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The solid potentiometric electrode for determination of chromium (III, VI) ions

The possibility of determining of chromium (III) ions was investigated in this paper. It is shown that the electrode on a basis of heazlewoodite shows high selectivity to chromium (III) ions. Also the stability constants of complexes of chromium (III) ions with a carbamide were determined by potentiometric titration. The amount of chromium (VI) ions in model solutions and wastewater JSC «Mittal Steel Temirtau» (Kazakhstan) was determined by amperometric and potentiometric methods. The data were processed by methods of mathematical statistics.

Key-words: synthesis, heazlewoodite, electrochemistry, ion-selective electrode, chromium (III, VI) ions, potentiometric method, amperometric method, application.

Prospects of development of potentiometry in the creation of new electrode systems and theoretical generalizations are promising enough; Gas, liquid as well as solid membranes, the example of which is an intercalate compound selectivity, ensuring polaron nature of charge carrier localization, are used as the main materials [1].

It is known that ion-selective electrodes (ISE) are widely used in environmental analytical monitoring of environment, medicine, manufacturing analysis. A distinctive feature of chalcogenide materials is the possibility of realization at the electrode-solution reactions of both electron and ion-exchange, which allows the use of chalcogenide ISE as ion metric and red-ox metric electrodes depending on the choice of conditions. In this regard, this paper is the first to be devoted to the research into the possibility of using the solid-state chalcogenide electrode based on heazlewoodite (Ni_3S_2) in determining the chromium ions.

The special literature claims the fact that chromium is used to determine the ISE, where the quaternary onium basis chromates [2], tetrakis(thiocyanate)chromate [3], diphenylguanidine [4], and chromium (III) ions, introduced in polymer matrix on the basis of acrylonitrile are used as an electrodeactive substance. Rudoy and his coworkers [5] proposed a new electrode for the determination of chromium (VI) based on a set of chromium ions with diphenylcarbazide, where methylbuthylketone is used as the complex organic extractant. The lifetime of the proposed electrode without the change of membrane is at least 60 days. The response time with and without stirring is 4. Drift capacity per day is less than ±1 mV, the detection limit, however, remains constant.

Potentiometric method for the determination is based on the oxidation of chromium (III) to dichromate ion in sulfuric acid medium in the presence of ammonium persulphate catalyst — silver nitrate. Dichromate ion is titrated with a solution of iron sulfate double-ammonium by countervailing and non-countervailing methods with platinum and saturated calomel electrode. The most extensively studied systems among electrodes based on liquid cation are the systems with dionylnaphthalenesulfur acid, sensors of which are sensitive to many cations including Cr (III) ions.

However, the main drawbacks of these electrodes are the lack of selectivity, short lifetime, the complexity and irreproducibility in the manufacture, drift potential and long response time. At the same time, along with the potentiometric method researchers use other methods for the determination of chromium, in particular, amperometric method, which suggests to use only the recovery of chromium (III) with any reducing agent. Several methods for the determination of chromium (III) have been developed as well, namely the titration by EDTA and diamincyclohexantetraacetate acid, and the use of hydrogen peroxide for the determination of chromium (III) [6], and determination of chromium (III) silver — persulphate method in the presence of vanadium [7].

Experimental part

Materials and Reagents

The powders of nickel, elemental sulfur, chromium chloride (III), potassium nitrate, potassium dichromate, urea, Mohr's salt were obtained from Karaganda Chemical Reagent Company (Kazakhstan). All chemicals were mark «analytical grade, ≥ 99 %».

Method of synthesis

The powder of nickel and elemental sulfur were used for solid-phase synthesis of metal chalcogenide. Ampoule was evacuated with carbon pump and then was sealed with an oxygen torch. A strong exothermic effect followed the initial reaction of sulfur with nickel. As a result, the ampoule was subjected to slow preheating. For the initial reaction of nickel with chalcogen the exposure was being carried out at 573 K for 2 hours. If there are initial reactions, further interaction takes place in a phase which has become solid. The main reaction was occurred at 773–873 K. The exposure was being carried out at this temperature for 4 hours, then slowly heated to 1073 K (melting point of chalcogenide) and kept at this temperature for 6 hours for the final synthesis.

The obtained chalcogenide was being slowly cooled in the furnace while the current strength was being gradually reduced; a total synthesis was proceeding for about 24 hours. In the synthesis ampoule explosion occurred only in insufficient evacuation of the ampoule. In order to have homogeneous samples, chalcogenides obtained after fusion were removed from the vials and triturated in an agate mortar to powder, then tablets were made from this powder on the press to strengthen the tablets; they were placed again in a quartz ampoule, this ampoule again were evacuated with carbon pump and sealed, placed in a furnace and heated up to 1273 K. Resultant samples were non-porous and durable; the contacts were deposited on the samples and the measurements were carried out. Making the samples of nickel sulfides is one of the most important issues since any impurities significantly affect electrochemical properties.

Identification of the material was carried out using X-ray phase analysis. Diffraction peaks of the samples were complied with data in [8].

Preparation of electrodes to work

Chalcogenide electrode (solid phase) were cleaned by magnesium oxide deposited on wet filter paper, were rinsed with distilled water and were finally polished with a dry filter before each new measurement.

The potentiometric titration

The millivoltmeter pH-121 with the rating measurement error ±2.5 mV was used as a measuring instrument. Silver chloride electrode EVL-1M was always separated from the working solution by electrolytic bridge filled with agar-agar gel 0.1 M KNO_3. Countdown readings were carried out after the establishment of potential value, not changing within the error of a measuring instrument for 1.5 min. Electrode potentials given in the text or tables are translated correspondingly to the normal hydrogen electrode. Calibration curves were constructed in the coordinates E–lg$C$ with standard solutions, prepared by successive dilutions. The initial solution was prepared from the accurately weighed salt sample. All standard solutions contained background electrolyte (0.1 M) KNO_3.

The reference electrodes EVL-1M3, pH-metric glass electrode ESL-63–07 and ESL-43–07, platinum point electrode were used in work. The solution was stirred with a magnetic stirrer. Titrations were carried out in phases, namely approximately and exactly according to the method of drops, the end point of titration was found from the integral and derivative curves. The calculation of errors in the determination was carried out according to the results of titration [9].

The amperometric titration

The amperometric titration was performed on a setup consisted of a galvanometer with a shunt, voltmeter, rheostat, the current source electrode, protective bottle, titration vessel, a rotating platinum indicator electrode [10]. The thermostat UTU-2/77 was used for maintain the standard temperature (298 K).

Discussion of Results

Analytical performance

We investigated the selectivity of the solid electrode based on nickel sulfide composition Ni_3S_2. The experimental values $k_{A/B}^{pot}$, of selectivity factors found by the method of mixed solutions are shown in Table 1 [11].

Table 1

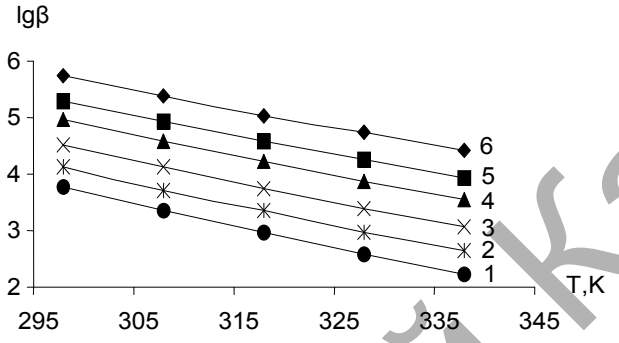
Analytical characteristics of electrodes based on nickel sulfides

Sulfide	S (mV/pFe)	Detection limit, mole·l^{-1}	Interval of admissible values pH	Response time, min	$k_{Cr^{3+}/Cu^{2+}}^{pot}$
Ni_3S_2	29±3	$6\cdot10^{-5}$	1–5	0.5–1.5	0.05
NiS	10±5	$1\cdot10^{-2}$	0.5–4.5	0.5–1.5	0.50

In the data of the table we can see that the relatively high selectivity for Cr^{3+} ions has an electrode of Ni_3S_2. This fact allows us to admit that the selectivity of electrodes based on heazlewoodite to chromium ions (III) is mainly due to ion-exchange function.

The statement is supported by the fact that nickel sulfides such as Ni_3S_2 refer to those compounds, in which the metal *p*-type conductivity has been found. According to the results presented in [12] narrow, partially filled bands fall into the valence band in Ni_3S_2; *d*-zone is filled by electrons from the *sp* valence band and as a result, in the valence band there are free holes, which are carriers, and, consequently, cause of the current, and in contact with the electrolyte — the stationary potential. Consequently, electrode of composition Ni_3S_2 can be used as indicator in the potentiometric titration with chromium (III) ions.

So, the complex formation processes of Cr(III) ions with low molecular compounds in aqueous solutions have been studied by Leden Method, results are given in Figure 1 [13].



Ionic strength: *1* — 1.0; *2* — 0.75; *3* — 0.5; *4* — 0.25; *5* — 0.1; *6* — 0

Figure 1 The dependence of the stability constants of complexes of chromium (III) ions with urea on temperature and ionic strength

The data show that at low temperatures stationary electrode potential takes quite high values over the entire range of concentrations of the ligand, this indicates the presence of chromium ions in the electrode layer. With increasing temperature, as well as with increasing ligand concentration the value of the stationary potential shifts to the negative region, which confirms the occurrence of both the hydrolysis reactions chromium chloride (III), resulting in the formation of hydroxo, and urea complexation [14]. In some cases, these processes are complicated by the presence of nitrate ions in solution that can compete with the ligand in the formation of bonds with the metal ion complexing agent in the inner sphere [15].

On the other hand, this electrode can be used to assess the stability constants of complexes of chromium ions not only with low molecular weight, but also with macromolecular compounds [16].

Oxidation-reduction methods of analysis

It is a well-known fact in literature that chalcogenide electrodes can behave as ion-selective and as redox ones [9]. Therefore, it becomes interesting to trace the dependence of the stationary electrode potential when used as an indicator of redox titration with dichromate-ions.

Change of electrode potential of Ni_3S_2 in the potentiometric titration of potassium dichromate by solution of Mohr's salt was presented in figure 2.

The data show that the titration curve of potassium dichromate solution with Mohr's salt used as an indicator platinum electrode does not have the sound potential drop, whereas the dependence of the stationary potential of threenickel disulfide electrode on the volume of titrant is characterized by a fairly sharp change in potential at the equivalence point. The results of the titration are shown in Table 2.

Table 2

Results of potentiometric determination of chromium (VI) ions with electrode Ni_3S_2

№ sample	pH	Δ*E*, mV	It was introduced, Cr^{6+} ions, mole·l^{-1}	It was detected, Cr^{6+} ions, mole·l^{-1}	S_r
1	1.89	60	0.016	0.015	$1.58 \cdot 10^{-3}$
2	1.87	62	0.016	0.016	
3	1.92	58	0.016	0.014	

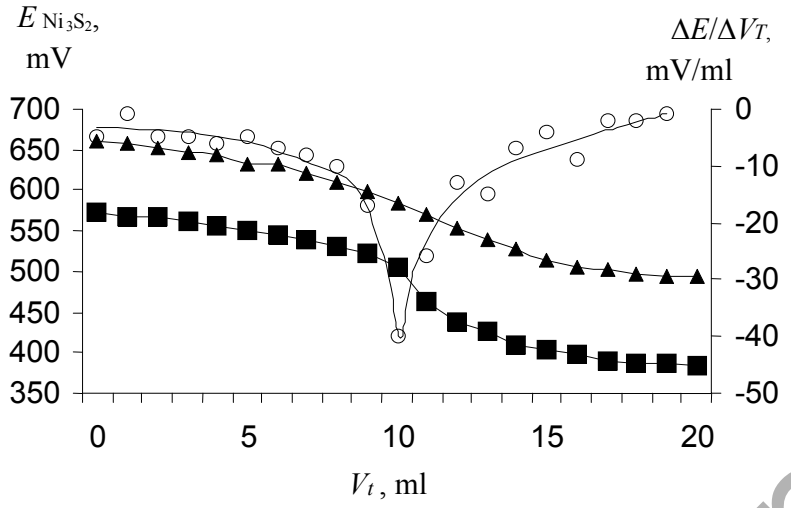


Figure 2. Change in electrode potential of Ni_3S_2 in the potentiometric titration of potassium dichromate solution of Mohr's salt: the titration curve with Ni_3S_2, Pt, the differential curve

The results presented above confirm the existence of electron exchange function along with the ion-exchange one in the case of nickel sulfide (Ni_3S_2), found for other metal chalcogenides, which significantly broadens the scope of semiconductor materials [17].

Application in the analysis of real objects

Potentiometric titration of wastewater samples was performed using the electrode based on heazlewoodite (Ni_3S_2). The amperometric titration was carried confirm the results.

There are many techniques that are based on the titration of chromium (VI) with Mohr's salt, but the principle of the method is the same: titration on platinum (or other solid electrode) by the oxidation current of iron (II). The results of determining the concentration of chromium in wastewater by two methods were presented in Table 3.

Table 3

Results of the determination of chromium in the effluent of JSC «Mittal Steel Temirtau»

Method	N	C, g·l^{-1}	pH	S	F_{exp}	F_{cryt}
Potentiometric	3	$4.7\cdot10^{-3} \pm 0.001$	6.3	$0.58\cdot10^{-3}$	6.69	19
Amperemetric	3	$3.3\cdot10^{-3} \pm 0.004$	6.2	$1.50\cdot10^{-3}$		

The results of the two methods were evaluated by Fisher test. The necessary condition for this criterion is the inequality $F < F_{cryt}$ [18]. Calculations showed that this inequality was satisfied. Consequently, the results of both methods can be considered equally accurate. According to the results, it was found that the potentiometric method of study using chalcogenide electrode based on heazlewoodite (Ni_3S_2) is applicable to the determination of small amounts of chromium (III, VI) in the wastewater [17]. Despite the numerous advantages of the amperometric method of research, potentiometric method using chalcogenide electrodes is easy to install, quick processing of results, minimal time.

Conclusion

Thus, reproducibility and stability of the parameters of sensitivity of the electrode based on nickel sulfide on chromium ions make it possible to analyze other objects, as well as to apply the potentiometric method using chalcogenide electrodes to monitoring mode.

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Ш.К.Әмерханова

Хром (III, VI) иондарын анықтауға арналған қатты потенциометрлік электрод

Мақалада хром (III, VI) иондарын анықтау мүмкіндігі көрсетілген. Хизлевудит негізіндегі электрод хром (III) иондарына қатысты жоғары селективтілікке ие. Сонымен қатар потенциометрлік әдіспен хром (III) иондарының карбамидпен түзетін комплекстерінің тұрақтылық константалары анықталды. Потенциометрлік және амперометрлік әдістермен модельді ерітінділер мен «МиттalСтил Теміртау» АҚ (Қазақстан) ағынды суларындағы хром (VI) иондарының мөлшері белгіленді. Алынған мәліметтер математикалық статистика әдістерімен өңделді.

Ш.К.Амерханова

Твердый потенциометрический электрод для определения ионов хрома (III, VI)

В работе исследована возможность определения ионов хрома (III, VI). Показано, что электрод на основе хизлевудита проявляет высокую селективность относительно ионов хрома (III). Также методом потенциометрического титрования определены константы устойчивости комплексов ионов хрома (III) с карбамидом. Потенциометрическим и амперометрическим методами было определено содержание ионов хрома (VI) в модельных растворах и сточных водах АО «МиттalСтил Темиртау» (Казахстан). Данные были обработаны методами математической статистики.