



Highly selective solid-state sensor for iodide based on the combined use of platinum (IV) phthalocyanine and solidified pyridinium ionic liquid

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Abstract

Solid-state iodide-selective electrodes based on the commercial screen-printed electrodes modified with readily available low-melting ionic material (ionic liquid solidifying at room temperature), such as *N*-cetylpyridinium bromide, CPBr, and a specially synthesized metallo-complex, namely, platinum (IV) phthalocyanine, $\text{Pc}^{\text{t}}\text{PtCl}_2$, are obtained. For comparison, PVC-membrane ion-selective electrodes (ISE) based on the same compounds and solid-state ISEs with other solid matrices (*N*-cetylpyridinium chloride, 1,3-dicetylimidazolium iodide) are studied. Plasticized PVC-membrane ISEs exhibit normal selectivity corresponding to the Hofmeister series: interfering effect of large hydrophobic ions (perchlorate, dodecyl sulfate, etc.) is significant. Incorporation of $\text{Pc}^{\text{t}}\text{PtCl}_2$ metallo-complex into plasticized membranes improves selectivity to a certain extent, but not dramatically. At the same time, the CPBr-based solid-state ISEs demonstrate high selectivity toward iodide even in the presence of hydrophobic anions: the interfering effect of perchlorate and dodecyl sulfate decreases by 3 and 6 orders of magnitude, respectively. The introduction of the metallo-complex into the matrix improves selectivity even more significantly. The CPBr- $\text{Pc}^{\text{t}}\text{PtCl}_2$ -based solid-state sensor demonstrates a reversible and reproducible response to iodide. The electrode function slope $S = -(54 \pm 1)$ mV/dec, $C_{\text{min}} = 1.9 \times 10^{-5}$ M, response time is 5–10 s.

Keywords Ion-selective electrodes · Iodide-selective electrodes · Platinum phthalocyanine · Ionic liquids · Low-melting ionic materials · *N*-Cetylpyridinium chloride · *N*-Cetylpyridinium bromide · 1,3-Dicetylimidazolium iodide · Iodide · Synthesis of platinum (IV) phthalocyanine

Introduction

Direct potentiometry [1] occupies an important position among the methods for determining ions in aqueous solutions. In addition to the simplicity of hardware and short analysis time, it is attractive in that, by choosing an appropriate electrode active component (EAC) of ion-selective electrode (ISE), it is possible to create an electrochemical sensor for many anions and cations. A wide variety of materials, from classic plasticized polyvinylchloride in combination with various ionophores [2] to now popular ionic liquids (ILs) [3], is available nowadays.

One particularly important class of EAC is metallo-complexes of porphyrins [4–9] and phthalocyanines [10, 11], which were successfully applied for creating ISEs for anions. Because of the particular features of electronic structure, these compounds are prone to either additional coordination of the ion to be determined or ligand exchange. Due to the planar structure of their molecules, there are almost no steric difficulties for the target ion in accessing a metal atom, which nature to a high extent determines selectivity of binding. Usually, metallo-complex ligands used are rather hydrophobic, which has a positive influence on the service life of ISE. Phthalocyanine metal complexes were used to modify electrode surface in voltammetry [12] and other electrochemical methods due to their electrocatalytic activity [13–16].

Introduction of an ionic additive into the membrane phase based on the neutral carrier [17] improves ionic conductivity and favorably affects all electrochemical characteristics of the sensor: the slope of the electrode function approaches theoretical one, the detection limit and response time decrease, and

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reproducibility improves. In recent years, many works have appeared where ILs of various nature were used as ionic additives.

The most important characteristic of ISE is potentiometric selectivity, which is an indicator of electrochemical sensor quality. Recently, we introduced [18, 19] solid-state sensors based on relatively high-melting ILs solidifying at room temperature (alternatively, such ILs may be called low-melting ionic materials, LMIMs) as an alternative to ISEs with a liquid plasticized membranes. It was shown that using LMIM—serving either as ion-sensing layer itself or as a matrix for additional ionophores—can result in significantly improved selectivity toward a target ion in the presence of bulky foreign anions. A reason for this can be the discrimination of large ions due to the steric hindrances exhibited by a solid (crystalline) sensitive layer, as well as the absence of plasticizer capable of unspecific anion solvation in the solid sensitive layer.

For example, solid-state sensor based solely on 1,3-dicetylimidazolium bromide IL shows high selectivity toward bromide [18]. In addition to providing ionic conductivity of the membrane, increasing its hydrophobicity and participating in the formation of potentiometric response to analyte due to the contribution of ion exchange, LMIM can serve as a matrix which embeds the other EACs [10, 20, 21]. High selectivity is expected for the solid-state sensors in which the solidified IL serves as a matrix including metal complex as an ionophore. Using a composition containing diphenylbutylethylphosphonium hexafluorophosphate (LMIM) and cobalt (III) tetrakis-*tert*-butylphthalocyanine iodide (additional EAC) allowed us to achieve high selectivity toward iodide [22]. Compositions containing alkylimidazolium LMIMs and cobalt (III) tetrakis-*tert*-butylphthalocyanine iodide were also successfully used for preparing iodide-selective solid-state electrodes [23]. The additional advantages of the solid-state ISE obtained by the modification of miniature printed planar electrodes are compactness, ease of operation and transportation, and possibility to work with small volumes of liquid.

In the current work, we investigated the possibility of using platinum (IV) metallo-complex with substituted phthalocyanine. The synthesized complex, platinum (IV) tetra-*tert*-butylphthalocyanine dichloride ($\text{Pt}^{\text{IV}}\text{Cl}_2$), contains two chloride ions coordinated to the metal, which can be subjected to the ligand exchange for a target ion (iodide) providing increased selectivity of detection. As an additional means of increasing selectivity—in particular, to reduce the interfering effect of large hydrophobic anions—this ionophore was immobilized in a solid matrix of LMIM. For the first time, LMIMs containing cetylpyridinium cation, namely, cetylpyridinium chloride and bromide (CPCl and CPBr, respectively) were tested as matrices. These compounds are commonly used as detergents and components of antiseptics and disinfectants and are much more affordable and easily

available than previously studied LMIMs. Crystallinity of those compounds is supported by the X-ray diffraction analysis data (for monohydrates of *N*-cetylpyridinium chloride and bromide. Codes of the Cambridge crystal-structure data Bank are LABKAA and PUDJON, respectively [24, 25]), which allowed us to expect a significant discriminating effect toward interfering ions of inappropriate size. For comparison, ISE with a solid matrix based on the previously used LMIM 1,3-dicetylimidazolium iodide (DCImI, $T_m = 64^\circ\text{C}$) as well as plasticized PVC-membrane ISEs, which were similar to the solid-state sensors in their composition, were investigated.

Experimental

Synthesis of metallo-complex

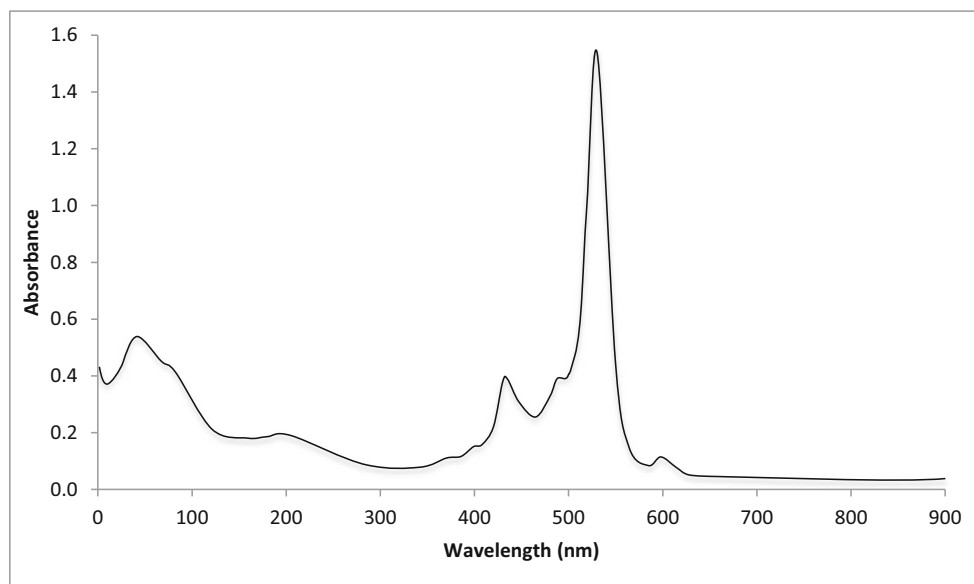
Platinum (IV) tetra-*tert*-butylphthalocyanine dichloride ($\text{Pt}^{\text{IV}}\text{Cl}_2$) was synthesized according to the following procedure: a mixture of *tert*-butyl-substituted phthalodinitrile (1.0 g, 5.4 mmol) and platinum (IV) chloride (0.5 g, 1.5 mmol) was mixed thoroughly in a glass vessel, placed in a microwave oven, and irradiated at 360 W for 2 min. After the mixture melting, the power was increased to 750 W and irradiation continued for 3 min to complete the reaction. During that time, the colorless mixture turned dark blue. Monitoring the completion of the reaction was carried out by thin layer chromatography (TLC) with toluene as an eluent. The target compound was isolated on the column packed with neutral alumina, with toluene also being used as an eluent. Such a method of purification made it possible to get rid of the initial phthalodinitrile impurity. The resulting solutions were concentrated under reduced pressure. As a result, 0.973 g of $\text{Pt}^{\text{IV}}\text{Cl}_2$ complex was obtained with a yield of 70.5%. That complex was also synthesized by fusion at 220–230 °C. However, it took much longer (2 h) to obtain the target compound, while its yield was only 58.3%.

The obtained complex was characterized by electronic absorption spectroscopy (EAS). The respective spectrum of platinum (IV) phthalocyanine dichloride solution in benzene is shown in Fig. 1.

From the data presented, it can be seen that the spectrum of the synthesized complex is characterized with absorption in the range of 650–660 nm, which is characteristic for the most of phthalocyanines metallo-complexes. EAS confirmed the complete conversion of phthalodinitrile into the corresponding phthalocyanine complex of platinum (the Soré strip was not more than one third of the main peak height). This is also supported by the data of TLC. The structure of platinum phthalocyanine complex was proved by means of MALDI-TOF/TOF mass spectrometry.

According to the results of TLC and EAS, synthesized complex was an individual compound of high purity. Those data also

Fig. 1 Electronic absorption spectrum (EAS) of platinum (IV) tetra-*tert*-butylphthalocyanine dichloride



confirmed the absence of the original phthalodinitrile, which indicated its complete conversion into the target complex or the products of linear polymerization. The main absorption maximum of Pc^1PtCl_2 is located at 651 nm (Fig. 1), the molar absorption coefficient $\varepsilon = 1.16 \times 10^5$.

According to MALDI results (Fig. 2), peaks at 1002, 968, and 933 mass units are observed corresponding to the complexes containing two ($M = 1002.2432$ g/mol), one ($M = 966.5133$ g/mol), or zero ($M = 931.1242$ g/mol) chloride atoms. This indicates gradual elimination of chloride ions as a result of laser exposure, which is also characteristic for other phthalocyanine complexes containing extra-ligands [26–28].

Reagents and solutions

CPCl and CPBr were purchased from “Merck” (Germany). 1,3-Dicetylimidazolium iodide ($(\text{C}_{16}\text{H}_{33})_2\text{ImI}$) was synthesized in the Institute of Physical Chemistry and Electrochemistry of Russian Academy of Science (IPCE

RAS) by Dr. V.E. Baulin and co-workers. Structural formulae of platinum (IV) phthalocyanine dichloride and IL/LMIM are given in Table 1.

For preparing plasticized ISE membranes, the following chemicals were used: polyvinyl chloride (PVC) C-70, *o*-nitrophenyloctyl ether (*o*-NPOE, Fluka, Germany) as a plasticizer, freshly distilled tetrahydrofuran (THF, Himmed, Russia) as a solvent.

Initial 0.01-M solutions of the salts of potential determining (POI) and foreign ions were prepared by dissolving the exact sample in distilled water; solutions of lower concentrations were obtained by successive dilution. Sodium salts, namely, sulfate, fluoride, sulfite, nitrate, bromide, benzoate, salicylate, *N*-lauroylsarcosinate, dodecyl sulfate, bis(2-ethylhexyl) sulfosuccinate, as well as potassium chloride, iodide, thiocyanate, perchlorate of reagent, or analytical reagent grade were used. Structural formulae of the salts of organic anions are presented in Table 2.

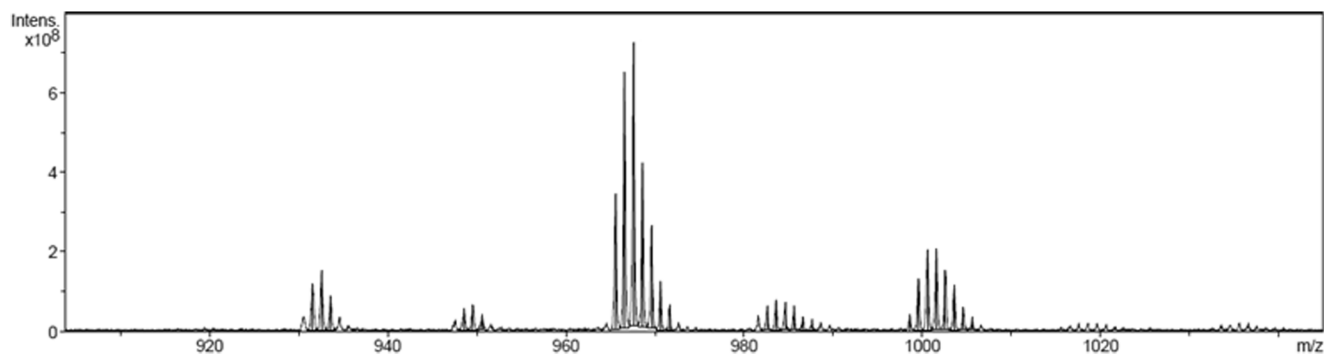
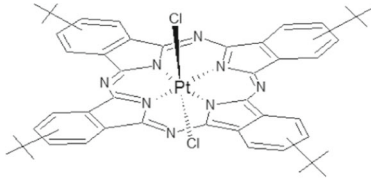
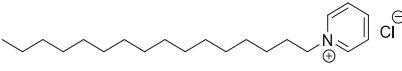
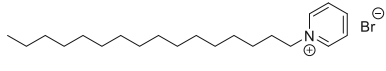
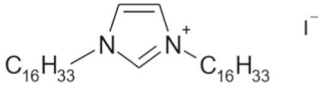


Fig. 2 MALDI-TOF/TOF spectrum of platinum (IV) tetra-*tert*-butylphthalocyanine dichloride

Table 1 Formulae of electrode active components of ISE membranes

Component	Structural formula	Abbreviation
Platinum (IV) tetra- <i>tert</i> -butylphthalocyanine dichloride		Pc ⁴ PtCl ₂
Cetylpyridinium chloride ($T_m = 85^\circ\text{C}$)		CPCl
Cetylpyridinium bromide ($T_m = 65^\circ\text{C}$)		CPBr
1,3-dicetylimidazolium iodide ($T_m = 64^\circ\text{C}$)		DCImI

Instrumentation and experimental technique

Plasticized film membranes were prepared in accordance with the procedure described in Ref. [29] by successive dissolving PVC, plasticizer (*o*-NPOE), electrode active compound (Pc⁴PtCl₂), and ILs (DCImI or CPCl/CPBr) in tetrahydrofuran at stirring.

For preparing solid-state sensors, screen printed planar electrodes (produced by “Rusens,” Russia; kindly supplied by Prof. A.A. Karyakin, MSU) were used. Such sensor has a polymeric support coated with graphite ink and a layer of insulator; the dimensions of the electrode are 10 × 28 × 0.35 mm. The working surface ($s = 0.2 \text{ cm}^2$) is free from insulating layer.

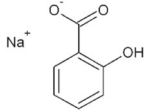
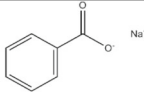
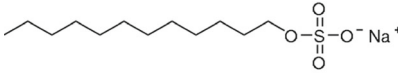
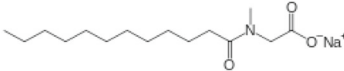
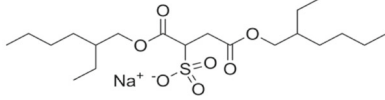
For preparing the electrodes modified only with LMIM (CPBr, DCImI), a sample of IL (~0.5 mg) was applied to the indicator surface of the solid-state sensor with subsequent melting over the electric hot plate. After 2–3 min of cooling at

room temperature, the electrode modified with a thin ion-sensitive layer of solidified IL was obtained.

Modification of planar printed electrodes (Fig. 3) with compositions containing metallo-complex was carried out in accordance with the following procedure. Platinum (IV) phthalocyanine and IL were mixed in a ratio of 1:4 [23]; the resulting mixture was dissolved in 2–3 drops of freshly distilled tetrahydrofuran and applied to the indicator surface of the electrode with a glass rod. Thus, electrodes modified with a mixture of Pc⁴PtCl₂ with DCImI, and also a mixture of Pc⁴PtCl₂ with either CPCl or CPBr were obtained and they were ready for operating after solvent volatilization. Total mass of the obtained ion-sensing layer was around 0.5 mg. The composition of the electrode active mixtures is given in Table 3.

Potentiometric measurements were carried out on an ionometer “Expert 001” (Ekoniks-Expert, Russia). Prior to the measurements, the electrodes with plasticized membranes

Table 2 Structural formulae of organic anion salts

Component	Structural formula	Abbreviation
Sodium salicylate		Sal
Sodium benzoate		Benz
Sodium dodecyl sulfate		DDS
Sodium N-lauroyl sarcosinate		LS
Sodium bis(2-ethylhexyl) sulfosuccinate		BEHSS

were conditioned in the studied solution for a day. The internal ISE solution consisted of 1×10^{-3} -M solution of potential determining ion and 1–2 drops of saturated KCl solution. Silver chloride electrode from “EVL-1M3T” (Russia) was used as an external reference electrode. Electrochemical properties of the prepared plasticized membranes were studied by measuring electromotive force of the following electrical circuit with a transfer.

Solid state planar electrodes were used for measuring the potential after conditioning in 1×10^{-3} -M solution of potential determining ion for 1–2 h. In the case of using solid state sensors, the electrical circuit scheme was as follows:

The potential was recorded, when its drift was not more than 1 mV/min ($\Delta E/\Delta t \leq 1$ mV/min). Period of time from the moment of electrode immersion into the studied solution till the establishment of equilibrium potential was taken as the electrode response time.

Limit of detection (C_{\min}) was evaluated according to the IUPAC recommendations as a magnitude of deviation $(\log 2) \times S$ of electrode function extrapolated rectilinear section from the experimental curve [30]. The coefficients of potentiometric selectivity were determined by a separate solutions method [31]. For iodide determination in pharmaceutical preparations, standard addition method was used.

Results and its discussion

For choosing a potential determining ion, electrode potentials of ISEs of different compositions and constructions were measured in $1 \cdot 10^{-2}$ -M solutions of salts containing various inorganic and organic anions (sulfate, fluoride, sulfite, nitrate, bromide, chloride, iodide, thiocyanate, perchlorate, benzoate, salicylate, *N*-lauroylsarcosinate, dodecyl sulfate, and bis(2-ethylhexyl) sulfosuccinate). It was found that in all cases ISEs possessed significant and well-reproducible anionic response in KI solution.

ISE potentiometric response in iodide solutions

Potentiometric response was studied for the solid-state and PVC-membrane ISEs based on platinum (IV) phthalocyanine dichloride and such low-melting ionic materials as CPCl, CPBr, and DCImI (they all may be considered also as non-room-temperature ILs, according to the common definition [32], since their melting points are significantly below 100 °C). The abbreviations used for the electrodes and their electrochemical characteristics are presented in Table 3. The response time of all ISEs based on $Pc^I PtCl_2$ and ILs does not exceed 5–10 s even in diluted solutions.

Ag/AgCl	Internal reference solution	Membrane	Investigated solution	Saturated KCl solution	Ag/AgCl
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Plasticized PVC-membrane electrode PVC:Pc⁴PtCl₂ based on platinum (IV) complex (Pc⁴PtCl₂) without ionic additives showed only a weak response to iodide ($S = -(26 \pm 3)$ mV/dec, $C_{\min} = 1.8 \times 10^{-4}$ M). The introduction of IL/LMIM additives to the membrane improves the response of ISE (Table 3). Such ISE as PVC:CPCl + Pc⁴PtCl₂ (plasticized membrane based on CPCl and Pc⁴PtCl₂) has the sub-Nernst electrode function slope: $S = -(45 \pm 1)$ mV/dec, linear range $1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-1}$, $C_{\min} = 2.1 \times 10^{-5}$ M. The electrode function slope of the electrode with a membrane based on CPBr and Pc⁴PtCl₂ is $-(54 \pm 1)$ mV/dec, linear range $1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-1}$, $C_{\min} = 3.5 \times 10^{-5}$ M. The electrochemical characteristics of the membrane plasticized with o-NFOE and based on one ion exchanger, namely, PVC: CPBr are as follows: $S = -(46 \pm 2)$ mV/dec, $C_{\min} = 3.0 \times 10^{-4}$ M, linear range $1.0 \cdot 10^{-3}$ – $1.0 \cdot 10^{-1}$ (Table 3).

It is noteworthy mentioning that IL, introduced as an ionic additive, reduces the electrical resistance of the membrane, which positively affects the characteristics of the sensor.

Solid-state sensor SS:CPCl + Pc⁴PtCl₂ (electrode was modified with a mixture of CPCl and Pc⁴PtCl₂) shows good response to iodide: $S = -(51 \pm 1)$ mV/dec in concentration range $1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-1}$ and $C_{\min} = 5.3 \times 10^{-5}$ M. However, it turned out that the modifying layer is washed off the electrode surface after 2–3 h of operation. This is probably caused by too high aqueous solubility (that is, insufficient hydrophobicity) of cetylpyridinium chloride salt.

Replacement of LMIM of solid-state sensor for more hydrophobic bromide salt of the same cation eliminates unwanted leaching and improves operating characteristics of ISE. For the electrode SS:CPBr + Pc⁴PtCl₂ $S = -(54 \pm 1)$ mV/dec, linear range $1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-1}$, $C_{\min} = 1.9 \times 10^{-5}$ M. The similar effect is noted after substituting LMIM for imidazolium salt, and for ISE SS:DCImI + Pc⁴PtCl₂, the characteristics are as follows: $S = -(57 \pm 2)$ mV/dec, linear range $1.0 \cdot 10^{-4}$ – $1.0 \cdot 10^{-1}$, $C_{\min} = 1.8 \times 10^{-5}$ M. For ISE based only on a solid layer of such LMIM as CPBr, $S = -(50 \pm 1)$ mV/dec, linear range $1.0 \cdot 10^{-3}$ – $1.0 \cdot 10^{-1}$, $C_{\min} = 1.0 \times 10^{-4}$ M.

Notably, the slope of electrode function for both PVC and solid-state ISE is close to theoretical one, which is an indicative of the reversibility of the electrochemical reaction [29].

In general, the developed ISEs show a satisfactory response to iodide. However, the significant differences between the ISEs of different design and composition, demonstrating the superiority of solid-state design, are observed in potentiometric selectivity.

Potentiometric selectivity of iodide ISE

Potentiometric selectivity of ISEs is influenced by various factors including hydrophobicity of the potential determining and interfering ions.

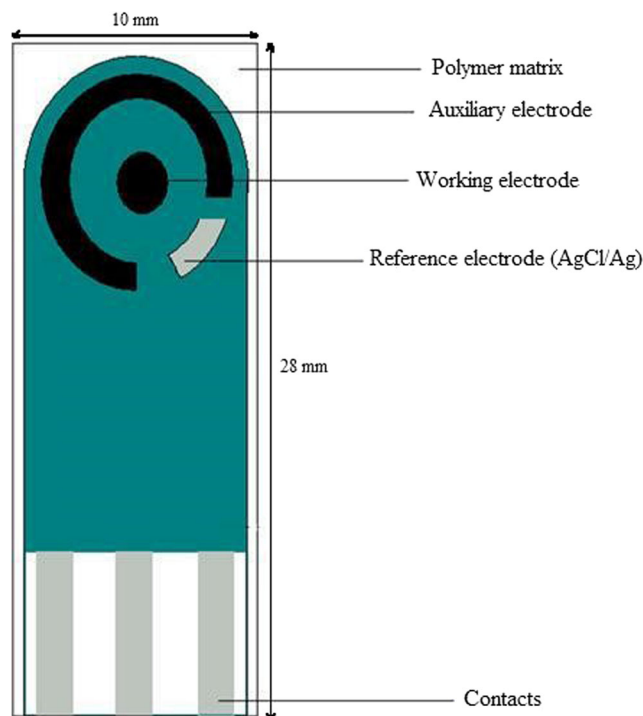


Fig. 3 Solid-state planar electrode construction

It is well known that anion-selective electrodes with plasticized membranes based on ion exchangers typically exhibit selectivity to the target anion corresponding to the Hofmeister series [33–35]. The interfering effect of foreign ions increases along with their hydrophobicity (recovery during the extraction from water into a nonpolar solvent); for monovalent anions, the series is $F^- < Cl^- < Br^- < NO_3^- < Sal^- < SCN^- < ClO_4^- < \text{large organic ions (picrate, dodecyl sulfate } DDS^-, \text{ etc.)}$.

Changing this order is necessary for achieving high and controllable selectivity. The most successful approach is to use the specific carriers interacting with analyte, especially metallo-complex compounds. Normally, the order of anion's affinity for the metal ion of the complex ionophore differs from Hofmeister selectivity pattern.

As shown in Fig. 4, quasi-liquid PVC membrane based only on CPBr ion exchanger shows all the signs of selectivity corresponding to the Hofmeister series. The greatest influence on the potentiometric response to iodide is demonstrated by hydrophobic inorganic (ClO_4^-) and large organic anions, such as $BEHSS^-$ and, especially, DDS^- . It is interesting to note that ISE for DDS^- based on *N*-cetylpyridinium salt dissolved in a fixed liquid membrane is described in literature [36].

The introduction of an additional metallo-complex additive into the membrane composition slightly improves selectivity. ISE based on CPBr and Pc⁴PtCl₂ exhibits higher selectivity

Table 3 Content and electrochemical characteristics of ISE in iodide solutions ($n = 3, P = 0.95$)

Name	Composition, mass. %	Electrochemical characteristics of ISE		
		Electrode function slope, S , mV/dec	Linearity range, M	LOD, C_{\min} , M
PVC-membrane plasticized ISE (with <i>o</i> -NPOE as a plasticizer)				
	Plasticizer/PVC/LMIM/Pc ^I PtCl ₂			
PVC: Pc ^I PtCl ₂	65.3/32.7/0/2	-26 ± 3	1.0×10^{-3} – 1.0×10^{-1}	1.8×10^{-4}
PVC:CPCl + Pc ^I PtCl ₂	65.2/32.3/0.5/2	-45 ± 1	1.0×10^{-4} – 1.0×10^{-1}	2.1×10^{-5}
PVC:CPBr + Pc ^I PtCl ₂	65.2/32.3/0.5/2	-54 ± 1	1.0×10^{-4} – 1.0×10^{-1}	3.5×10^{-5}
PVC:CPBr	65.3/32.7/2/0	-46 ± 2	1.0×10^{-3} – 1.0×10^{-1}	3.0×10^{-4}
Solid-state ISE				
Name	LMIM/ Pc ^I PtCl ₂			
SS:CPCl + Pc ^I PtCl ₂	80/20	-51 ± 1	1.0×10^{-4} – 1.0×10^{-1}	5.3×10^{-5}
SS:CPBr + Pc ^I PtCl ₂	80/20	-54 ± 1	1.0×10^{-4} – 1.0×10^{-1}	1.9×10^{-5}
SS:CPBr	100/0	-50 ± 1	1.0×10^{-3} – 1.0×10^{-1}	1.0×10^{-4}
SS:DClmI + Pc ^I PtCl ₂	80/20	-57 ± 2	1.0×10^{-4} – 1.0×10^{-1}	1.8×10^{-5}

toward iodide in the presence of SO_4^{2-} , SO_3^{2-} (tenfold amounts), F^- , Cl^- , and Benz^- (hundredfold amounts). The interfering effect of thiocyanate is reduced by an order of magnitude. However, there is no fundamental change in selectivity: large hydrophobic anions (ClO_4^- , DDS^- , BEHSS^-) strongly interfere with the determination of iodide.

The situation changes dramatically when switching to solid-state ISE, in which LMIM serves as an ion-sensitive layer and/or a matrix embedding the metallo-complex.

As seen in Fig. 5, significant discrimination of large hydrophobic anions is achieved even without a help of metallo-complex additive, simply by switching to solid ion-exchange material, such as CPBr. The interfering effect of ClO_4^- , BEHSS^- , and DDS^- decreases by 3, 5, and 6 orders of magnitude, respectively. Probably, the crystallinity of the LMIM

structure is responsible for the discrimination of anions, which are too large for the particular matrix.

The introduction of platinum (IV) phthalocyanine dichloride additive into CPBr matrix reduces the interfering effect even more (though not that significantly), and such an effect is noted for almost all anions (Fig. 5).

It is important that the same effect of a sharp selectivity increase toward large hydrophobic ions can also be achieved using the imidazolium LMIM as a matrix (Fig. 6). However, the alkylpyridinium salt as a solid matrix provides better selectivity in general. It is difficult to explain this difference at the moment; one can only assume that this is due to the different structures (packing, channels, distance between the layers and the chains) of the corresponding solid materials.

Fig. 4 Potentiometric selectivity of PVC-membrane (with *o*-NPOE as a plasticizer) iodide-selective ISE based on (1) CPBr or (2) CPBr + Pc^IPtCl₂

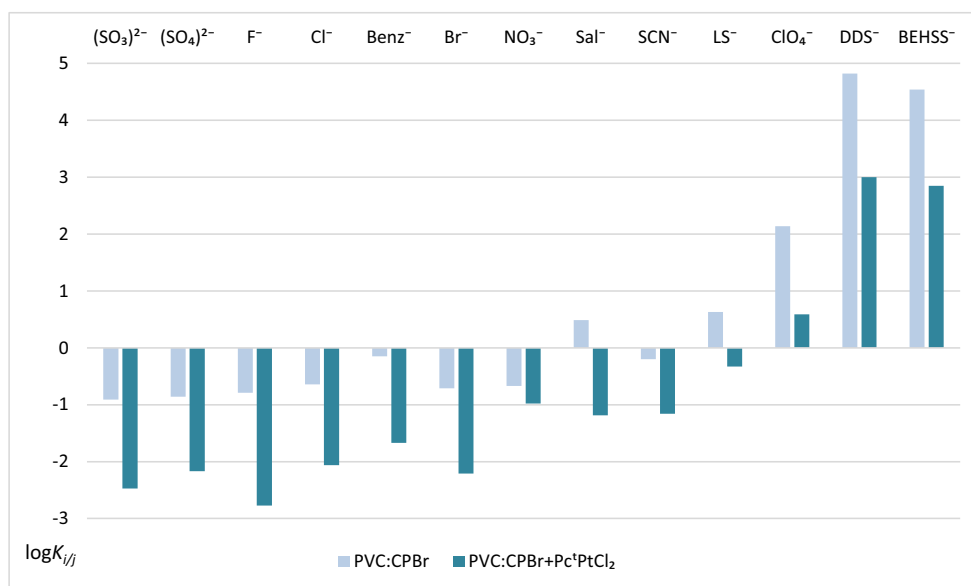
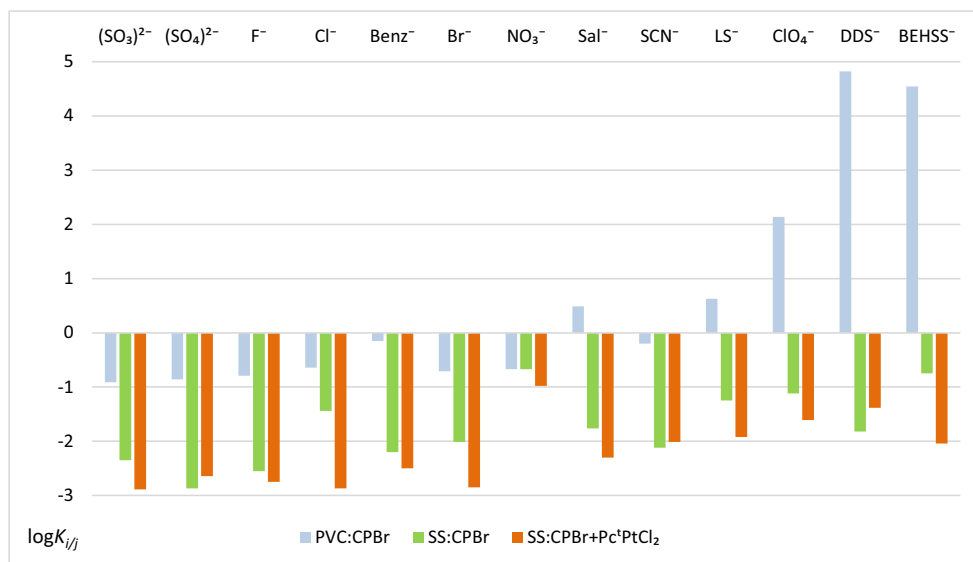


Fig. 5 Selectivity improvement for ISE based on CPBr when switching from PVC-membrane to solid-state construction, also with addition of metallo-complex ionophore, such as $\text{Pc}^{\text{IV}}\text{PtCl}_2$



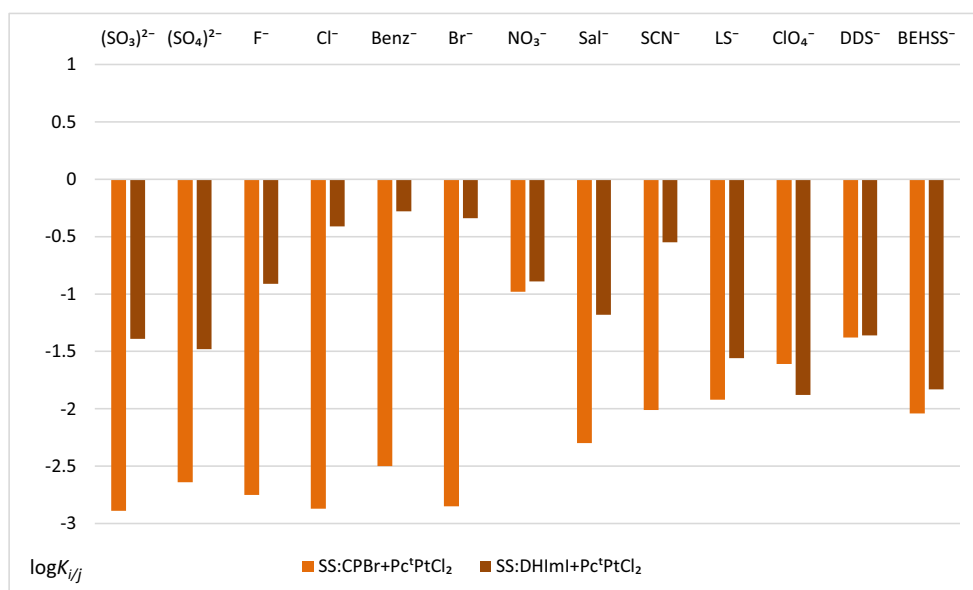
Thus, the solid-state ISE based on readily available LMIM, such as CPBr and a specially synthesized metallo-complex, namely, platinum (IV) phthalocyanine exhibits high selectivity toward iodide. In comparison with PVC-membrane ISE containing only CPBr ion exchanger, the interfering effect of most inorganic ions is reduced by 1 or 2 orders of magnitude, while for the large hydrophobic ions, it decreases by 3–6 orders of magnitude. We believe that this is achieved due to the combined effect of the analyte–metallo-complex ionophore interaction specificity, on one hand, and the discrimination of large anions by the crystalline solid matrix, on the other hand.

In addition, metal phthalocyanine is supposed to provide a smoother transition from ionic conductivity in sensing layer to electronic conductivity in a conductor. Operation of solid-state

ISE relies on both ionic and electronic conductivity. Membrane/sensing layer has an ionic conductivity, and the inter-phase potential (membrane/aqueous solution) is determined by electrochemical equilibrium involving ions of both phases. Solid contact base of screen-printed electrode (metal, graphite) has an electronic conductivity. Whence, to obtain stable ISE potential, a fast and reversible ion-to-electron transduction is necessary, which is achieved by using electroactive materials having mixed electronic and ionic conductivity [1]. Metal phthalocyanines are well known by the ability to participate in reversible redox processes, so we suppose that Pt (IV) phthalocyanine immobilized in solid matrix provides a transition from ionic to electronic conductivity.

Comparing the developed electrodes with those containing metallated electrode-active components, which were recently

Fig. 6 The comparison of potentiometric selectivity of solid-state iodide-selective ISE based on $\text{Pc}^{\text{IV}}\text{PtCl}_2$ metallo-complex immobilized in pyridinium (CPBr) and imidazolium (DCImI) LMIM



described in literature [19, 22, 23, 37–40], one can conclude that their characteristics are close. Plasticized polymer membrane electrodes [37–40] are, in general, less selective in the presence of relatively hydrophobic ions. For example, urea-derived ionophore ISE shows potentiometric selectivity coefficients for iodide in the presence of salicylate and thiocyanate at the level of 10^{-1} [39]. Solid-state sensors previously developed in our group [19, 22, 23] have the characteristics which are similar to those reported herein. However, solid-state ISEs described in this paper benefit from the use of matrix formed by cetylpyridinium salts, which are much more easily available than low-melting ionic compounds employed previously.

Analytical application

Solid-state ISE based on CPBr and Pc^1PtCl_2 was used for determining iodide in pharmaceutical preparations “Iodomarine 100” (“Berlin-Chemie,” Germany) and “Iodobalans 100” (“Merck KGaA,” Germany).

Sample preparation technique was as follows: 4 pills of pharmaceutical preparation (either “Iodomarine 100” or “Iodobalans 100”) were crushed and grinded in an agate pounder; a sample of the obtained substance was weighed, placed in a 10-ml glass, and dissolved in distilled water at stirring. Then, the resulting solution was filtered through the “Blue tape” filter; the precipitate was thoroughly washed. The filtrate was evaporated, transferred to a 50-ml flask, and adjusted with distilled water. The resulting solution was used for the determination of iodide by standard addition method. The ISE and the reference electrode were immersed into a 10-ml aliquot and the potential was registered, then 500 μl of $1.0 \cdot 10^{-1}\text{-M}$ potassium iodide solution was added and the potential was registered again. The iodide content was found using the respective formula [29].

As a result, 0.132 ± 0.004 ($S_r = 0.01$) and 0.130 ± 0.008 ($S_r = 0.02$) mg of iodide were found in pharmaceutical preparations “Iodomarine 100” and “Iodobalans 100,” respectively, which is in accordance with the prescription data, since the declared content of iodide in both drugs is 0.131 mg. The results were also confirmed by the literature data: 0.127 and 0.130 mg of iodide in “Iodomarine 100” and “Iodobalans 100,” respectively, as determined by argentometric titration [41]. Thus, the proposed ISE can be used for the determination of iodide in pharmaceuticals.

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References

- Bobacka J, Ivaska A, Lewenstam A (2008) Potentiometric ion sensors. *Chem Rev* 108(2):329–351
- Pechenkina IA, Mikhelson KN (2015) Materials for the ionophore-based membranes for ion-selective electrodes: problems and achievements. *Russ J Electrochem* 51(2):93–102
- Koel M (ed) (2016) Analytical applications of ionic liquids. World Scientific Publishing Europe Ltd., London, pp 339–360
- Malinowska E, Meyerhoff ME (1995) Role of axial ligation on potentiometric response of Co (III) tetraphenylporphyrin-doped polymeric membranes to nitrite ions. *Anal Chim Acta* 300(1-3): 33–43
- Malinowska E, Górski Ł, Meyerhoff ME (2002) Zirconium (IV)-porphyrins as novel ionophores for fluoride-selective polymeric membrane electrodes. *Anal Chim Acta* 468(1):133–141
- Skripnikova TA, Starikova AA, Shumilova GI, Ermolenko YE, Pendin AA, Mourzina YG (2017) Towards stabilization of the potential response of Mn (III) tetraphenylporphyrin-based solid-state electrodes with selectivity for salicylate ions. *J Solid State Electrochem* 21(8):2269–2279
- Amini MK, Shahrokhian S, Tangestaninejad S (1999) PVC-based Mn (III) porphyrin membrane-coated graphite electrode for determination of histidine. *Anal Chem* 71(13):2502–2505
- Mitchell-Koch JT, Pietrzak M, Malinowska E, Meyerhoff ME (2006) Aluminum (III) porphyrins as ionophores for fluoride selective polymeric membrane electrodes. *Electroanalysis* 18(6):551–557
- Shvedene NV, Otkidach KN, Gumerov MR, Tarakanov PA, Tomilova LG (2015) New metalloporphyrins as active components of membranes of anion-selective electrodes. *J Anal Chem* 70(1):72–80
- Leyzerovich NN, Shvedene NV, Blikova YN, Tomilova LG, Pletnev IV (2001) Comparative study of the metal phthalocyanates as active components in salicylate-selective electrodes. *Electroanalysis* 13(3):246–252
- Shvedene NV, Leyzerovich NN, Rybakova MM, Kostalyndina EV, Koval YA, Pletnev IV (2000) Aluminium (III) phthalocyanine as an active component of salicylate-selective membrane electrode. *Vestn Mosk Univ Seriya 2 Khimiya* 41:34–36
- Galal A, Darwish SA, Ahmed RA (2007) Hybrid organic/inorganic films of conducting polymers modified with phthalocyanines. I—film preparation and voltammetric studies. *J Solid State Electrochem* 11(4):521–530
- Akinbulu IA, Ozoemena KI, Nyokong T (2011) Formation, surface characterization, and electrocatalytic application of self-assembled monolayer films of tetra-substituted manganese, iron, and cobalt benzylthio phthalocyanine complexes. *J Solid State Electrochem* 15(10):2239–2251
- Hebié S, Bayo-Bangoura M, Bayo K, Servat K, Morai C, Napporn TW, Kokoh KB (2016) Electrocatalytic activity of carbon-supported metallophthalocyanine catalysts toward oxygen reduction reaction in alkaline solution. *J Solid State Electrochem* 20(4): 931–942
- Nyoni S, Mashaz P, Nyokong T (2016) Electrode modification using nanocomposites of electropolymerised cobalt phthalocyanines supported on multiwalled carbon nanotubes. *J Solid State Electrochem* 20(4):1075–1086
- Pavez J, Páez M, Ringuedé A, Bedioui F, Zagal JH (2005) Effect of film thickness on the electro-reduction of molecular oxygen on electropolymerized cobalt tetra-aminophthalocyanine films. *J Solid State Electrochem* 9(1):21–29
- Bakker E, Malinowska E, Schiller RD, Meyerhoff ME (1994) Anion-selective membrane electrodes based on metalloporphyrins:

- the influence of lipophilic anionic and cationic sites on potentiometric selectivity. *Talanta* 41(6):881–890
18. Rzhavskaia AV, Shvedene NV, Pletnev IV (2014) Solidified ionic liquid as crystalline sensing element of the bromide selective electrode. *Sens Actuators B Chem* 193:563–567
 19. Otkidach KN, Shvedene NV, Tarakanov PA, Tomilova LG, Pletnev IV (2016) Cobalt (II) porphyrine as an active component of iodide-selective electrodes. *Mosc Univ Chem Bull* 71(4):270–276
 20. Wei D, Ivaska A (2008) Applications of ionic liquids in electrochemical sensors. *Anal Chim Acta* 607(2):126–135
 21. Shvedene NV, Chernyshev DV, Gromova YP, Nemilova MY, Pletnev IV (2010) Hydrophobic ionic liquids in plasticized membranes of ion-selective electrodes. *J Anal Chem* 65(8):861–865
 22. Shvedene NV, Rzhavskaia AV, Pletnev IV (2012) Ionic liquids based on quaternary phosphonium cation as active components of solid-state iodide selective electrode. *Talanta* 102:123–127
 23. Shvedene NV, Avramenko OA, Baulin VE, Tomilova GL, Pletnev IV (2011) Iodide-selective screen-printed electrodes based on low-melting ionic solids and metallated phthalocyanine. *Electroanalysis* 23(5):1067–1072
 24. Paradies HH, Habben F (1993) Structure of N-hexadecylpyridinium chloride monohydrate. *Acta Crystallogr C* 49:744–747
 25. Ballirano P, Caminiti R, Sadun C, Coiro VM, Mancini G, Mara A (2010) Single crystal structure determination of cetylpyridiniumammonium bromide and Rietveld structure determination of cetylquinuclidinium bromide. *Z Für Krist—Cryst Mater* 213:123–129
 26. Tolbin AY, Pushkarev VE, Tomilova LG (2012) Methodology for the selective synthesis of homo- and heteroligand phthalocyanine complexes. The chapter in the book - "Organic Chemistry in the Works of NS Zefirov". Gilem. Ufa. Bashkortostan. 296 p.
 27. Tolbin AY, Tomilova LG (2011) Subphthalocyanines and their analogues: methods for the synthesis and structure modification. *Russ Chem Rev* 80(6):531–551
 28. Balashova IO, Pushkarev VE, Shestov VI, Tomilova LG, Koifman OI, Ponomarev GV (2015) Synthesis and spectral properties of phthalocyanine–methylphosphoribide a covalently linked dyad. *Macrocyclics* 8(3):233–238
 29. Kamman K (1980) *Work with ion-selective electrodes*. Mir, Moscow
 30. Currie LA, Svehla G (1994) Nomenclature for the presentation of results of chemical analysis (IUPAC Recommendations 1994). *Pure Appl Chem* 66(3):595–608
 31. Lindner E, Umezawa Y (2008) Performance evaluation criteria for preparation and measurement of macro- and microfabricated ion-selective electrodes (IUPAC technical report). *Pure Appl Chem* 80: 85–104
 32. Wilkes J (2002) A short history of ionic liquids—from molten salts to neoteric solvents. *Green Chem* 4(2):73–80
 33. Egorov VV, Lyaskovskii PL, Taribo MG, Nazarov VA, Rahman'ko EM, Stanishevskii LS, Okaev EB (2010) Influence of the nature of liquid anion exchanger on the selectivity of anion selective electrodes. *J Anal Chem* 65(11):1181–1190
 34. Hofmeister F (1888) Zur Lehre von der Wirkung der Salze. *Arch Für Exp Pathol Pharmacol* 25(1):1–30
 35. Kunz W, Henle J, Ninham BW (2004) 'Zur Lehre von der Wirkung der Salze' (about the science of the effect of salts): Franz Hofmeister's historical papers. *Curr Opin Colloid Interface Sci* 9(1-2):19–37
 36. Arvand-Barmchia M, Mousavi ME, Zanjanchi MA, Shamsipur M (2013) A new dodecylsulfate-selective supported liquid membrane electrode based on its N-cetylpyridinium ion-pair. *Microchem J* 74: 149–156
 37. Ganjali MR, Poursaberi T, Hosseini N, Salavati-Niasary N, Yousefi M, Shamsipur N (2002) Highly selective iodide membrane electrode based on a cerium salen. *Anal Sci* 18:289–292
 38. Farhadi K, Maleki R, Yamchi RH, Sharghi H, Shamaipur M (2004) [Tetrakis(4-N,N-dimethylaminobenzene)porphyrinato]-manganese (III) acetate as a novel carrier for a selective iodide PVC membrane electrode. *Anal Sci* 20(5):805–809
 39. Jeong DC, Lee HK, Jeon S-W (2006) Polymeric iodide-ion selective electrode based on urea derivative as a ionophore. *Bull Kor Chem Soc* 27:1985–1988
 40. Pouretedal HR, Keshavarz MN (2004) Copper(I)-bathocuproine complex as carrier in iodide-selective electrode. *Talanta* 62(1): 221–225
 41. Lisina SV, Lyakhov AI (2013) Qualitative and quantitative determination of iodide content in medicinal preparations and table salt. *Sovremennie Naukoemie Technologii (in Russian)* 9:82–84