THE DETERMINATION OF Cu, Pb, Cd, AND Zn IN NONFERROUS METALLURGY PRODUCTS WITH AN ALTERNATING CURRENT POLAROGRAPH

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Translated from Zavodskaya Laboratoriya, Vol. 29, No. 4,
pp. 395-401, April, 1963

To determine thousandths and ten thousandths of a per cent of Cu, Cd, Pb, and Zn in various products of nonferrous metallurgy using an alternating current polarograph, the following new supporting electrolytes are proposed: 0.5 M $HClO_4$+ 1 M H_3PO_4 for the determination of all these elements and alkaline solutions of sodium perchlorate, chloride, and tartrate for the determination of Cu and Pb.

The alternating-current polarograph [1-3] has high sensitivity and resolving capacity compared with a direct-current polarograph and can be used to determine Cu, Pb, Cd and Zn in the presence of a much larger amount of the interfering element. However, when there is a very low potential difference of the half-waves we must separate the interfering elements. For example, the determination of lead with a supporting electrolyte of chlorides or hydrochloric acid is affected by Sn, W, Sb, and As; the determination of cadmium is affected by indium. With an ammonium-ammonia supporting electrolyte cobalt affects the determination of zinc and thallium affects the determination of copper. We looked for other electrolytes in which we could determine Cu, Pd, Cd and Zn in the presence of high concentrations of the interfering elements. We conducted the investigations with a Mervin Instruments polarograph, model 3; the anode was a mercury bottom, the cathode was a mercury-drop electrode with drop period of 2.8-3.5 sec (capillary diameter 60-70 μ).

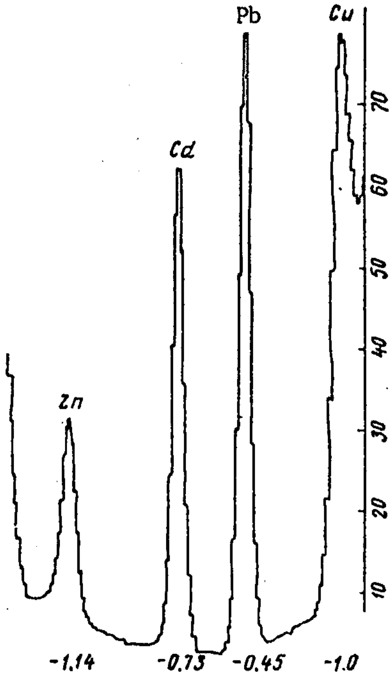

Fig. 1. Polarogram of Cu, Cd, Pb and Zn with a supporting electrolyte of a solution which was 1 M with respect to orthophosphoric acid and 0.5 M with respect to perchloric acid; concentration 10^{-4} mole/liter; sensitivity $^1/_{160}$.

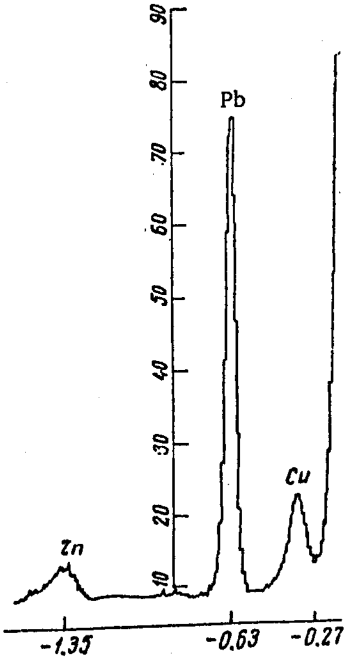

Fig. 2. Polarograms of Cu, Pb, and Zn with a supporting electrolyte of a solution which is 0.5 M with respect to sodium perchlorate and 0.9 M with respect to alkali; concentration 10^{-4} mole/liter; sensitivity $^1/_{160}$. Oxygen removed by sodium sulfite.

Using a supporting electrolyte of 1 M phosphoric acid [2, 4] the potentials of the peaks Cu, Pb, Cd and Zn were +0.01, −0.39, −0.58 and −1.0 V respectively and the potential difference was sufficient for the determination of these elements without separating Sn, Sb, W, Co and In.

To obtain reproducible results during the determination of zinc the solution had to be boiled for a certain length of time to destroy the polyphosphoric acids which form during evaporation. However, in nonferrous metallurgy products there is always a large amount of iron, which means that phosphoric acid alone cannot be used as the supporting electrolyte.

TABLE 1. Characteristics of Polarograms of Various Elements at a Concentration of 10^{-4} mole/liter With a Supporting Electrolyte of a Solution Which is 1 M With Regard to Orthophosphoric Acid and 0.5 M With Regard to Perchloric Acid

Element	mg/liter	H_p mm	σ, mV	E_p, V	$K = \frac{H_p}{C}$
Cu	6.35	960	58	−0.18	151
Pb	20.7	1280	47	−0.55	64.0
Cd	11.2	1056	47	−0.73	94.0
Zn	6.53	576	52	−1.15	88.2
Fe	5.85	2780	20	0.00	475
Pt	19.6	2112	41	0.00	108
Mo First peak	9.59	832	41	−0.18	87.0
Mo Second peak	9.59	160	1300	−0.70	18.7
Re First peak	18.6	17	2000	−0.22	0.94
Re Second peak	18.6	22	290	−0.45	1.2
Pd	10.6	37	1700	−0.40	3.5
As	7.49	–	200	−0.42	–
Mn	5.49	27	2350	−0.45	4.9
V	5.09	22	2000	−0.55	4.3
Se First peak	7.89	64	20	−0.10	8.13
Se Second peak	7.89	2304	18	−0.72	293
Tl	20.4	480	94	−0.77	23.5
Te First peak	12.7	76	153	−0.27	5.2
Te Second peak	12.7	80	200	−0.47	6.3
Te Third peak	12.7	7040	20	−1.03	554
Ni	5.87	43	117	−1.22	7.3
Ge, Sb, Sn, Co, W, Ga and In		Not reduced			

Hydrochloric and nitric acids are usually used to decompose the samples, after which the chloride ions must be completely removed; the interfering elements (Sn, Co, Sb, In, W) are reduced in the presence of chloride [2, 3].

Heating with sulfuric acid may only be used when it is not necessary to determine lead.

In the determination of zinc using a mixture of phosphoric and sulfuric acids as the supporting electrolyte it is essential that the concentration of the latter should be not more than 4% (by volume) since otherwise the zinc peak is deformed.

To remove the hydrochloric and nitric acids we heated the solution with perchloric acid ($t_b = 203°C$) until fumes appeared. With all the elements to be determined perchloric acid forms nonvolatile, readily soluble compounds. The best medium for the determination of Cu, Pb, Cd, and Zn is a solution which is 1 M with respect to orthophosphoric acid and 0.5 M with respect to perchloric acid. In this solution these elements are reversibly reduced, which can be seen by comparing their half-wave widths σ with the theoretical values [5, 6] for reversible processes with the participation of two electrons $\sigma = (88/2) = 44$ mV.

Figure 1 gives the polarograms of Cu, Pb, Cd, and Zn, from which the value of σ calculated for each element is close to the theoretical and is 58, 47, 47, and 52 mV for Cu, Pb, Cd, and Zn respectively.

The linear relationship between the concentration and height of the peak is preserved for copper and zinc from $0.7 \cdot 10^{-6}$ mole/liter, for lead and cadmium from $1 \cdot 10^{-7}$ mole/liter. The maximum concentration of each element should not exceed $5 \cdot 10^{-4} - 1 \cdot 10^{-3}$ mole/liter.

The presence of hydrochloric and nitric acids has little effect on the height (H_p) and σ of lead and cadmium and has a greater effect on these quantities for copper and zinc in view of the closeness of the reduction potentials of Cl^- and NO_3^- to the reduction potentials of copper and zinc respectively.

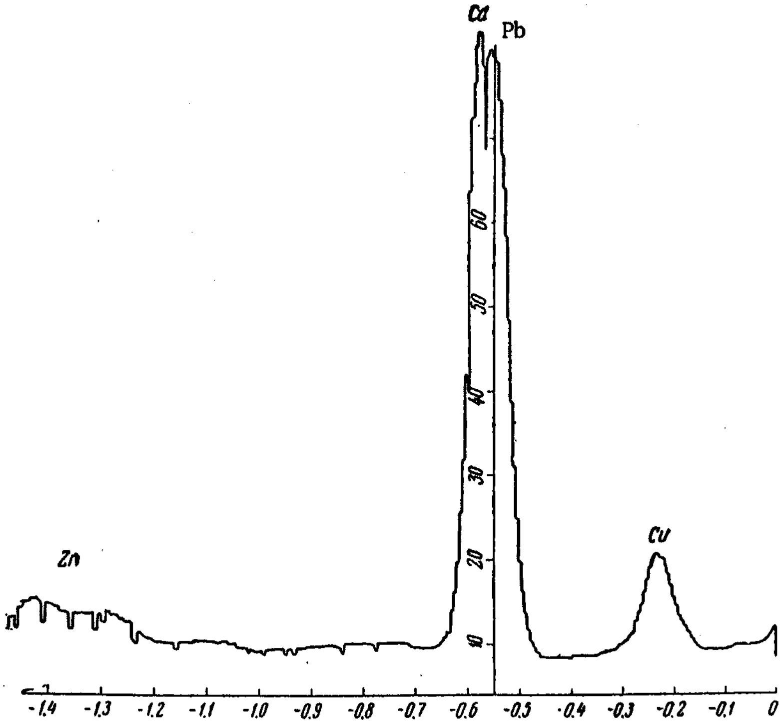

Fig. 3. Polarograms of Cu, Pb, Cd, and Zn in the presence of iron with a supporting electrolyte of a solution which is 1 M with respect to alkali, 0.09 M with respect to sodium tartrate and 0.65 M with respect to sodium chloride; concentration 10^{-4} mole/liter; sensitivity $^1/_{160}$.

Iron does not interfere with the determination of Zn, Pb, and Cd with a ratio Fe : Me = 400 : 1 and for copper Fe : Cu = 200 : 1. It was found that copper could be determined with a ratio Cu : Pb : Cd : Zn = 1 : 500 : 1000 : 1000; lead with Pb : Cu : Cd : Zn = 1 : 200 : 1000 : 1000; cadmium with Cd : Cu : Pb : Zn = 1 : 1000 : 1000 : 1000 and zinc with Zn : Cu : : Pb : Cd = 1 : 600 : 200 : 600.

By detailed analysis of the data provided by Table 1, we can demonstrate, for example, that Pb can be determined without the separation of Sn, Sb, W and As; Cd without the separation of In; Zn without the separation of Co; and Cu without the separation of Tl. The data also indicate the possibility of developing sensitive methods for the determination of low concentrations of Te, Se, Pt, Fe and Mo since the heights of the peaks of the first four elements with equal molar concentrations are 6, 2, 1.5 and two times greater respectively than the heights of the peaks of Pb and Cd and to a greater extent Cu and Zn, and the height of the Mo peak is 1.5 times greater than the height of the Zn peak. For high concentrations of these elements, phosphoric and perchloric acids therefore cannot be used as the supporting electrolyte for the determination of Cu, Pb, Cd and Zn.

It is a well-known fact that these elements are reduced reversibly when an alkali solution is used as the supporting electrolyte [7, 8], the copper in this case forms several peaks, whose determination will not be interfered with by Sn, Mo, Sb, or W since the latter are not revealed polarographically. The reduction potential of tellurium is much more negative than the reduction potentials of copper and lead, but is close to the reduction potential of zinc, and should therefore interfere only with its determination ($E_{1/2}$ for Cu, Pb, Zn, Te (IV) and Te (VI) is −0.21, −0.76, −1.49, −1.2 and −1.57V respectively).

As the supporting electrolytes we also studied mixed electrolytes—caustic soda and sodium perchlorate, and also caustic soda and sodium chloride.

Figure 2 shows polarograms of Cu, Pb, and Zn with reduction using a supporting electrolyte of an alkaline solution of sodium perchlorate (potentials of the Cu, Pb, and Zn peaks were −0.27, −0.63 and −1.35 V respectively). The values of σ for Cu,* Pb, and Zn of 88, 47, and 135 mV respectively point to the reversible character of the reduction of lead and copper and the irreversible character of zinc, which contradicts certain literature data. The linear relationship between the concentration and height of peaks was found for Cu, Pb, and Zn within the limits $3 \cdot 10^{-7}$, 10^{-7} and 10^{-6} mole/liter respectively up to $2 \cdot 10^{-4}$ mole/liter for all elements.

TABLE 2. Characteristics of the Polarograms of Cu, Pb, Cd, and Zn with a Supporting Electrolyte of Various Main Electrolytes (Concentration 10^{-4} mole/liter)

Composition of electrolyte	Cu			Pb			Cd			Zn		
	H_p, mm	E_p, V	σ, mV	H_p, mm	E_p, V	σ, mV	H_p, mm	E_p, V	σ, mV	H_p, mm	E_p, V	σ, mV
1 M H_3PO_4 + 1 M $HClO_4$	196	−0.18	47	210	−0.18	47	167	−0.73	47	73	−1.14	52
0.2 M $Na_2C_2H_4O_6$	300	−0.20	41	128	−0.56	59	172	−0.74	53	8	−1.30	280
0.5 M $NaClO_4$+ + 1 M NaOH	30	−0.17	88	185	−0.55	47	In precipitate			14	−1.32	135
3.5 N NaOH+ + 0.2 M $Na_2C_4H_4O_6$	30* 7**	−0.22 −0.33	88 82	160	−0.62	41	120	−0.67	41	7	−1.33	100
1 M NH_4OH + 1 M $(NH_4)_2SO_4$	13* 49**	−0.42 −0.154	164 76	Not reduced			155	−0.72	47	21	−1.40	100

* First peak.

** Second peak.

Tellurium interferes with the determination of zinc for all ratios and with the determination of lead and copper for ratios of Te : Cu and Te : Pb > 800 : 1.

Copper and lead cannot be determined with a supporting electrolyte of caustic soda in the presence of iron in the material investigated; in this case a complex former must be added to keep the iron in solution, e.g., a tartrate. Experiments showed most suitable medium for determination of Cu, Pb, and Cd to be a solution which is 0.5-2M with respect to Na OH and 0.1 M with respect to sodium tartrate. The peak potentials for Pb, Cu, and Cd are −0.55, −0.24 and −0.57 V respectively (Fig. 3). In this solution Zn is reduced irreversibly and its determination is impracticable.

The linear relationship between the concentration of copper, lead, and cadmium and the height of their peaks is maintained from 10^{-6}, $3 \cdot 10^{-7}$ and 10^{-6} mole/liter respectively to $2 \cdot 10^{-4}$ mole/liter for all elements. Iron is reduced irreversibly and forms peaks over a wide voltage range(E_pFe = −1.1 V), interfering with the determination of lead with a ratio Fe : Pb > 300 : 1, copper for Fe : Cu > 200 : 1 and cadmium for Fe : Cd > 150 : 1.

Table 2 compares the character of reduction of Cu, Pb, Cd, and Zn in electrolytes which we investigated and those mentioned in the literature. With a supporting electrolyte of phosphoric and perchloric acids these elements

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* According to theory, with the participation of one electron in the reaction σ = 88 mV.

are reduced reversibly with the participation of the maximum possible number of electrons (2). With this supporting electrolyte the sensitivity of the determination is therefore greatest. The exception is copper, the sensitivity of whose determination is still higher with a supporting electrolyte of sodium tartrate. It is an important fact that lead and cadmium are reduced reversibly with the participation of two electrons in all solution.

The data obtained with the solutions made it possible to develop rapid methods for the determination of Cu, Pb, Cd and Zn with a content from 0.001 to 3% in some nonferrous metallurgy products without the separation of the interfering elements.

Copper and lead in tellurium concentrate and tellurium were determined without separation of the tellurium when it was present in amounts from 0.001 to 3%. In the determination of lead and copper in tellurium concentrate containing antimony, after decomposition of the sample it is essential to remove most of the antimony by evaporation with bromine and hydrobromic acid. Antimony cannot be separated in the form of metaantimonic acid since some of the lead and copper is lost with the precipitate.

TABLE 3. Results for the Determination of Lead and Copper in Tellurium and Selenium

Object of analysis	Found, Pb, %		Found, Cu, %	
	Polarographically	Spectrally	Polarographically	Spectrally
Tellurium	0.00014; 0.00011; 0.00010	0.0001	0.00006; 0.00005; 0.00008	0.0001
	0.00010; 0.00011; 0.00014	0.0001	0.00013; 0.00014; 0.00009	0.0002
Selenium	0.00006; 0.00008; 0.00007	0.0001	0.00015; 0.00015; 0.00010	0.0001
	0.00035; 0.00040; 0.00046; 0.00040	0.0002	0.0025; 0.0020; 0.0028; 0.0024	0.0030; 0.0030; 0.0025; 0.0025

Note. The last column contains the results of the polarographic and colorimetric determination of Cu and Pb in the presence of 0.14% Fe and 0.009% Te.

To determine ten-thousandths of a per cent of elements it is essential to separate most of the interfering elements. For example, lead was determined in bronze and brass after its separation by ammonia from most of the copper and nickel in the form of hydroxide together with Fe, Al, Sn and Mn, which do not intefere with the determination of lead.

For the determination of ten-thousandths of a per cent of lead and copper in tellurium used the experience of the Pyshminsk plant laboratory, in which lead and copper are separated from tellurium by sodium sulfide in an alkaline solution.

The determination of ten-thousandths of a per cent of lead and copper in selenium was conducted after removing most of the selenium by evaporation with hydrochloric acid. An alkaline solution of tartrate is used as the supporting electrolyte if there is a large amount of iron. The results for the determination of Cu and Pb in selenium and tellurium are given in Table 3.

Determination of Cu, Pb, Cd, and Zn with a Supporting Electrolyte of a Mixture of Phosphoric and Perchloric Acids in Ores and Their Enrichment Products. A sample weighing 0.1-0.5 g, depending on the content of elements to be determined (from 0.001 to 3%), was decomposed in a mixture of hydrochloric and nitric acids with the addition of a few drops of bromine. The insoluble residue was removed and 4 ml of concentrated perchloric acid was added to the filtrate; the solution was evaporated until fumes appeared. The liquid was diluted with a small amount of water, heated to boiling, cooled, transferred to a 100-ml measuring flask, 28 ml of H_3PO_4 (1 : 3) was added and the solution was made up to the mark with water. After mixing, some of the solution was transferred to a container, blown with nitrogen for 10-15 min and polarographed on an instrument with the application of alternating voltage in an electrolyzer with a mercury bottom.

The potentials of the peaks for Cu, Pb, Cd and Zn were −0.10, −0.45, −0.73 and −1.14 V respectively. The calculation was performed by the method of standard curves or by the method of additions.

Determination of Lead in Bronze, Brass, and Nickel. A sample weighing 1-2 g (with content of Pb from 0.0001 to 0.001%) was dissolved in HNO_3 (1 : 3), diluted with water and the lead was precipitated together with ferric hydroxide by ammonia. If there was no iron in the sample or an insufficient quantity of it, then iron was added ($Fe : Pb \approx 10 : 1$). If there was a high content of manganese, ammonium chloride was added to the solution before the precipitation of the hydroxides. The hydroxide precipitate was filtered off, washed and dissolved in hydrochloric acid. We added 1 ml of perchloric acid to the liquid, evaporated until its vapor appeared and then proceeded as described above.

Determination of Cu, Cd, and Zn in Products Containing Organic Substances. The sample was decomposed as laid down for ores; 2 ml of H_2SO_4 (1 : 1) was added to the liquid after it had been filtered or to the residue after removal of the organic solvent (after extraction) and evaporated until SO_3 vapors appeared.

The organic substances were decomposed by adding nitric acid dropwise during the liberation of SO_3 vapors. The process was then continued as described in the method for the analysis of ores and their enrichment products.

Determination of Lead and Copper in Tellurium and Tellurium Concentrate Using a Supporting Electrolyte of an Alkaline Solution of Sodium Chloride. A sample of weight 0.1-0.5 g was dissolved in a mixture of HCl and HNO_3 (10 : 1). When there was a high content of antimony the solution was evaporated two or three times with bromine and hydrobromic acid. When sulfur was present a few drops of bromine were added in the cold. After decomposition of the sample, the solution was evaporated two or three times to the state of moist salts and then to a volume of 5-7 ml; HCl (1 : 1) was added to bring the volume to exactly 10 ml, the liquid was transferred to a 100-ml measuring flask, 35 ml of a 20% solution of NaOH was added and the liquid was made up to the mark with water. We then proceeded as in the method for the analysis of ores and their enrichment products.

The potential of the copper peak was −0.33 V, that of lead was −0.6 V.

Determination of Lead and Copper in High-Purity Tellurium. The sample was decomposed as described in the previous method. The solution was evaporated to 5 ml, 5 ml of HCl (1.19) and 50 ml of water were added; the liquid was cooled and a 20% solution of NaOH was carefully added until the initially precipitated tellurium hydroxide was dissolved (the liquid was then slightly opalescent). We then added another three or four drops of NaOH and 5 ml of a 5% solution of Na_2S was added slowly with mixing. The liquid was allowed to stand on a boiling water bath for 1 h to coagulate the precipitate which only forms after 15-20 min. The precipitate of copper and lead sulfides was filtered off on a white-band filter and carefully washed with hot water and then dissolved in 40 ml of hot HCl (2 : 1) containing perhydrol. We then continued as described in the previous method.

Determination of Lead and Copper in Selenium. We decomposed the sample with nitric acid, distilling off most of the selenium by evaporating the solution with hydrochloric acid. We then proceeded as above.

If there was a high content of iron in the sample we added to the measuring flask 4 ml of a 44% solution of sodium tartrate, 35 ml of a 20% solution of NaOH; we made the liquid up to the mark with water and then proceeded as above.

The calculation was performed by the method of additions. For this purpose an aliquot part of standard solution was transferred to a 50-ml beaker, 5 ml of HCl (1 : 1) was added and the liquid was evaporated to 1 ml. The solution was transferred to a 10-ml measuring cylinder, made up to 3 ml (accurately) with HCl (1 : 1). The liquid was then transferred to a 50-ml measuring flask, the cylinder being rinsed with a small amount of water. If iron was present in the sample, 1.2 ml of a 44% solution of sodium tartrate was added. We then added 9 ml of a 20% solution of NaOH and 20 ml of the sample solution; the liquid was made up to the mark with water and mixed. Some of the solution was blown with nitrogen and the polarograph taken.

The calculation was performed from the following formula:

$$\% Me = \frac{Hp \cdot 100 \cdot v_2}{K \cdot 1000 \cdot 1000 \cdot g},$$

$$K = \frac{H_t - H_p \cdot \frac{v_1}{v_2}}{C}.$$

Here H_p is the height of the peak of the metal being determined, mm; v_2 is the volume of solution in ml; g is the weight of the sample, g; H_t is the height of the total peak (sample and additions), mm; v_1 is the volume of the aliquot part of the solution of the sample, ml; C is the concentration of addition, mg/liter.

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THE DETERMINATION OF V^{4+} AND V^{5+} BY AMPEROMETRIC TITRATION WITH TWO INDICATOR ELECTRODES

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Translated from Zavodskaya Laboratoriya, Vol. 29, No. 4,
pp. 401-402, April, 1963

The determination of V^{4+} and V^{5+} in their mixtures is carried out by amperometric titration with two indicator electrodes, in a 2 N sulfuric acid medium, at a potential difference of 0.4 V. The V^{5+} is first titrated with ferrous ammonium sulfate, and then the total vanadium is titrated with potassium permanganate. The error is <1% relative to V^{5+} and about 1.5% relative to V^{4+}.

A method has been described [1] for the determination of pentavalent and tetravalent vanadium, when present together, by coulometric titration with electrically generated Ti^{3+}, the end point being determined amperometrically with two indicator electrodes.

We have found that direct amperometric titration of pentavalent and tetravalent vanadium could be carried out, using two indicator electrodes and the normal reagents for vanadium determination, ferrous ammonium sulfate and potassium permanganate [2]. This method was considerably simpler than coulometric titration, and was more sensitive than the normal methods of visual or potentiometric titration.

We used 1 cm^2 platinum electrodes; the current was measured with a type M-198/3 microamperevoltmeter; 0.1 N ferrous ammonium sulfate and permangante solutions were used; the medium was 2-4 N sulfuric acid.

It was necessary to select the correct emf in order to get a sharp end point. This was determined by the difference in potentials for anodic oxidation and cathodic reduction for some "participants" in the titration, and was deduced from the corresponding voltage-current curves [3]. In this case the titration was carried out at 0.4 V, since this ensured "operation" of the system Fe^{3+}/Fe^{2+}, formed in the process of V^{5+} titration, and of the system $MnO_4^- - O_2$, produced at the titration end point.