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DETERMINATION OF MICROGRAM AMOUNTS OF TELLURIUM IN AN AC POLAROGRAPH

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A method has been developed for determining 10^{-4}-10^{-3}% tellurium in some nonferrous metallurgical products in an ac polarograph in an acid medium (1-M). The character of tellurium reduction under these conditions, and the inhibiting effect of other elements, are examined. The error of a determination is 5-20 rel. % and the duration is about four hours.

Polarographic determination of tellurium is currently carried out against a background of ammoniacal or alkaline solutions, using a dc polarograph [1-3]. Polarographic determination of tellurium is possible at a concentration of not less than 4 mg/liter ($3.2 \cdot 10^{-5}$ mole/liter) and on not less than 0.01% of a 2 g sample. There is little information on the character of tellurium reduction against an acid background; it is known [4, 5] that on a dc polarogram tellurium forms a maximum which is not eliminated by surface-active substances. Determination of tellurium against an orthophosphoric acid background [6] has also been carried out in an ac polarograph; the minimum concentration was 10^{-6} mole/liter Te, but the character of the reduction process was not examined in this paper.

In [7] we showed that against the background of a solution 1 M with respect to orthophosphoric acid and 0.5 M with respect to perchloric acid the height of one of the tellurium peaks is much greater than the height of the peaks of other elements, e.g., of lead and cadmium which are reduced irreversibly against this background.

This communication* deals with an investigation of the behavior of tellurium with use of an ac polarograph and the development of a determination method for Te contents of 10^{-3}-10^{-4}%. Solutions of various acids were tried as backgrounds, because, according to [8] tellurium is reduced irreversibly against a background of ammoniacal or alkali solutions.

The work was carried out in a Barker polarograph with a rectangular voltage, and in a TsLA vector-polarograph with a sinusoidal voltage. 1-M solutions of HCl, HBr, HI, H_2SO_4, H_3PO_4, $HClO_4$, and tartaric acid were investigated as backgrounds. It was found that the relation between peak height and concentration has a break. In Fig. 1 this relation is given for tellurium against a background of 1 M H_2SO_4, HBr, HI, and tartaric acid; the graphs were similar in the case of the other investigated acids. A change in the half-wave width σ corresponds to the break in the curve. Against a tartaric acid background (see Fig. 1, curve 4) a break was not observed and the change in σ was not so marked. This indicates that the tellurium compounds reduced against this background are identical in a wide range of concentrations.

The linear relation between peak height and tellurium concentration is retained against a background of 1 M acids in the following ranges: $7.8 \cdot 10^{-8}$-$1.6 \cdot 10^{-5}$ mole/liter (0.01-2.0 mg/liter) for HCl, HBr, and HI; $1.5 \cdot 10^{-7}$-$1.6 \cdot 10^{-5}$ mole/liter (0.02-2.0 mg/liter) and $7.8 \cdot 10^{-5}$ mole/liter (0.1-10.0 mg/liter) for tartaric acid. The tellurium peak height at a concentration of $7.8 \cdot 10^{-8}$ mole/liter is 32 mm, the sensitivity being $^1/_5$ (Fig. 2). Therefore, any of these acids can serve as a background for determining small amounts of tellurium.

Determination of such tellurium concentrations against an acid background using a dc polarograph is impeded by the presence of a current maximum on the polarogram, which appears as a result of reduction of the polytellurides formed by the presence of a $Te^2 \rightarrow Te^0$ pari [4]. Elemental tellurium dissolves in alkali, therefore its addition to a neutral solution will evidently eliminate this maximum. Experiments showed that with an increase in alkali concentration above 0.1% or more the maximum on a dc polarograph decreases and finally disappears (Fig. 3).

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* L. N. Vasil'eva helped in this work.

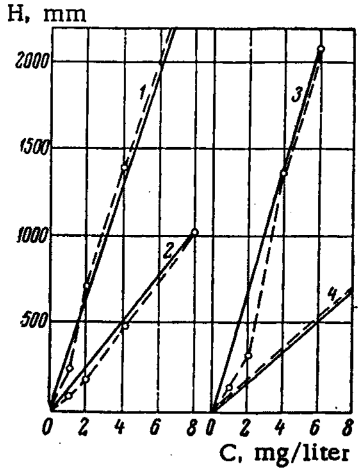

Fig. 1.

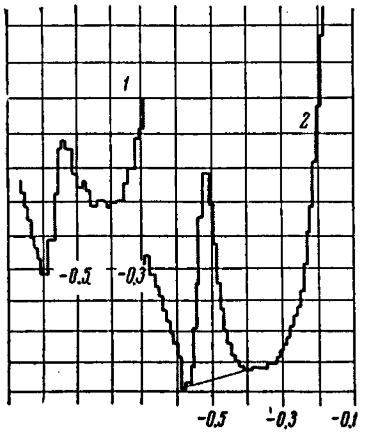

Fig. 2.

Fig. 1. Relation between peak height and tellurium concentration against a 1-M background of solutions of: 1) H_2SO_4; 2) HBr; 3) HI; 4) tartaric acid. The theoretical and experimental curves are denoted by the solid and dotted lines respectively; sensitivity $^{1}/_{80}$.

Fig. 2. Polarograms of tellurium against a background of 0.5 M HI. Tellurium concentration: 1) $7.8 \cdot 10^{-8}$; 2) $7.8 \cdot 10^{-7}$ mole/liter.

To investigate the character of tellurium reduction against an acid background, we determined the number of electrons taking part in the reaction, investigated the effect of Cl^-, Br^-, and I^- ions combined with tellurium before reduction, the effect of the solution pH on the potentials of the tellurium peak and the effect of the height of the mercury level on the current value.

Employing the microcoulombometric method [9] it was found that six electrons take part in the reduction reaction $Te\,(IV) \rightarrow Te^{2-}$. Fig. 4 shows the graph from which the number of electrons was determined.

It is known [10] that for reversible processes the width of the half-wave of an ac polarogram $\sigma = 88/n$ mv, where $\underline{n}$ is the number of electrons taking part in the reaction. If the process is reversible, for a six-electron process $= {}^{88}/_{6} = 14.7$ mv. The value obtained by experiment is 21 mv or more; therefore it follows that reduction of tellurium is not a completely reversible process.

To determine the effect of I^-, Cl^-, and Br^- ions combined with tellurium before reduction, we employed the fact that the peak potentials of tellurium chloride, bromide and iodide complexes differ markedly from the peak potential of tellurium against a perchloric acid background, which does not form complexes (the potential difference is 100-110 mv). Tellurium was polarographed against a background of 1 M $HClO_4$, with a variable concentration of halide ions. Their introduction displaces equilibrium towards formation of a halide complex of tellurium, which reacts at the electrode. The data obtained so far do not give sufficient grounds for determining the composition of the compound reacting at the electrode.

To determine the effect of the hydrogen-ion concentration on Te(IV) reduction, we carried out polarographic determination in 1 M KBr and KI with variable concentrations of hydrobromic and hydriodic acids: 0.006 and 0.01 M respectively. The pH of the solution was measured each time before the polarographic determination.

From the known equation we calculated the number of hydrogen ions taking part in tellurium reduction. It was found that two hydrogen ions participate in the presence of bromide ions, but only one in the presence of the iodide ion. In the first case, hydrogen telluride H_2Te is formed (evidently as a result of an electrode reaction) which requires two hydrogen ions. In the second case the solution contains elemental iodine as a result of partial oxidation of hydriodic acid. The elemental iodine present in the acid solution can oxidize Te^{2-} which has a higher reducing capacity and whose concentration in the solution is too low; therefore HTe^-, not H_2Te, is formed. Its presence in the solution agrees with data for the dissociation constant of H_2Te: $K_1 = 10^{-3}$ and $K_2 = 10^{-11}$ [11].

We found that tellurium reduction in a solution of acids is determined not only by diffusion, but by other processes [12]. In the presence of an electrode reaction telluride ions are formed, these being oxidized by tellurite ions

TABLE 1. Values of the Potentials (E_p), Half-Wave Widths (σ) and Peak Heights (H_p) of Different Elements* during Polarographic Determination of Tellurium against a Background of 1 M Acids (concentration of the elements 10^{-4} mole/liter, sensitivity $^1/_{160}$)†

Back-ground	Peak char-acteristics	Cu	Ag‡	Au‡	Zn	Cd	Sn	Pb	Mo	Te	Pd‡	Pt
HCl	E_p, V	−0.25	−0.20	−0.25	−1.02	−0.66	−0.46	−0.45	−0.10 I −0.90 II	−0.81	−0.20	−0.25
	σ, mv	94	260	—	71	41	40	53	— I 165 II	29	236	100
	H_p, mm	140	96	—	54	272	24	280	— I 47 II	1248	85	65
HBr	E_p, V	−0.18	−0.3	—	−0.82	−0.51	−0.30	−0.32	−0.72	−0.60	−0.53	−0.81
	σ, mv	170	—	—	53	43	47	47	200	26.4	50	82
	H_p, mm	192	12	—	130	300	50	708	36	752	57	92
HI	E_p, V	−0.18	−0.79	−0.60	−0.69	−0.39	−0.20	−0.26	−0.79	−0.52	−0.53	−0.10 I −0.80 II
	σ, mv	82	—	59	53	50	100	70.5	70	29.4	50	—
	H_p, mm	168	—	107	168	600	96	576	176	2044	57	—
$HClO_4$	E_p, V	−0.22	−0.50	−0.175 I −0.60 II	−1.21	−0.87	−0.40	−0.64	−0.42	−0.97	−0.50	−1.15
	σ, mv	64.5	—	— I 59 II	70	43	—	47	130	29.4	—	—
	H_p, mm	100	—	— I 107 II	59	272	—	280	82	1064	—	—

Back-ground	Peak char-acteristics	Cu	Ag‡	Au‡	Zn	Cd	Sn	Pb	Mo	Te	Pd‡	Pt
H_2SO_4	E_p, V	—0.05	—0.50	—	—1.27	—0.25	Not inves-tigated	0.55	—0.11 I —0.30 II —0.40 III	—0.95	—0.06 I —1.20 II	—
	σ, mv	88	300	—	82	41		40	76 I 200 II+III	35.0	—	—
	H_p, mm	488	20	—	23	224		27	40 I 40 II+III	1416	—	—
H_3PO_4	E_p, V	—0.20	—0.30 I —0 60 II	—0.30	—1.17	—0.73	—0.40 I —0.70 II	—0.51	—0.18 I —0.54 II	—0.95	—	—
	σ, mv	130	— I — II	—	58	53	— I — II	41	— I 147 II	26	—	—
	H_p, mm	168	— I — II	—	116	228	— I — II	236	— I 10 II	1464	—	—
$C_4H_6O_6$	E_p, V	—0.19	—	—1.20 I —1.30 II	—1.17	—0.81	—	—0.56	—0.32 I —0.63 II	—1.02	—	—1.33
	σ, mv	130	—	— I 50 II	59	53	—	41	88 I 153 II	41	—	165
	H_p, mm	188	—	100 I 32 II	94	200	—	195	65 I 11 II	376	—	880

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* Arsenic impedes tellurium determination against all backgrounds, bismuth and antimony do not impede against a background of HCl, HBr, and HI.

† A stroke signifies that H_p, σ, and E_p are difficult to measure, because of the extreme irreversibility of the process; the Roman numeral indicates the wave number.

‡ Sensitivity $^1/_{20}$.

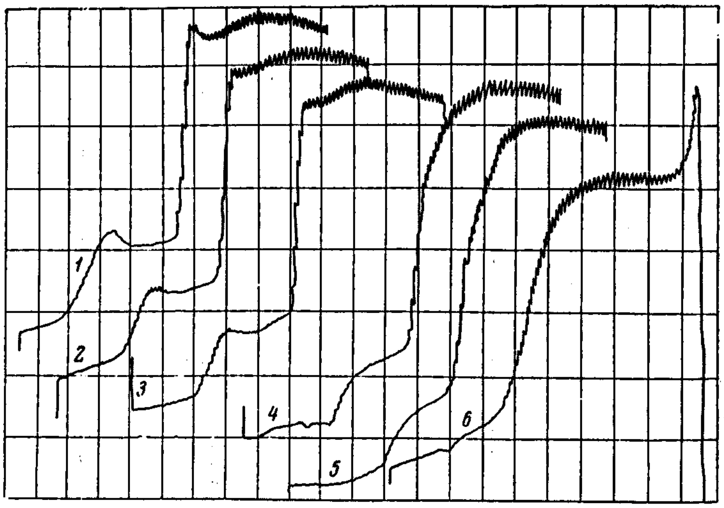

Fig. 3.

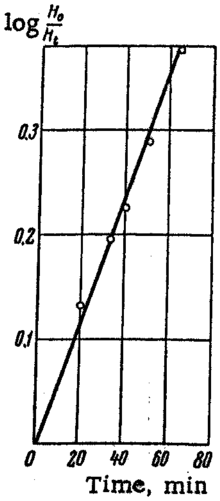

Fig. 4.

Fig. 3. Direct-current polarograms of tellurium (8 mg/liter) against the background of a 1 M solution of KBr in absence (1) and presence of an alkali solution; 2) 0.025 M (0.1%); 3) 0.05 M (0.2%); 4) 0.2 M (1%); 5) 0.5 M (2%); 6) 1 M KOH (94%) without potassium bromide. Current maximum: 1-3) 12; 5 and 3 mm respectively; 4-6) no maxima. Sensitivity $^1/_5$; initial voltage 0.5 V, final voltage 1.5 V.

Fig. 4. Relation between $\log(H_0/H_t)$ and the duration of electrolysis (H_0 is the initial height of the tellurium wave corresponding to the time elapsed since commencement of electrolysis, mm). Background-1 M HBr.

in the vicinity of the electrode to elemental tellurium. Therefore the rate of feed of Te (IV) ions to the electrode is also affected by the rate of this redox reaction.

We also investigated the behavior of other elements under tellurium determination conditions (Table 1) and found that many elements (Cu, Tl, Cd, Sn, As, Sb, Bi, Fe, Se) are reduced at a more positive potential than tellurium.

It is known that tellurium can form insoluble tellurides with many elements, therefore those which are reduced on a dropping mercury electrode at a more positive potential must be separated. Tellurium determination is particularly determined by selenium, which always accompanies it, and against a background of any of the acids used (except hydriodic acid) is reduced at a more positive potential. In a solution of hydriodic acid selenium is not revealed polarographically because it is reduced by the iodide to the elemental state. Nor does iron impede the determination, because in an acid medium it is reduced by hydriodic acid to the bivalent state [13], which is reduced at a dropping mercury electrode at a higher potential than tellurium.

To separate tellurium from other elements, we used the known method of separating the sum of selenium and tellurium by hydrazine and a tin chloride solution [14]. From data of work with isotopes carried out in the Gintsvetmet analytical laboratory in 1959, the tellurium loss when precipitated with an equal content of selenium is not more than 4%. Our experimental data agree with these results.

From the data obtained, we have developed a polarographic method of determining 10^{-3}-10^{-4}% in some nonferous metallurgical products by the following system: decomposition of the sample in a mixture of nitric and hydrochloric acids; precipitation of the total selenium and tellurium from a 14 vol-% HCl solution by a tin chloride solution in the presence of hydrazine; dissolution of the precipitate in a mixture of hydrochloric and nitric acids; evaporation of the solution and dissolution of the residue in hydriodic acid and, after appropriate dilution, polarographic determination in an ac polarograph. The relative error of a determination is 5-10% for thousandths of one percent Te and 10-20% for ten thousandths of one percent Te. The minimum determinable tellurium content is 0.0001%. The duration of a determination in one sample and two weighed portions is about four hours.

The results of analysis of industrial products are given in Table 2.

TABLE 2. Results of the Polarographic Determination of Tellurium in Ores

Weight, g / Dilution, ml	Tellurium found, %		Content of other elements, %
	Polarographic method (ave.)	Photocolorimetric method	
0.25/50	0.0053	0.005	Cu — 1.5; Pb — 7.4; Zn — 34; Fe — 8.5; Cd — 0.16; SiO_2 — 12.4; Se — 0.004; Sb — 0.01; As — 0.02
0.5/50	0.0019	0.002	Cu — 0.5; Pb — 1.7; Zn — 7.4; Fe — 5.9; Cd — 0.04; SiO_2 — 40.6; Se — 0.002; Sb — 0.01; As — 0.02
1/25	0.0006	0.0005	Cu — 0.15; Pb — 0.7; Zn — 3.4; Fe — 0.9; Cd — 0.016; SiO_2 — 0.12; Se — 0.0004; Sb — 0.001; As — 0.002
2/25	0.0002	0.0002	Cu — 0.05; Pb — 0.17; Zn — 0.74; Fe — 0.6; Cd — 0.04; SiO_2 — 4.0; Se — 0,0002; Sb — 0.001; As — 0.002
2/25	0.0001	<0.0002	Fe — 2; SiO_2 — 70; Al — 15
1/25	0.00055	0.0006	Fe — 10; SiO_2 — 40; Al — 15

ANALYTICAL PROCEDURE

To a 0.25-2 g sample (depending on its tellurium content) is added 0.5 g of NaCl, a mixture of hydrochloric and nitric acids (3:1) and three drops of bromine; if the sulfur content is high the mixture is left for 1-2 hours (preferably overnight). One mg of Se is added, the sample is decomposed and the solution evaporated on the water bath, first to small volume and then almost to dryness; 1-2 ml of HCl is added and it is again evaporated. This operation is repeated twice to remove nitric acid.

Seven ml of HCl (1.19) is added to the residue, gently heated to dissolve the salts, 40 ml of hot water is added and the mixture is heated to boiling. If an insoluble residue is present in the solution it must be filtered and washed with 15% HCl.

To precipitate the total Se + Te, 1 g of hydrazine chloride is added to the solution and the mixture boiled for about 5 min, 1 or 2 ml of a 25% $SnCl_2$ solution is added and it is boiled again. The precipitate is coagulated on the water bath for an hour, filtered through a No. 4 funnel with a porous bottom, washed 5-6 times with hot 10% HCl containing 0.5 g of hydrazine per 100 ml of solution, and then 4 times with cold water. The precipitate is dissolved on the funnel with a small amount of a hot HNO_3 + HCl mixture (3:1), collecting the solution in the same flask from which filtration was carried out. The filter is washed with hot water, the liquid is evaporated to small volume, 0.2 ml of concentrated $HClO_4$ is added and evaporation continued until fumes of the latter appear. One or two ml of HI (1.54*) is added to the residue, the mixture is transferred to a 25 or 50 ml measuring flask respectively and made up to the mark with water. After the solution has been mixed, part is transferred to a vessel through which nitrogen is passed for 5-10 min and the polarographic analysis is carried out in an electrolyzer with mercury on the bottom† having a dropping period of 3 sec.

The half-wave potential of tellurium is −0.52 V. Calculation is by the method of additions. The tellurium concentration in the solution subjected to polarographic analysis must not be more than 10^{-5} mole/liter.

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* The hydriodic acid may contain only a small amount of iodine. It must be kept in a dark, cool place.

† The duration of the period between preparation of the solutions and their polarographic analysis should not be more than 4-6 h, otherwise elemental iodine is liberated and the reproducibility of the results impaired.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.