

The Electrode for Potentiometric Determination of Chromium (III, VI) in Water Solutions

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ABSTRACT

The possibility of determining of chromium (III, VI) ions was investigated in this paper. It is shown that the electrode on a basis of heazlewoodite has high selectivity to chromium (III) ions. Also the stability constants of complexes, forming in system “Cr³⁺-Mohr’s salt-Ca(OH)₂-PVA ÷ PAA” were determined by potentiometric titration with ion-selective electrode.

KEYWORDS

Heazlewoodite; Chromium (III, VI) Ions; Potentiometric Method

1. Introduction

The growing interest in the development of analytic techniques for chromium determination originates from wide spread industrial use of this element and by the fact that its two main oxidation forms have negative various influences on humans [1,2]. Therefore, one of the most urgent problems is to develop new and effective methods for determining of chromium (III, VI). In the scientific literature, there are many methods for determining chromium of different valence, for example, ion-chromatography method [3], potentiometric method [4], determination method using polymers [5,6].

The transition metals chalcogenides used in thermal and photo voltaic converters and also often used as a unique model objects in solid state physics. The unique combination of semiconductor, fluorescent, photo-and piezoelectric properties is as the basis of chalcogenide in microelectronics. Nowadays electrochemistry of solid state is a progressive growing direction in the research world. In modern electrochemistry as electrodes various materials are used as conductors and semiconductors, and composite materials, while the specifics of each individual class and undeniable. 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 redox-metric electrodes depending on the choice of conditions [7]. 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 (Ni₃S₂) in determining the chromium ions.

2. Experimental Part

2.1. Materials and Reagents

The powders of nickel, elemental sulfur, chromium chloride (III), potassium nitrate, potassium dichromate, urea, Mohr’s salt were obtained from Karagandy Chemical Reagent Company (Kazakhstan). All chemicals were marked “analytical grade, ≥99%”.

2.2. 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 pre-heating. 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

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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 anagatemortar 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 was 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]. Also for analysis used the amperometric method for the determination of chromium (VI) ions [9].

2.3. Preparation of Electrodes

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.

2.4. 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-IgC 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 [7].

2.5. 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** [10].

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 [11] narrow, partially filled bands fall into the valence band in Ni_3S_2 ; d—zone is filled by electrons from the spvalence 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** [12].

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 [13]. In some cases, these processes are complicated

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	$k_{Cr^{3+}/Cr^{2+}}^{pot}$
Ni_3S_2	29 ± 3	$6 \cdot 10^{-5}$	1 - 5	0.5 - 1.5	0.05
NiS	10 ± 5	$1 \cdot 10^{-2}$	0.5 - 4.5	0.5 - 1.5	0.50

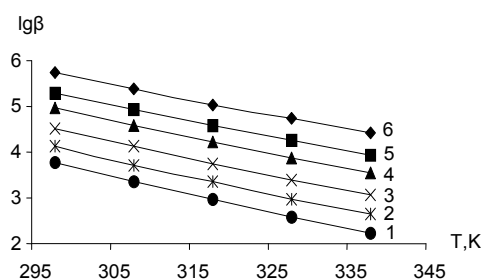


Figure 1. The dependence of the stability constants of complexes of chromium (III) ions with urea on temperature and ionic strength: 1) 1.0 2) 0.75 3) 0.5, 4) 0.25, 5) 0.1, 6) 0.

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 [14].

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 [15].

2.6. Oxidation-Reduction Methods of Analysis

Further the model solution of wastewater containing chromium (III) ions, particularly, system Cr^{3+} -Mohr's

salt- $\text{Ca}(\text{OH})_2$ -PVA ÷ PAA was investigated by potentiometric method (B'errum method).

Mohr's salt concentration (C_{Red}) in the range 0.5 - 0.05 mole·L⁻¹, calcium hydroxide concentration ($C_{\text{Ca}(\text{OH})_2}$) in the range 1 ÷ 10, 1 ÷ 1 vol. %, ratio of PVA ÷ PAA ($C_{\text{PAA} \div \text{PVA}}$) in the range 1 ÷ 5, 5 ÷ 1, are used as variable parameters. We use 6-factorial 5-level matrix [16] as a base (Table 2).

The mathematical models describing the extraction process of chromium (III) ions from wastewater, are obtained on the basis of experimental data, and are listed below general equation:

$$y(E_{ST}) = \frac{(-0.0081T^3 + 0.81T^2 - 22.59T + 467.99)}{314,72^3} \times \frac{(7463.50C_{\text{Red}}^3 - 6118.70C_{\text{Red}}^2 + 1423.10C_{\text{Red}} + 225.60)}{1} \times \frac{(66270.00C_{\text{alk}}^4 - 112969.00C_{\text{alk}}^3 + 56070.00C_{\text{alk}}^2 - 9849.30C_{\text{alk}} + 834.37)}{1} \times \frac{(-24.65C_{\text{HMC}}^4 + 207.37C_{\text{HMC}}^3 - 481.28C_{\text{HMC}}^2 + 307.66C_{\text{HMC}} + 280.90)}{1}$$

Table 2. Change of stationary electrode potential of Ni_3S_2 in the system Cr^{3+} -Mohr's salt- $\text{Ca}(\text{OH})_2$ -PVA ÷ PAA.

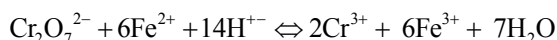
№ exp.	T K	C_{Red} mole·L ⁻¹	$C_{\text{Ca}(\text{OH})_2}$ %	C_{HMC} %	E_{NHE} mV
1	298	0.5	1:10	5:1	303
2	298	0.25	1:7.5	2.5:1	256
3	298	0.1	1:5	1:1	252
4	298	0.075	1:2.5	1:2.5	303
5	298	0.05	1:1	1:5	316
6	308	0.01	1:7.5	1:1	293
7	308	0.025	1:2.5	1:2.5	349
8	308	0.1	1:5	1:5	357
9	308	0.075	1:1	5:1	316
10	308	0.05	1:10	2.5:1	294
11	318	0.5	1:5	1:5	413
12	318	0.25	1:2.5	5:1	390
13	318	0.005	1:1	2.5:1	403
14	318	0.001	1:10	1:1	338
15	318	0.75	1:7.5	1:2.5	297
16	328	0.5	1:2.5	2.5:1	393
17	328	0.1	1:1	1:1	348
18	328	0.05	1:10	1:2.5	349
19	328	0.01	1:7.5	1:5	303
20	328	0,005	1:5	5:1	284
21	338	0,001	1:1	1:2,5	399
22	338	0,75	1:10	1:5	234
23	338	0,5	1:7,5	5:1	206
24	338	0,1	1:5	2,5:1	249
25	338	0,05	1:2,5	1:1	218

For estimation the adequacy of the response function values of obtained experiment and by calculation, the multiple correlation coefficients were calculated on base of generalized equations: $E_{\text{NHE}} = f(T) - 0.99$; $E_{\text{NHE}} = f(\text{PVA/PAA}) - 0.99$; $E_{\text{NHE}} = f(C_{\text{Red}}) - 0.99$; $E_{\text{NHE}} = f(C_{\text{alk}}) - 0.99$. The possibility of using these equations is confirmed by the values of the correlation coefficient. Consequently, the use of electrode on the basis of heazlewoodite mineral is valid not only in the model systems, but in the real multicomponent systems.

2.7. Application in the Analysis

Potentiometric titration of waste water samples was performed using the electrode based on heazlewoodite (Ni_3S_2). 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).

Determination of chromium (VI) was carried out with double ferrous-ammonium salt sulfate solution. Electrochemical reactions occurring with participation of redox-system in presence of $\text{Cr}^{6+}(\text{Cr}_2\text{O}_7^{2-})$ is expressed by equation:



The method is as follows: electrode is placed in a cup with a liquot part of test solution of sulfuric acid in the background, and conduct potentiometric titration, *i.e.* made graphical dependence $E_{\text{Ni}_3\text{S}_2} - \text{Vml. of } (\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ titrant.

After addition of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ titrant solution, chromium(VI) ions reduced to Cr(III). The results of chromium (VI) ions titration with double ferrous—the ammonium salt of sulfuric acid on the background on a compact telectrode are presented in **Table 3**.

Ni_3S_2 composition electrode is sensitive to electrons, which allows, successfully using these properties to determine chromium (VI) ions by oxidation-reduction method [17]. Control of results was performed by classical platinum electrode, with advantage of sulfide electrode compared to other clear.

Table 3. Results of potentiometric determination of chromium (VI) ions with Ni_3S_2 electrode.

values	Electrode types	
	Pt	Ni_3S_2
ΔE , mV	16,000	60,000
It was taken, mole·L ⁻¹	0,016	0,016
It was found, mole·L ⁻¹	0,010	0,015
S,	0,0078	0,0016

2.8. 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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