Chemistry

STUDY OF CHROMIUM(VI) INTERACTION WITH 2-(3-(AZEPAN-1-YL)-2-HYDROXYPROPYLTHIO)ACETIC ACID

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The interaction of chromium(VI) with 2-(3-(azepan-1-yl)-2-hydroxypropil-thio)acetic acid has been studied by means of potentiometric, amperometric and spectrophotometric titration methods. The titration is possible to carry out in the acidity range $3.0 - 7.0\ mol/L$ by sulfuric acid. Molar ratio of the reacting agents is $[Cr(VI)] : [Reagent] = 2 : 3$.

Conformity to the Beer's law is preserved when $8.3 \cdot 10^{-6} - 2.0 \cdot 10^{-3}\ mol/L$ at $E = +0.2\ V$ and when $2.0 \cdot 10^{-5} - 2.0 \cdot 10^{-3}\ mol/L$ at $E = +1.2\ V$ chromium(VI) solutions were titrated.

The technique elaborated has been approved during the analysis of standard chromium-containing ore with standard relative deviation 0.61%. Possible scheme describing the interaction of chromium(VI) with the reagent has been suggested.

**Keywords**: ion-chromatographic determination, amperometric titration method, spectrophotometric titration method.

Literary data about methods for determination of chromium(VI) are rather diverse. It is necessary to carry out preliminary concentration and selective separation for micro-amounts determination. For example, a technique had been suggested for selective isolation of $Cr(VI)$ from solid matrices and its separation from $Cr(III)$ by means of super-critical fluid extraction. Supercritical carbon dioxide adding of methanol, water and lithium bis-(trifluoroethyl)-dithiocarbamate small quantities had been used as extraction agent. The method had been applied for $Cr(VI)$ determination in soil [1].

An ion-chromatographic determination of $Cr(VI)$ in potable water had been described. $Cr(VI)$ was eluted by ammonium sulfate and ammonium hydroxide solution. Then after-column color reaction of $Cr(VI)$ with diphenylcarbazide and

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photometric detection was carried out at $530\ nm$. The calibration curve is linear within $0.1-10\ \mu g/L$ range and the detection limit is $0.02\ \mu g/L$ [2].

Among electrochemical methods the amperometric titration method attracts attention. The methods elaborated are based on the reduction reactions of $Cr(VI)$ to $Cr(III)$ as well as on the oxidation of $Cr(III)$ [3].

Definite interest offers the reactions of $Cr(VI)$ interaction with sulfur-containing reagents – thiourea and phenylthiourea. Methods of potentiometric and amperometric titration of dichromate-ion by thiourea [4] and phenylthiourea [5] had been elaborated.

The aim of the present work is the study of $Cr(VI)$ interaction with newly synthesized substance – 2-(3-(azepan-1-yl)-2-hydroxypropilthio)acetic acid.

Experimental Part. The solution of potassium dichromate has been prepared from fixanal (standard-titre). The 2-(3-(azepan-1-yl)-2-hydroxypropilthio) acetic acid (R) working solution has been prepared by solving the reagent sample in distilled water. "Pure for analysis" quality sulfuric acid solutions have been used.

The study of the interaction of dichromate-ions with reagent has been carried out on pH-121 pH-meter-millivoltmeter. Amperometric titration has been carried out at the self-composed amperometric setting using platinum microelectrode $(l=5\ mm)$ and mercury iodide comparison electrode $(E=+0.2\ V)$. Spectrophotometric titration has been realized by means of СФ-16 spectrophotometer.

Preliminary study of $Cr(VI)$ interaction with the reagent has been done by means of qualitative reactions, which showed that in the presence of sulfuric acid the orange color of dichromate-ions solution turns to blue-green when the reagent is gradually added. Such change of color witnesses about the formation of $Cr(III)$ and redox character of the interaction. And it makes possible to study the system $Cr(VI)-R$ by means of potentiometric titration method.

The potentiometric titration has been carried out in wide range of acidity by sulfuric acid $(1.0-9.0\ mol/L)$. The potential leap corresponds to molar ratio $\big[Cr(VI)\big]:\big[R\big]=2:3$. This ratio remains invariable in the presence of sulfuric acid in $3.0-7.0\ mol/L$ concentration. At lower and higher acidity this molar ratio gets broken. In the sequel all the determinat-ions were carried out at medium values of sulfuric acid concentration $(3.5-4.5\ mol/L)$.

Voltage-current characteristics of the reacting components have been taken away to choose the potential value for amperometric titration. It is interesting that R displays electro-activity and notably undergo anodic oxidation at potential values higher than $1.2\ V$, and $Cr(VI)$ gives cathodic reducing wave starting with $0\ V$. The amperometric titration curves are __/ and __ shaped correspondingly. The inflection at the titration curves is observed at molar ratio of reacting components 2 : 3, which confirms the data of potentiometric titration. At optimal sulfuric backgrounds the linear dependence between $Cr(VI)$ concentration and the

diffusion current holds true for $8.3 \cdot 10^{-6} - 2.0 \cdot 10^{-3}$ mol/L solutions of $Cr(VI)$ at $E = +0.2\,V$, and at $E = +1.2\,V$ the range of determined concentration for $Cr(VI)$ is $2.0 \cdot 10^{-5} - 2.0 \cdot 10^{-3}$ mol/L.

Since blue-green colored $Cr(III)$ is a product of the interaction of $Cr(VI)$ with the reagent, the system has been studied also by means of spectrophotometric titration method. With this aim series of solutions with constant $Cr(VI)$ concentration and increasing concentration of the reagent have been prepared. Measuring of optical density of solutions has been carried out at $\lambda=370$ nm (Fig. 1).

Complete de-coloration of the dichromate-ions solution takes place when molar ratio $\left[Cr(VI)\right]:[R] = 2:3$, which coincides with the data of potentiometric and amperometric titration.
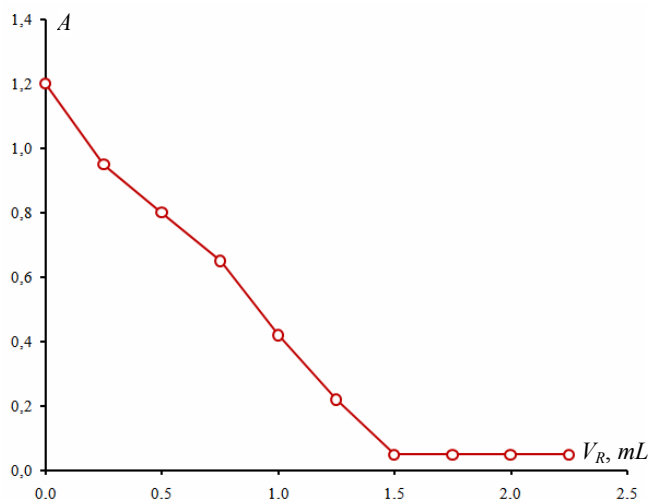

Fig. 1. Spectrophotometric titration curve:
$V_{Cr(VI)}$=1.0 mL; [Cr(VI)]=1·10^{-2} mol/L; [R]=1·10^{-2} mol/L; l=1 cm; [H$_2$SO$_4$]=4.0 mol/L.

Thereby, it has been stated by means of the three independent methods that the interaction of chromium(VI) with 2-(3-(azepan-1-yl)-2-hydroxypropilthio) acetic acid accomplishes at molar ratio between the reacting components 2 : 3, which allows to present the given interaction by the following Scheme:
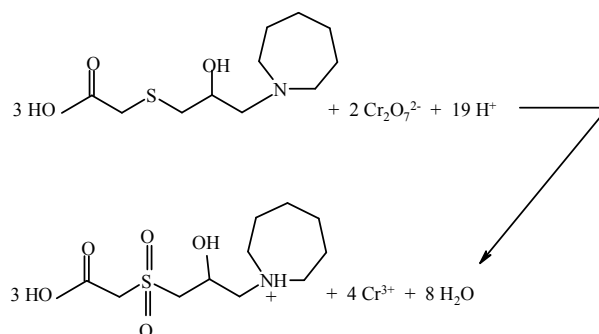
Inasmuch as the data of the three methods are reproducible and coincided, the potentiometric titration has been applied for determination of chromium in standard chromium-containing ore (the sample № 10.42) having the following certificated content (mass. %): $Al - 5.31$; $Si - 6.23$; $Mg - 8.22$; $Ca - 0.68$; $Fe - 12.1$; $Cr - 32.8$.

Procedure. Decomposition of the chromic ore may be achieved by sintering with the mixture of two mass parts of sodium carbonate and one mass part magnesium oxide (by weight) at $800 - 900\,^0C$ temperature. The sample of fine-grained ore ($0.5\,g$) was mixed on watch glass with sixfold quantity of the above mentioned sintering mixture, carried into the quartz crucible on the bottom, of which some soda with magnesium oxide was preliminary placed and cover with thin layer of the same sintering mixture. The crucible was covered then placed to the muffle and sintered during $2 - 3\,h$. On the expiration the cake comes off walls and the mixture covering it becomes colored yellow. The cake was cooled and leached by boiling water. Insoluble residue was filtered and rinsed by hot water. Iron, manganese and other metal ions remain in residue and chromium(VI) pass on to the filtrate as dichromate ion [6]. The solution obtained was neutralized by sulfuric acid (1:2) and the volume was led to $250.0\,mL$ by distilled water. The aliquote part of the solution ($5.0\,mL$) was titrated potentiometrically by $1 \cdot 10^{-2}\,mol/L$ working solution of 2-(3-(azepan-1-yl)-2-hydroxypropilthio)acetic acid in optimal acidity conditions (3.5 *mol/L* sulfuric acid) (Fig. 2).
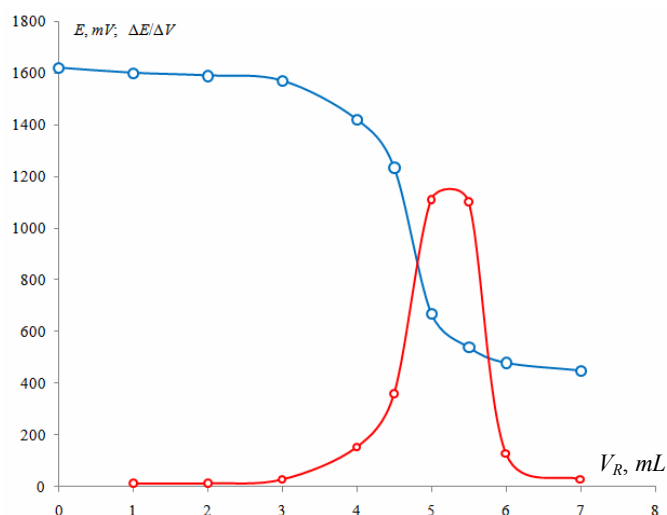

Fig. 2. Potentiometric titration curves. Aliquote volume $5.0\,mL$, [R]=$1 \cdot 10^{-2}$ *mol/L.*

When analizing standard ore with 32.8 mass.% chromium content 33.0% has been obtained. Standard relative deviation value is 0.61% at $P = 0.95$, so, it may serve as a cause to use 2-(3-(azepan-1-yl)-2-hydroxypropilthio)acetic acid as a new reagent for determination of chromium.

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