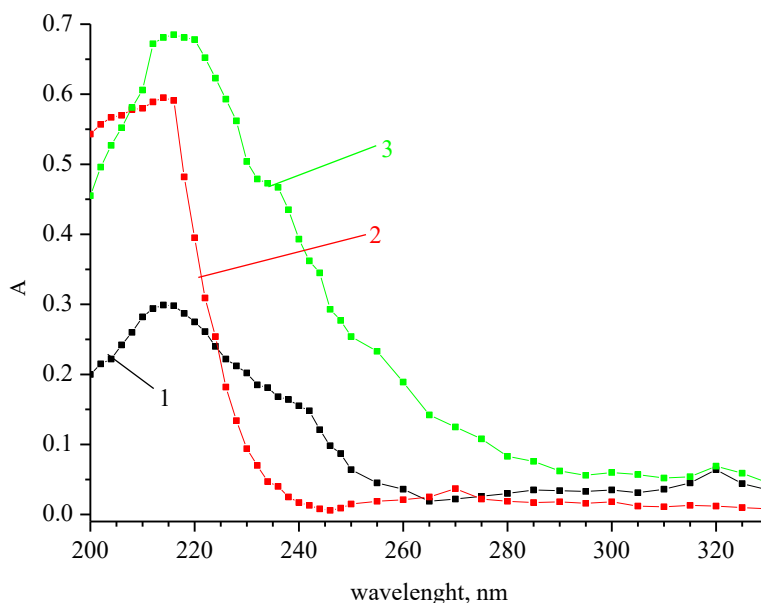


Figure-6. The UV absorption spectrum of the MPhA (1), HMDA (2) (alkaline destruction PHMG), associate HMDA-MPhA (3).

Table-3 shows the spectral characteristics of the organic cations of polyhexamethylene guanidine, hexamethylene diamine, the anion of 12-

molybdophosphate heteropoly acid and the products of its interaction.

Table-3. Spectral characteristics of the studied substances.

Substance	wavelength, nm	$E_{exp.}, l \cdot mol^{-1} \cdot cm^{-1}$
$H_3PMO_{12}O_{40}$	215	60000
	235(shoulder)	34000
	320	12000
PHMG	215	218200
	270	39800
$(PHMG)_x(PMO_{12}O_{40})_y$	215	170000
	235(shoulder)	103000
	268	34000
	320	4000
HMDA	216	96000
$(HMDA)_x(PMO_{12}O_{40})_y$	215	122000
	235(shoulder)	94000
	320	16000

The interaction of guanidine compounds with a 12-molybdophosphate heteropoly acid results in a significant increase in absorption which can be used in the development of spectrophotometric methods for determining the studied guanidine compounds in industrial facilities.

The spectral characteristics of the interaction products contain absorption bands that are characteristic of both the studied guanidine compounds and the heteropoly acid, which indicates the immutability of the chromophore system during the reaction, which confirms the formation of compounds with the ionic bond.



The ratio of the components and the composition of the formed ionic associates of polyhexamethylene guanidine and hexamethylene diamine with a 12-molybdophosphate heteropoly acid were determined spectrophotometrically by the saturation method. The aqueous solutions of the researched guanidine compounds were saturated with an aqueous solution of heteropolyacid and the absorption of the resulting solutions was measured. (Figures 7, 8).

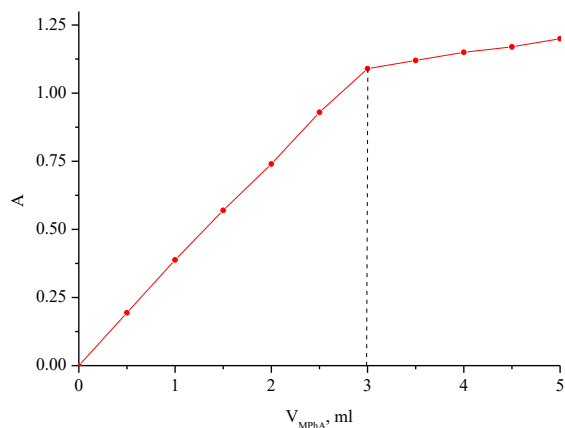


Figure-7. Saturation curve of PHMG with MphA.

According to the results of photometric determination of polyhexamethylene guanidine (Figure-7), it was found the ratio is $[\text{PHMG}^+] : [\text{PMo}_{12}\text{O}_{40}^{3-}] = 3 : 1$. It means that the interaction of polyhexamethylene guanidine with a 12-molybdophosphate heteropoly acid forms an ionic associate of the composition $(\text{PHMG})_3\text{PMo}_{12}\text{O}_{40}$.

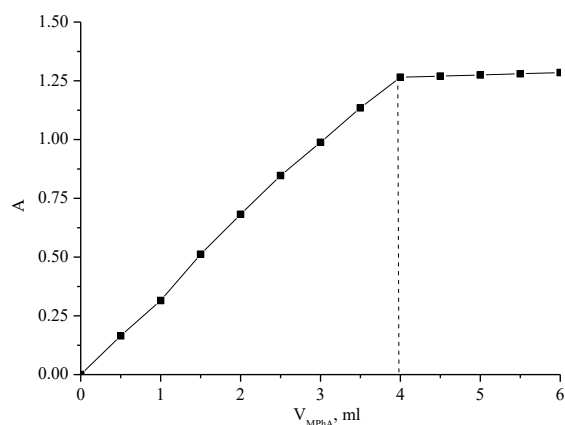


Figure-8. Saturation curve of the HMDA with MphA.

It was found, the ratio of components in complex with 12-molybdophosphate acid is 3: 2, that is, an ionic associate of composition is $(\text{HMDA})_3(\text{PMo}_{12}\text{O}_{40})_2$, according to the results of the photometric determination of hexamethylenediamine (Figure-8).

4. CONCLUSIONS

- The influence of the solution acidity on the properties of polyhexamethylene guanidine salts was researched using UV spectroscopy.
- The influence of degradation conditions of polyhexamethylene guanidine salts on the properties of the formed hexamethylene diamine salts was investigated.
- The reactions of the interaction of organic cations of polyhexamethylene guanidine and hexamethylenediamine with a 12-molybdophosphate heteropoly acid were studied. The ion-associative nature of the interaction of reacting compounds was confirmed.
- The ratio of the components and the composition of the formed associates during the interaction of the organic cations of guanidine compounds with the anion of a 12-molybdophosphate heteropoly acid were determined spectrophotometrically by the saturation method. The ratio of reacting components is 3:1 in the interaction of polyhexamethylene guanidine with MPA, i.e., a compound with $(\text{PHMG})_3\text{PMo}_{12}\text{O}_{40}$ composition is formed. The ratio of reacting components in the reaction is 3:2 for hexamethylenediamine, i.e., the resulting compound has $(\text{HMDA})_3(\text{PMo}_{12}\text{O}_{40})_2$ composition.

REFERENCES

- Gembickij P. A., Voinceva I. I. 1998. Polimernyj biocidnyj preparat poligeksametilenguanidin. Zaporozh'e: Poligraf. 44.
- Efimov K. M., Gembickij P. A., Snezhko A. G. 2000. Poliguanidiny - klass malotoksichnyh dezsmidstvovannogo dejstviya. Dezinfekcionnoe delo. 4, 25-31.
- Sidorenko S. A., Dudla I. A. 2004. Vliyanie upakovochnyh materialov na kachestvo pishchevoj produkcii. Izvestiya vuzov. Pishchevaya tekhnologiya. 1, 112-114.
- Gladishev V. V., Fedorchuk V. V., Baranova G. I., Gusakova N. V., Golovkin A. V. 2002. Rozrobka gelyu z novim antiseptichnim preparatom poligeksametilenguanidin fosfatom. Visnuk.farmacii. 2, 58-59.
- Voinceva I. I., Nizhnik T. Yu., Strikalenko T. V., Baranova A. I. 2018. Antikorrozionnye svojstva



- obezzarazhivayushchih reagentov na osnove poligeksametilenguanidina gidrohlorida. Voda: himiya i ekologiya. 10-12, 99-108.
- [6] Kosheleva O. E., Popova E. N. 2002. Proizvodnye poligeksametilenguanidina v proizvodstve kozhi i mekha. Novosibirsk: NIPKiPRO. 94.
- [7] Pat. 287320 S2, RU MPK A61K 8/36, A61K 8/37, A61K 8/42, A61K 8/43, A61K 8/72, A61Q 5/12. Shampun' protiv perhoti. Borodkina T. V. (RU), Bezhanishvili A. E. (RU); Borodkina T. V. (RU), Bezhanishvili A. E. (RU). - 2005102045/15; pending patent. 8.01.28; published patent. 20.11.2006. Bul. № 32. p. 8.
- [8] Voinceva I. I., Hranina T. I., Gembickij P. A. 1994. Antikorrozionnyj baktericidnyj lak na osnove poligeksametilenguanidina. Lakokrasochnye materialy i ih primenenie. 1, 22-23.
- [9] Konstantinovskaya S. V. 2006. Issledovanie dejstviya biocidov (na primere poligeksametilenguanidinov) na ekologo-funkcional'noe sostoyanie vodorosli *Chlorella Pyrenoidosa*: abstract of the dissertation for the degree of candidate of biological sciences, scientific specialty 03.00.16 «Ecology», 03.00.18 «Gidrobiologiya», Moscow, Peoples' Friendship University of Russia. 26.
- [10] Nizhnik T. Yu., Baranova A. I., Rokickaya O. V., Nizhnik V. V. 2004. Kompleksoobrazovanie ionov medi s poligeksametilenguanidinom v vodnoj srede. Zhurnal hromatograficheskogo tovarishchestva. 4(2): 16-25.
- [11] Krejngol'd S. U. 2002. Prakticheskoe rukovodstvo po himicheskomu analizu dezinfekcionnyh preparatov. M.: Ekspressprint. 39.
- [12] Malysheva A. F., Dedkov Yu. M. 1985. Fotometricheskoe opredelenie v vode nekotoryh fungicidnyh veshchestv s guanidinovoj funkciej. Zavodskaya laboratoriya. 5, 3-4.
- [13] Buzlanova M. M., Karandi I. V., Kitaeva D. H. 2003. Fotometricheskoe opredelenie poligeksametilenguanidina v vodnyh rastvorah v vide kompleksa s jodom, Zavodskaya laboratoriya. 4, 18-19.
- [14] Goncharuk V. V., Terleckaya A. V., Ievleva O. S., Bogoslovskaya T. A., Kushchevskaya N. F. 2006. Novyj fotometricheskij metod opredeleniya ostatocnyh koncentracij poligeksametilenguanidina v pit'evykh i prirodnyh vodah. Himiya i tekhnologiya vody. 28(6): 558-569.
- [15] Chmilenko T. S., Gamblievskaya E. A., Chmilenko F. A. 2010. Obrazovanie bromfenolovym krasnym ionnykh asociatov i ih vzaimodejstvie s poligeksametilenguanidinom v vodnyh rastvorah. Metody i ob'ekty himicheskogo analiza. 5(1): 19-28.
- [16] Arhipova V. V., Apyari V. V., Dmitrienko S. G. 2015. Opredelenie poligeksametilenguanidina gidrohlorida s ispol'zovaniem nanochastic zolota i penopoliuretana. Vestnik Moskovskogo universiteta. Himiya. 56(1): 34-40.
- [17] Chmilenko F. A., Obratcov V. B., Korobova I. V., Portretnyj V. P., Danilenko L. N. 2001. Amperometricheskoe opredelenie sodержaniya poliguanidina. Issues of Chemistry and Chemical Technology. 1, 40-42.
- [18] Pat. 2381501 Rossijskaya Federaciya, MPK7 G 01 N 33/15 G 01 N 27/26. Sposob kolichestvennogo opredeleniya anavidina metodom inversionnoj vol'tamperometrii / Slepchenko G. B., Moiseeva E. S., Hazanov V. A. - № 2008114568/15; zayavl. 20.10.2009; opubl. 10.02.2010, Byul. № 15.
- [19] Rudnev A. V., Dzherayan T. G. 2006. Opredelenie poligeksametilenguanidina metodom kapillyarnogo elektroforeza. Zhurnal analit. himii. 61(10): 1086-1089.
- [20] Efros I. E. 2003. Izuchenie vzaimodejstviya nekotoryh kationnykh poverhnostno-aktivnykh veshchestv s laurilsul'fatom natriya. Uchenye zapiski MITHT. 7, 37-40.
- [21] Matyushina G. P., Popkov V. A., Krasnyuk I. I., Abrikosova Yu. E., Timofeeva M. Yu., Zaderejko L. V. 2005. Razrabotka metoda kolichestvennogo opredeleniya solej poligeksametilenguanidina na osnove yavleniya gasheniya fluorescencii. Himiko-farmaceuticheskij zhurnal. 1, 48-50.
- [22] Tkach V. I. 1999. Geteropolianiony struktury Keggina kak analiticheskie reagenty na azotsoderzhashchie organicheskie veshchestva: Thesis of the degree of Doctor of Chemical Sciences: specialty 02.00.02 Analytical Chemistry Dnipropetrovsk: National University. 321.



- [23] Pashinova O. V., Tkach V. I. 2012. Pryame potentsiometrične viznachennya sintetichnogo pidsolodzhuvacha aspartam (harchova dobavka E-954) v bezalkogol'nih napoyah. *Issues of Chemistry and Chemical Technology*. 1, 102-106.
- [24] Volnyanska O. V., Labyak O. V., Tkach V. I. 2015. Ionometrične viznachennya tiabendazolu v harchovij produkcii. *Issues of Chemistry and Chemical Technology*. 4(102): 4-8.
- [25] Lutsenko N. V., Mironyak M. O., Tkach V. I. 2015. Viznachennya glicirrizinovoï kisloti v korinni solodki goloï metodom pryamoï potentsiometriï. *Issues of Chemistry and Chemical Technology*. 4(102): 35-40.
- [26] Lutsenko N., Mironyak M., Panchenko J., Tkach V. 2016. Ionometric determination of tannins in industrial production. *Chemistry & Chemical Technology*. 10(1): 73-80.
- [27] Volnyanska O. V., Labyak O. V., Blazheevskiy M. Ye., Brizitskiy O. A., Tkach V. I. 2016. Amperometric and spectrophotometric determination of food additive thiabendazole (E-233) in Bananas. *International Journal of Advances in pharmacy, biology and Chemistry*. 5(3) 271-281.
- [28] Lutsenko N. V., Mironyak M. A., Labyak O. V., Volnyanska O. V., Tkach V. I. 2016. Determination of the total content of diterpene glycosides in Stevia rebaudiana plant by the method of direct potentiometry. *Der Chemica Sinica*. 7(1): 9-19.
- [29] Lutsenko N., Mironyak M., Tkach V. 2016. Electrochemical determination of tannins in industrial products. *Methods and objects of chemical analysis*. 11(1): 16-24.
- [30] Volnyanskaya O., Mironyak M., Nikolenko M. 2018. Potentsiometrični sensori dlya viznachennya nitroghenvmisnih rechovin. Saarbrücken (Germany): LAP LAMBERT Academic Publishing. 109.
- [31] Volnyanska O. V., Mironyak M. O., Manzyuk M. V., Labyak O. V., Nikolenko M. V. 2019. Membrannij potentsiometričnij sensor dlya viznachennya etoniyu. *Naukovij visnik Uzhgorods'kogo universitetu. Seriya" Himiya*. 1(41): 51-67.
- [32] Mironyak M., Volnyanska O., Labyak O., Kovalenko V., Kotok V. 2019. Development of a potentiometric sensor sensitive to polysorbate 20. *Eureka: Physics and Engineering*. 4, 3-9.