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DEVELOPMENT OF A POTENTIOMETRIC EDTA METHOD FOR DETERMINATION OF MOLYBDENUM. USE OF THE ANALYSIS FOR MOLYBDENITE CONCENTRATES

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16. Abstract Based on considerations of principles and experimental data, the interference of sulfate ions in potentiometric titration of EDTA with $FeCl_3$ was confirmed. The method of back complexometric titration of molybdenum of Nonova and Gasheva has thus been improved by replacing hydrazine sulfate with hydrazine hydrochloride for reduction of Mo(VI) to Mo(V). The method can be used for one to tenths of mg of molybdenum with 0.04 mg standard deviation. The specific method of determination of molybdenum in molybdenite concentrates is presented.					
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DEVELOPMENT OF A POTENTIOMETRIC EDTA METHOD FOR DETERMINATION OF MOLYBDENUM. USE OF THE ANALYSIS FOR MOLYBDENITE CONCENTRATES

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The complexometric method of determination of molybdenum is based /243 on the property of Mo(V) ions to form a stable complexon with EDTA with the composition  $Mo_2O_4Y^{2-}$ , molecular weight 608.15 and log. K-25-27 [1, 2]. The complex is stable in a wide interval of acidity, from 0.5 N to pH 10. A method of direct complexometric titration has not been developed, because of the lack of a suitable indicator. A number of authors propose back titration with xylenol orange, eriochrome black T and Cu(II)-EDTA-RAN system indicators [3]. The color transition close to the equivalent point is not very distinct in this method, because of which the reproducibility of results is not particularly good.

Of the instrumental methods of establishment of the equivalent point, the potentiometric method is of the greatest interest [4]. Back titration is applied in this case. Mo(IV) ions are reduced in a medium of 0.5 N sulfuric acid with hydrazine sulfate in the presence of a known excess of EDTA. The excess is titrated potentiometrically with  $FeCl_3$  solution in buffer at pH 2. A bright Pt plate is used as the indicator electrode, and a saturated calomel electrode is used as the comparison electrode. The potentiometric method has better selectivity and, compared with visual readout methods, better reproducibility.

In the sulfuric acid solution obtained following acid decomposition of molybdenum containing items, difficulties arise in reading the equivalent point, since the equivalent part of the potentiometric

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curve has a lower slope (Fig. 1). In comparison of the results obtained potentiometrically with those by the gravimetric method with oxine, it has been established that a negative error is permitted in the potentiometric method.

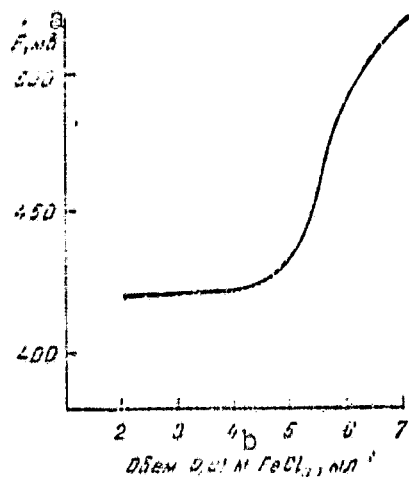


Fig. 1. Potentiometric curve of titration of EDTA with 0.01 M  $\text{FeCl}_3$  after reduction of Mo(VI) with 0.05 M hydrazine sulfate at pH 2.

Key: a. E, mV  
b. Volume of 0.01 M  $\text{FeCl}_3$ , ml

$$\text{pFe} = -0.5 \log c_{\text{EDTA}}^0 + 0.5 \log K_{\text{FeY}} - 0.5 \log \alpha_{\text{Y}(\text{H})},$$

where

$c_{\text{EDTA}}^0$  is the EDTA concentration of the solution before titration;

$K_{\text{FeY}}$  is the stability constant of the ferricomplexon =  $10^{25.1}$  [5];

$\alpha_{\text{Y}(\text{H})}$  is the stability of the alpha factor of  $\text{H}_2\text{Y}^{2-}$  at pH 2 =  $10^{18.5}$  [5].

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We suggest that the unfavorable appearance of the potentiometric curve is due to complex formation between sulfate ions and ferric ions introduced with the titration solution. To test this hypothesis, the equilibrium concentrations of  $\text{Fe}^{3+}$  in the solution titrated was calculated at different stages of the titration in the absence and in the presence of sulfate ions. The change in concentration of  $\text{Fe}^{3+}$  before the equivalent point is immaterial for the potential. At the equivalent point, the value of pFe in the absence of the sulfate ion is calculated by the equation

In the presence of sulfate, calculation of the excess by the similar equation

$$pFe = -0.5 \log C_{EDTA}^0 + 0.5 \log K_{FeY} - 0.5 \log \alpha_{Y(H)} + \log \alpha_{Fe(SO_4)^{2-}},$$

where  $\alpha_{Fe(SO_4)^{2-}}$  is the alpha factor for binding the ferric ions in the sulfate complexes; with  $[SO_4]^{2-} = 0.05$  M,  $\alpha_{Fe(SO_4)^{2-}} = 10^{1.7}$  [3].

The  $Fe^{3+}$  concentration after the equivalent point is calculated on the basis of dilution. In the presence of sulfate, the correction is made with the aid of the expression

$$pFe = pC_{Fe} + \log \alpha_{Fe(SO_4)^{2-}},$$

where  $C_{Fe}$  indicates total concentration of the addition to the excess ferric ions. To simplify the calculation, a correction is made for the activity and for the change in volume during titration.

With the lowest possible concentration of sulfate ions, i.e., introduced only with the reducing agent, of 0.05 M and with 0.01 M titration solution concentration, the following pFe values are obtained (Table 1):

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TABLE 1

His mllyk ot 0,01 M a FeCl <sub>3</sub> в ml	p Fe	
	b в отсутствие SO <sub>4</sub> <sup>2-</sup>	c в присутствии 0,05 M SO <sub>4</sub> <sup>2-</sup>
0	7,3	8,3
0,1	5,0	6,7
0,2	4,7	6,4
0,3	4,5	6,2
0,5	4,3	6,0

Key: a. Excess of 0.01 M FeCl<sub>3</sub> in ml  
 b. In absence of SO<sub>4</sub><sup>2-</sup>  
 c. In presence of 0.05 M SO<sub>4</sub><sup>2-</sup>

It is seen that, in the absence of sulfate, the first small excess of titration solution causes a 2.3 unit reduction of pFe. In

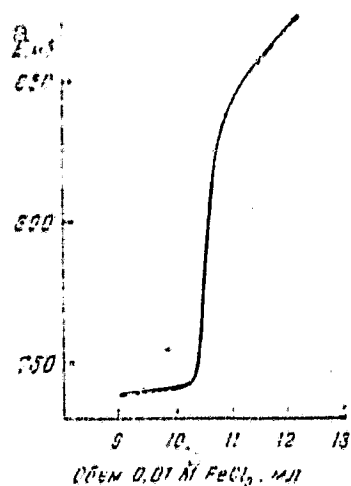


Fig. 2. Potentiometric curve of titration of EDTA with 0.01 M  $\text{FeCl}_3$  at pH 2.

Key: a. E, mV  
 b. Volume of 0.01 M  $\text{FeCl}_3$ , ml

of pFe (Fig. 1). The effect of the sulfate ion will be still more tangible at higher concentration.

The results obtained show that it is advisable to replace hydrazine sulfate with a reducing agent which does not contain the sulfate ion, and to use hydrochloric acid to acidify the solution instead of sulfuric acid. We experimentally tested the substitution of reagents under the following conditions. A specific volume of EDTA solution with a known concentration and 0.6 g of hydrazine hydrochloride is added to a solution containing molybdenum, and the solution is heated and boiled 5 min. It is cooled, neutralized with 1 N NaOH, 10 ml of monochloracetate buffer of pH 2 is added (one molar solution of monochloroacetic acid is neutralized by pH meter with NaOH to pH 2). The solution is diluted to approximately 80 ml, and the excess EDTA is titrated with 0.01 M  $\text{FeCl}_3$ .

The concentrations of the solutions used were determined by the

the Nernst response, approximately a 120 mV change in potential (for a single electron reaction at 25°) corresponds to this increase in concentration of the indicator ion potential. The values we obtained experimentally are close to theoretical (Fig. 2). The presence of the sulfate ion causes a reduction in the equilibrium concentration of  $\text{Fe}^{3+}$  at the equivalent point from  $10^{-7.3}$  to  $10^{-8.3}$  M. The latter concentration is very low, and the indicator electrode cannot record the relatively sharper reduction of pFe immediately beyond the equivalent point, i.e., there is not a sharp jump in the potentiometric curve. The experimentally obtained curves actually have a nearly constant slope in the equivalent section

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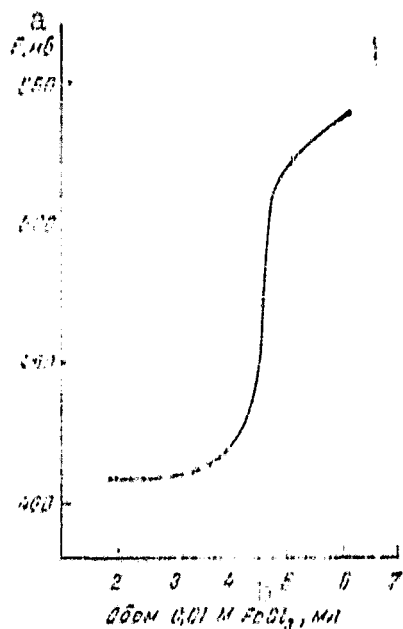


Fig. 3. Potentiometric curve of titration of EDTA with 0.01 M  $\text{FeCl}_3$  after reduction of Mo(VI) with hydrazine hydrochloride in hydrochloric acid medium.

Key: a. E, mV  
b. Volume of 0.01 M  $\text{FeCl}_3$ , ml

molybdenum. The volumes corresponding to the first jump of E were calculated and, from these, those corresponding to the maximum on the differential  $dE/dV$  curve. The results calculated from the initial volume are closer to the actual content, which is evident from Table 2.

As is evident, in calculation with the volumes which correspond to the differential curve maximum, the results are systematically lower. It was established that, in determination of molybdenum by this method, ions of divalent metals, Al(III) and W(VI) do not interfere [6].

following methods: ammonium molybdate gravimetrically with oxine; EDTA with solution of electrolytic copper;  $\text{FeCl}_3$  gravimetrically as ferric oxide and by potentiometric titration with EDTA at pH2. E was measured with the pH meter of a AT-2 automatic titrater.

The potentiometric curves obtained under these conditions have the form shown in Fig. 3. Exactly which moment has to be used for the end of titration is established from its value. From the table with the calculated values of pFe, it is seen that the jump is observed with the first excess of titration solution. Titration therefore has to be considered complete at the first jump in the potential noted after addition of a 0.05 ml portion of titration solution. To test the authenticity of this conclusion, we repeatedly titrated different, but precisely known amounts of

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TABLE 2.

а Содержание Mo в мг	б Объемы 0,005 и 0,01 M FeCl <sub>3</sub> в мл		е Определен Mo в мг	ф Объемы FeCl <sub>3</sub> решения по макс. наблюдения в мл		г Определен Mo в мг
	по измерению	по расчету		по макс.	по мин.	
1,03	3,11	3,11 3,13 3,10 3,10	1,04	3,20 3,23 3,20 3,20	0,95	
4,11	6,13	6,10 6,15 6,10 6,05	4,10	6,20 6,25 6,22 6,13	3,95	

- Key: a. Mo content in mg  
 b. Volume of 0.005 and 0.01 M ferrichloride, mg  
 c. Calculated  
 d. Reading at first jump  
 e. Mo determined in mg  
 f. Volume of FeCl<sub>3</sub>, reading at dE/dV max in ml

Use of Potentiometric EDTA Method for Determination of Molybdenum in Molybdenite Concentrates

Applicability of the method is tested on standard samples of molybdenite concentrates with a precisely known molybdenum content.

Several ways of putting the samples into solution were tested. In acid solution with hydrochloric and nitric acids, the results for molybdenum are systematically lower. Fusing with a mixture of alkaline carbonate and sodium peroxide also proves to be unsuitable, because a stable blue compound with Mo(V) forms in the presence of carbonate. In all likelihood, this is a complex compound which does not decompose upon boiling and which binds some amount of Mo(V). Preliminary removal of CO<sub>2</sub> from the solution proceeds slowly. Alkaline peroxide fusion proves to be most convenient. To reduce the amount of sulfur, a weighed sample is heated in a porcelain crucible for approximately one hour at 480±10°. The melt is dissolved in hot water, it is transferred to a 200 ml volumetric flask after cooling, and it is left until equilibrium of adsorption process is established. After passing the solution through a dry filter, an aliquot is pipetted from the filtrate for conduct of the titration.

It can be expected that, together with the molybdate ions,  $WO_4^{2-}$ ,  $VO_3^-$ ,  $AlO_2^-$  and  $PbO_2^{2-}$  will pass over into the filtrate. By means of spectral analysis of the dry residue obtained after evaporation of 20 ml of the filtrate, the presence of other component elements of the molybdenite concentrate is not established. The passage of foreign ions in the filtrate does not interfere with molybdenum determination under the titration conditions. According to data in the literature [5], the conditional stability constants of Al(III) and Pb(II) complexons under these conditions are  $10^{1.8}$  and  $10^{3.3}$  respectively, and it has been proved experimentally that tungsten does not bind measurably to EDTA [6] and that the V content is less than 0.01%. Consequently, with an alkaline peroxide melt, simultaneously with decomposition of the sample, removal of the interfering components is achieved.

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Based on the study results, the following method for determination of molybdenum was worked out. Approximately 0.25 g of finely ground concentrate dried at  $105^\circ$  is weighed out in a porcelain crucible, and it is heated in a muffle furnace with a heat regulator at  $480 \pm 10^\circ$  for one hour. Approximately 2.5 g of KOH (pure and  $CO_2$  free) is weighed out in an iron crucible and warmed on a heater. The hot sample of concentrate is transferred to the melt, 0.5 g of  $Na_2O_2$  is added, it is covered, and it is heated carefully on a burner until a smooth homogenous melt is obtained. The crucible is removed and shaken so as to distribute the melt over the walls, and it is immersed into a beaker of cold water. After this, the crucible is rinsed with distilled water and is placed into a short 250 ml beaker containing approximately 150 ml of hot water.

The beaker is covered with a watch glass and is warmed until the melt forms a puddle. The crucible and cover are removed and rinsed with distilled water. After it is cooled, the contents of the beaker are transferred to a 200 ml volumetric flask, it is tempered and filled up with water. Equilibrium of the adsorption process is reached in approximately one hour. The clarified solution is filtered through a dry filter into a dry beaker. The first portion is

discarded, and 25.0 ml is pipetted into a 250 ml beaker, 10.0 ml of 0.01 M EDTA solution, 4.7 ml of 2 N HCl and 6 ml of 10% solution of hydrazine hydrochloride are added. The solution is heated to boiling and is boiled for 5 min. It is neutralized with 1 N KOH with methyl red indicator, and 10 ml of monochloracetate buffer at pH 2 is added. After 15-20 min, the solution is diluted to approximately 80 ml and the excess of EDTA is titrated with 0.02 M  $\text{FeCl}_3$  solution tempered at 20° and placed in a 5 ml microburette. The electrodes described are used. Before each titration the platinum electrode is immersed briefly in hot concentrated  $\text{HNO}_3$  and rinsed with water. At first, the titration solution is added continuously, but slowly and dropwise while stirring with an electromagnetic stirrer. Close to the equivalent point, the solution is added in 0.02 ml portions, stirred, and the constant value of E is read. The volume at which the change of E amounts to 20 mV after addition of the last 0.05 ml portion is taken as the equivalent volume. One potentiometric curve obtained under the conditions described is presented in Fig. 4.

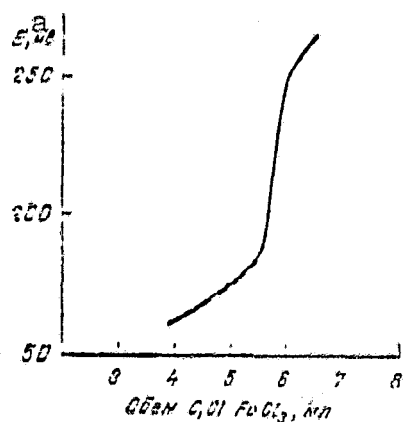


Fig. 4. Potentiometric curve of titration of excess EDTA with  $\text{FeCl}_3$  in solution of molybdenite concentrate.

Key: a. E, mV  
 b. Volume of 0.01 M  $\text{FeCl}_3$ , ml

The calculation is performed by the following formula, /249

$$\text{Mo}^{\text{a}}_{\text{b}} = \frac{(V_{\text{EDTA}} \cdot M_{\text{EDTA}} - V_{\text{FeCl}_3} \cdot M_{\text{FeCl}_3}) \cdot 2 \cdot \text{mgeq} \cdot \text{Mo} \cdot 8 \cdot 100}{a}$$

where  $V_{\text{EDTA}}$  is the volume of EDTA of molarity  $M_{\text{EDTA}}$  added,  $V_{\text{FeCl}_3}$  is the volume of titration solution of molarity  $M_{\text{FeCl}_3}$  with which the excess EDTA is titrated, the factor 2 comes from the ratio in which the Mo(V) ions react with EDTA, namely 2:1, the factor 8 is from the ratio of the total volume to the volume of the aliquot, and a is the initial weight of the sample.

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The EDTA and  $\text{FeCl}_3$  solutions have to be prepared very precisely. Reagents r.a. from companies of good repute are used. For 1 l of 0.01000 M solution of EDTA, 3.7228 g of the disodium salt, dried at  $60^\circ$  for 4 days is weighed to within  $\pm 0.1$  mg, and it is dissolved in double distilled water in a specially tested 1 l volumetric flask after tempering. The solutions can be prepared from pure ethylenediaminetetraacetic acid, if the equivalent amount of sodium hydroxide in the form of a solution of known concentration is added to the solution.

For preparation of 1 l of 0.02 M  $\text{FeCl}_3$  solution, 3.2242 g  $\text{FeCl}_3$  is weighed to within  $\pm 0.1$  mg, 8 ml of 2 N HCl and 10 ml of distilled water are added, and it is heated until dissolved. For oxidation of  $\text{Fe}^{2+}$ , 2 ml of 3%  $\text{H}_2\text{O}_2$  solution is added. The solution is boiled until the excess  $\text{H}_2\text{O}_2$  is decomposed. It is transferred quantitatively to a 1 l volumetric flask. The concentration of the solution is determined gravimetrically (as  $\text{Fe}_2\text{O}_3$ ) and volumetrically by potentiometric titration of a specific volume of EDTA solution buffered with monochloroacetate buffer, with the  $\text{FeCl}_3$  solution.

TABLE 3.

Вид образца а	b Содержание молибдена в %				Средняя стоимость е	S	C
	с по свидетельству	d определено					
Молибденитовый концентрат f	22,61	22,76	22,52	22,25	22,59	0,18	0,80
		22,69	22,77	22,62			
		22,77	22,77	22,67			
		22,36	22,61	22,37			
		22,69	22,60	22,98			
		22,77	22,37	22,61			

Standard deviation is denoted by "S," and the relative standard deviation in % by "C."

Key: a. Sample type  
b. Molybdenum content in %  
c. From certificate  
d. Determined  
e. Average value  
f. Molybdenite concentrate

The results obtained from multiple repetition of the analysis by the method described are presented in Table 3.

The reproducibility of the method can be improved, if a carbon electrode (CR-S-7112-S, Radelkis) is used in place of the platinum electrode and if the volume of the aliquot is increased. /250

Compared with the volumetric method used for determination of molybdenum in similar samples, the method we have compiled is more selective and reliable, and it has better reproducibility.

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