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Ion selective potentiometric sensor based on single crystalline $KTiOPO_4$ for determination of K^+-ions

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Abstract

New improved $\mathbf{K^+}$–selective electrode based completely on solid single crystal KTP with nano-capillary conductivity is developed. The crystal KTP grown by two different methods had an ordinary orthorhombic structure ($Pna2_1$) with the chain structure of shared TiO_6 octahedrons, where the vacantly mobilized $\mathbf{K^+}$ ions provide the ionic conductivity through nano-dimension capillary. The membranes of 0.8 mm thickness and 6 mm diameter were hermetically sealed without glue materials into a IONIKS 111.080 solid membrane electrode body together with an inner standard Ag/AgCl reference electrode. The 0.01 M KCl solution and a standard Ag/AgCl electrode were placed inside of reservoir. The electrode response was linear in the range of pK^+=1 – 5, with the electrode function slope equal to S=58.8 (0.4 at 25° C. The high selectivity coefficients for ions of alkali and earth-alkali elements were found. We find the difference in selectivity proposed electrode, glass electrode ESL-47-07 (Belarussia) and valinomycin electrode supplied by “IONIX alpha” Ltd. (Russia). Thus, the selectivity of proposed electrode permits to use it for practical application in a medicine. The electrode had a convenient response time, DL_K of pK^+ = 5.2 (0.1 and the reproducibility of electrode potential (0.2 mV in KNO_3 solutions during at least 28 months.

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Keywords: Potassium $\mathbf{K^+}$**;** ion-selective electrode; single crystal KTP; $KTiOPO_4$; ionic conductivity; solid membrane; selectivity of electrode

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1. Introduction

Ion-selective electrodes for determination of potassium are the most widely used in clinical chemistry and agriculture. The high precision of corresponding measurements should imply the highest sensibility and selectivity of the electrodes available. One could achieve this in several ways: by the improvement of ion-selective electrode construction, by the improvement of separate unit quality, by optimum selection of membrane composition (with already known components), by the search of the new electrodoactive components, as well as the new sensitive elements – membranes (from inorganic materials).

The several kinds of K^+-selective electrodes with membranes of a various compositions are developed and being produced at present. All of them are assigned to a type of electrodes based on neutral carriers and are described in reviews [1-2]. The well-known and received the wide use is the electrode based on valinomycin [3], which is included in production catalogs of many firms, engaging by production of ionometric equipment. Therefore, in our work we compared parameters of new electrode based on single crystal with valinomycin electrode.

2. Theoretical premises

The requirements to membrane materials have been formulated in the middle of 60's. In spite of it, until now the electrode based on LaF_3 remained the only electrode with single crystal membrane. Use of LaF_3 as a single crystal is indispensable condition to obtain the electrode with high analytical parameters. The active search of single crystals with high ionic conductivity (basically 60's–beginning of 70's) as membranes ion-selective electrodes had no positive result.

For the first time a single crystal of $KTiOPO_4$ (KTP) was identified by French researchers in 1971 [4] and was patented in 1974 for use in electrooptical devices, converting the frequent characteristics of laser radiation [5]. The single crystal KTP has an orthorhombic structure and concerns to point group mm2 (space group Pna21). For KTP lattice parameters a=12.814 , b=6.404 and c=10.616 Å were found. Each elementary cell contains 8 formula units. The structure is characterized by chains of TiO_6 octahedrons, which are connected on two corners and the chains are divided by PO_4 tetrahedrons. Potassium ions are located in the centers of high coordination number, are weakly bound to oxygen atoms, which surround of atoms titanium and phosphorus, and are able to move by vacancy mechanism. For the first time the information about low-temperature ionic conductivity of KTP crystals has appeared at the end of 80's [6]. Data, obtained by various authors have shown that electrical conduction in KTP in a wide range of temperatures occurs almost exclusively through the movement of potassium ions on channels, which perforate a framework along the c axis. Electron and anion conductivity are more isotropic and their summary upper limit can be evaluated from resistance of a crystal in perpendicular directions to c axis. According to work *197* this resistance makes about 10^{12} om·cm that on 6 - 7 orders of magnitude higher than resistance of a KTP crystal in a direction along the axis c with under conditions of cation transport. Thus, it is possible to conclude about overwhelming character of cation conductivity KTP. Research of impedance has demonstrated that greatest value of ionic conductivity of the crystal was $1.2 \cdot 10^6$ om·cm. Taking into account availability of low-temperature ionic conductivity and state stability, assumption about an opportunity of use of a KTP crystal (by analogy with LaF_3) as a membrane of K^+–selective electrode was made.

3. Experimental section

3.1. Equipment and procedure.

All measurements were carried out with use of an ionmeter Orion Research Model-901 (USA). The external reference electrode was an IONIKS-112.024 (Russia) double-junction Ag/AgCl electrode with 1M potassium chloride and 1M lithium sulfate bridge electrolyte. Electroanalytical parameters of the new ion–selective electrode were measured according to IUPAC recommendations [7]. The selectivity coefficients were measured by the method of mixed solutions.

3.2. Synthesis of membrane and the electrode design.

KTP crystals were grown by two methods: hydrothermal and from a solution in melt [8, 9]. The conductivity of crystals varied in a range of 10^7—10^6 om·cm. The membranes of about 0.8 mm thickness and about 6 mm diameter were mounted in an IONIKS 111.080 solid membrane electrode body, in which the hermetic sealing of a membrane was made without using any glue material. The 0.01 M KCl solution and a standard silver/silver chloride electrode were placed inside of reservoir.

4. Reagents.

In this work the standard reagents of the grade “chemically pure” Reakhim (Russia) were used. All standard solutions were prepared using deionized water.

5. Results and discussion

A typical electrode characteristic of single crystal K^+–selective electrode is given in Fig.1.

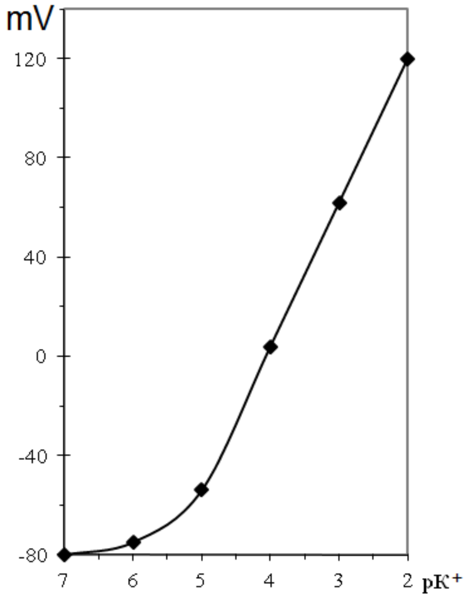

Fig.1. A typical electrode characteristic for the single crystalline K^+–selective electrode

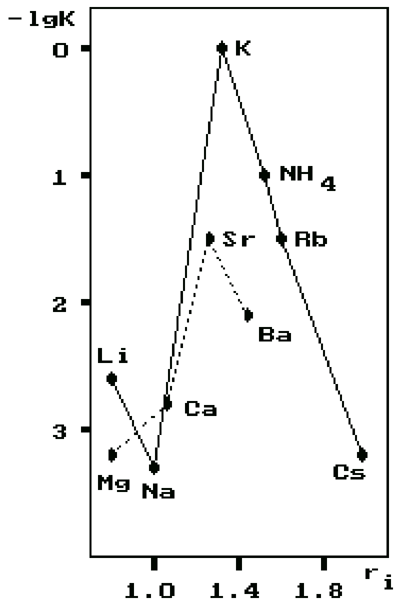

Fig.2 Correlation between metal ionic radii and cation selectivity coefficients.

The linear response of electrode potential was observed in a wide range of concentration $pK^+=1 - 5$. The electrode function slope was close to theoretical one and was equal S=58.8±0.4 mV at 20º C. The coefficients of selectivity for ions of alkali and alkali earth elements are given in Table 1. A correlation between ionic radius and selectivity coefficient is shown at fig.2.

Table 1. The selectivity coefficients $-lgK_i$ for the ions of alkali and earth-alkali elements as determined with the KTP single crystalline K^+–selective electrode

Ion	H^+	Li^+	Na^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	NH_4^+
$-lgK_i$	2.2	2.6	3.4	1.5	3.2	3.3	2.8	1.5	2.1	1.1

As follows from this figure, the size of a channel probably plays an essential role in selectivity, in which ionic transport of ions take place. So, when going from potassium to sodium ion selectivity changes almost on three order of magnitude. The Figure 3 evidently demonstrates the difference in selectivity between proposed electrode, glass electrode ESL-47-07 (Belarussia) and valinomycin electrode Potencial (Russia).

Thus, the selectivity of proposed electrode permits to hope for its practical application in a medicine. The results of the response time measurements are shown in Fig.3. (Electrode previously was soaked in a 10^{-3} m KCl solution during 12 hours).

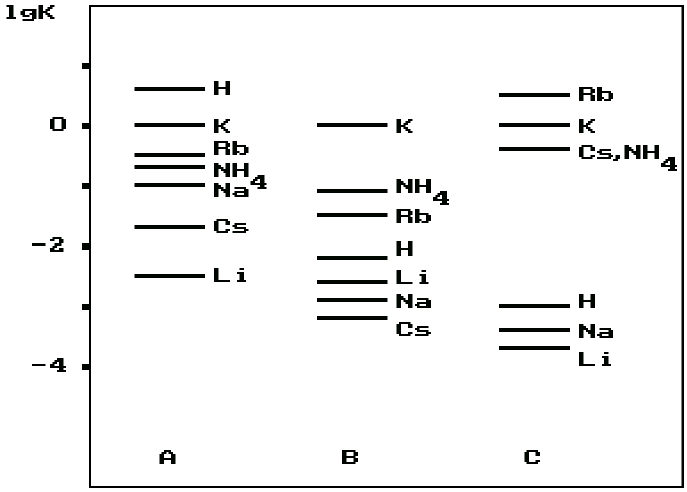

Fig.3. Lg K (A – glass electrode, B - electrode of single crystal K^+, C – valinomicin electrode).

It is evident that, the electrode has the response time, which does not prevent its practical application. The measured limit of detection in pure potassium nitrate solutions was pK^+= 5.2 (0.1. Reproducibility of electrode potential in potassium nitrate solutions pK^+= 3 was better than 0.2 mV. The changes of analytical parameters were not noted for the time of the study (14 months). Working mechanism of this membrane is not yet well investigated, and we hope, that the further study of the electrode characteristics will show if the proposed single crystal is a unique one as an ion-selective membrane.

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