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**THE EFFECT OF THIAZINE DYES ON POLAROGRAPHIC DETERMINATION OF TELLURIUM**

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Accepted August 5, 1990*Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.*

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The effect of thionine, azure I and methylene blue on the electroreduction of tellurium(IV) has been studied in the solutions of oxalic, tartaric and trihydroxyglutaric acids. It has been shown that the electrode process is complicated by adsorption of all components of the electrochemical reaction. This causes an increase of the tellurium analytical signal. The determination is not hampered by great excesses of various elements. Optimal conditions were found according to which determinations were carried out of tellurium in binary mixtures Pb-Te, Cd-Te, Fe-Te, Bi-Te and of tellurium admixtures in bismuth of high purity, doped by tellurium.

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The adsorption of surfactants on the electrode surface causes specific enhancement or inhibition of electrochemical processes that result in an increase or a suppression of the analytical signal. Thiazine dyes used as surfactants promote sensitivity and selectivity in the determination of tin. Methylene blue in solutions of oxalic acid makes it possible to determine tin in the presence of different quantities of lead<sup>1-5</sup>. It has been shown in our previous work<sup>6-8</sup> that electroreduction of tin in the presence of thionine and azure I is complicated by adsorption that causes an increase of the analytical signal of tin by more than one order. It allowed to determine tin in copper alloys, zinc, nickel and lead and tin in the alloys of lead-tin-tellurium from small samples. An oxalate solution of azure I has been used as supporting electrolyte.

The reduction of tellurium(IV) in acidic and slightly acidic solutions of salts was studied in several papers<sup>9-16</sup>. Three peaks could be seen on the a.c. polarograms in 1 mol l<sup>-1</sup> solutions of acids. The first two correspond to gradual reduction of Te(IV) to Te(0), the third one – of Te(0) to Te(2-). In a supporting electrolyte of more dilute acid solution the reduction of tellurium(IV) proceeds only in two stages: Te(IV) → Te(0) → Te(2-). As has been shown<sup>11</sup>, the second peak of Te(IV) is by two orders of magnitude greater than the first one. The sensitivity of tellurium determination is lower than in supporting electrolyte of oxalic and tartaric acid<sup>12,15,16</sup>, as more stable complexes of tellurium with these acids have been

described. In the mentioned work possibilities have been discussed of determining Te in metallic Sb, In, Ga, and Bi after separating elemental Te by co-deposition with sulfur<sup>9,10</sup>; Te in the presence of Zn and Cd (refs<sup>12,13</sup>); Pb, Sn and Te after their chromatographic separation on anionite<sup>14</sup>, and Pb and Sn in alloys of Pb-Sn-Te (ref.<sup>7</sup>). In order to improve sensitivity of determination of Te in some natural objects<sup>15,16</sup> chloride or oxalate supporting electrolytes with addition of  $6 \cdot 10^{-4}\%$  of methylene blue are used.

It has been shown in the present paper that the increase of sensitivity and selectivity of tellurium(IV) determination from oxalic, tartaric and trihydroxyglutaric solutions of thionine, azure I or methylene blue is related to the adsorption of both initial components of electrochemical reaction and products of their interaction.

## EXPERIMENTAL

### Equipment and Method

Polarographic measurements were carried out on a PU-1 polarograph (U.S.S.R.) in a thermostated ( $25 \pm 0.1$ )°C three-electrode cell. A three-electrode system was employed with a platinum auxiliary electrode and saturated calomel reference electrode. The dropping mercury electrode had drop-time of 3.6 s (in distilled water at an applied voltage of 0 V vs saturated calomel electrode, at the mercury reservoir height of 65 cm) and flow rate of  $2.6 \text{ mg s}^{-1}$ . The potential-scan rate,  $v$ , was  $-2 \text{ mV s}^{-1}$ , the amplitude of alternating voltage,  $\Delta E$ , was 15 mV.

The electrocapillary curves were obtained by measuring droptime in the three-electrode cell with a slowly dropping capillary (drop-time of 8.6 s in  $0.2 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$  at an applied voltage of 0 V and Hg column height of 65 cm).

The solution acidity was measured by a universal pH-meter of OP-204/1 type (Hungary). The analyzed solutions were degassed by electrolytic hydrogen.

### Reagents

Thiazine dyes were purified by recrystallization from ethanol. Solutions of thionine, azure I and methylene blue of  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  concentration were obtained by dissolving the recrystallized reagents in water. All the other solutions were prepared from p.a. chemicals without purification. Water used throughout was twice distilled in a quartz apparatus. A  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  tellurium standard solution was obtained by dissolving a metal sample of p.a. purity in 2–3 ml of the mixture of  $\text{HNO}_3$  and  $\text{HCl}$  (1 : 3) under heating on a water bath. After dissolving the sample 2–3 ml of  $\text{H}_2\text{SO}_4$  (1 : 1) were added to the solution which was then evaporated until dense vapours of  $\text{SO}_3$  were formed. After cooling the beaker walls were rinsed with water and the solution was quantitatively transferred into a 100 ml volumetric flask which was filled up to the mark. The solutions of lower concentration were obtained by diluting the initial standard tellurium solution. Standard solutions of  $10^{-5}$ – $10^{-6} \text{ mol l}^{-1}$  concentration were prepared daily by diluting the stock solution.

### Procedure

A finely divided sample of an alloy, of the mass of 0.01 g, was dissolved in 2–5 ml of the mixture of  $\text{HNO}_3$  and  $\text{HCl}$  (1 : 3) under heating on a water bath, 2 ml of  $\text{H}_2\text{SO}_4$  (1 : 9) were added and

the solution was then evaporated until dense vapours of  $\text{SO}_3$  were formed. After cooling the beaker walls were rinsed with 5 ml of  $\text{H}_2\text{SO}_4$  (1 : 9) and the solution was quantitatively transferred into a 10 ml volumetric flask which was filled up to the mark. An aliquot part of the solution (1–2 ml) from the 10 ml volumetric flask was mixed with 4 ml of  $1 \text{ mol l}^{-1}$  tartaric acid, 1 ml of  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  azure I and the pH was set at 1–1.5. The solution was then transferred into the polarographic cell, oxygen was removed and an a.c. polarogram was recorded under the following conditions: initial potential  $E_i - 0.45 \text{ V}$  (SCE),  $\Delta E 15 \text{ mV}$ ,  $v - 2 \text{ mV s}^{-1}$ . The tellurium content was found by means of a calibration graph for standard solutions of Te brought through all stages of analysis.

## RESULTS AND DISCUSSION

The a.c.polarograms of electroreduction of tellurium(IV) from oxalic ( $\text{H}_2\text{Ox}$ ), tartaric ( $\text{H}_2\text{Tart}$ ) and trihydroxyglutaric ( $\text{H}_2\text{THG}$ ) solutions of thionine, azure I or methylene blue display two peaks: the first one with the summit potential of  $-0.14 \text{ V}$  is irreversible and the second one – with the summit potential between  $-0.81$  and  $-0.86 \text{ V}$  – is reversible, complicated by adsorption. The second peak is considerably higher than the first one. A decrease of the depolarizer concentration leaves only the second peak on the polarogram. The peak height depends on the concentration of  $\text{H}_2\text{Ox}$ ,  $\text{H}_2\text{Tart}$  or  $\text{H}_2\text{THG}$ , of the thiazine dye, of the depolarizer and on pH of the solution. Figures 1–3 show the dependence of the height of the tellurium peak on the concentration of thionine and azure I in  $\text{H}_2\text{Ox}$  solutions (Fig. 1, curves 1 and 1'), azure I in  $\text{H}_2\text{Tart}$  solutions (Fig. 2, curve 1) and methylene blue in  $\text{H}_2\text{THG}$  solution (Fig. 3, curve 1). The saturation limits shown by these curves are characteristic of the processes accompanied by adsorption. The change of peak height with the increase of concentrations of  $\text{H}_2\text{Ox}$ ,  $\text{H}_2\text{Tart}$  or  $\text{H}_2\text{THG}$  is probably related with the formation of more saturated or mixed-ligand complexes. As described earlier<sup>15</sup>, in the supporting electrolyte of  $\text{H}_2\text{SO}_4$  containing methylene blue  $\text{Te(IV)}$  produced a wave with the half-wave potential of  $-0.96 \text{ V}$  due to reduction of the complex with the metal-to-ligand ratio 1 : 2. When  $\text{H}_2\text{Ox}$  was added to the solution containing tellurium and thiazine dye at concentration of  $[\text{H}_2\text{Ox}] > 0.1 \text{ mol l}^{-1}$  the peak height did not practically change what indicated formation of a  $\text{Te-thionine (azure I)-H}_2\text{Ox}$  complex. For  $\text{H}_2\text{Tart}$  and  $\text{H}_2\text{THG}$  these relations were of another character. At concentrations of  $[\text{H}_2\text{Tart}] < 0.5 \text{ mol l}^{-1}$  and  $[\text{H}_2\text{THG}] < 0.2 \text{ mol l}^{-1}$  probably a complex of one composition was formed and with the increase of concentration a transition to more saturated complexes occurred (Figs 2 and 3, curves 2).

The height of Te peak in dependence on pH for the  $\text{Te(IV)-H}_2\text{Tart-azure I}$  system is shown in Fig. 2 (curve 4). For the other systems this dependence is similar.

The relation between the peak height and the  $\text{Te(IV)}$  concentration is displayed in Figs 1 and 2 (curves 3 and 3'). At concentrations of  $[\text{Te(IV)}] > 4 \cdot 10^{-6} \text{ mol l}^{-1}$  the slope of the calibration curve changes; this is due to the complication of the electrode process by adsorption of the reactants of the electrochemical reaction.

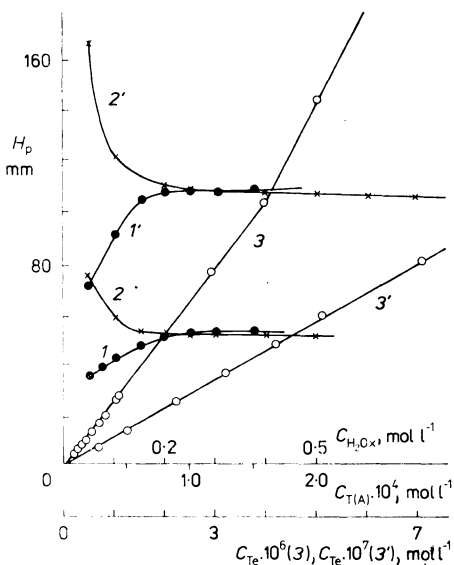


FIG. 1

Tellurium peak height vs concentration of thionine (1), azure I (1'),  $H_2Ox$  (2, 2'), tellurium (IV) (3, 3'). Concentrations:  $[Te(IV)] = 2 \cdot 10^{-6} \text{ mol l}^{-1}$  (1, 2) and  $[Te(IV)] = 4 \cdot 10^{-6} \text{ mol l}^{-1}$  (1', 2');  $[H_2Ox] = 0.2 \text{ mol l}^{-1}$  (1, 1', 3, 3');  $[thionine] = 1 \cdot 10^{-4} \text{ mol l}^{-1}$  (2, 3);  $[azure I] = 1 \cdot 10^{-4} \text{ mol l}^{-1}$  (2', 3'). Current range  $1 \times 100$  (3) and  $0.25 \times 100$  (3')

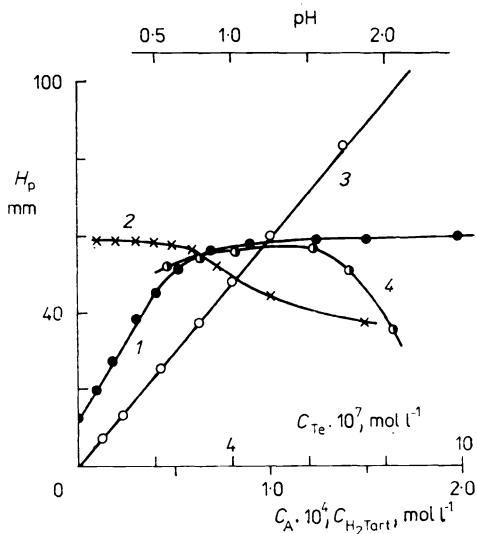
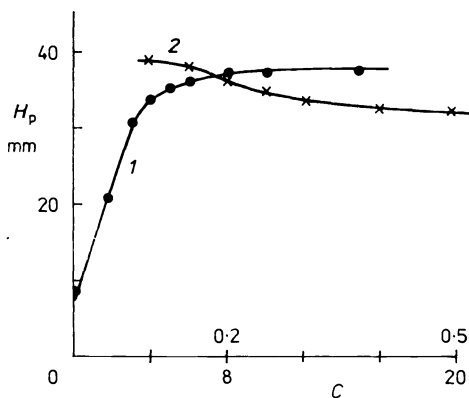


FIG. 2

Tellurium peak height vs concentration of azure I (1),  $H_2Tart$  (2), tellurium (IV) (3) and vs pH (4). Concentrations:  $[Te(IV)] = 5 \cdot 10^{-7} \text{ mol l}^{-1}$  (1, 2, 4);  $[H_2Tart] = 0.4 \text{ mol l}^{-1}$  (1, 3, 4);  $[azure I] = 1 \cdot 10^{-4} \text{ mol l}^{-1}$  (2-4). Current range  $0.25 \times 100$

FIG. 3

Tellurium peak height vs concentration of methylene blue ( $c \cdot 10^5, \text{ mol l}^{-1}$ ) (1) and  $H_2THG$  ( $\text{mol l}^{-1}$ ) (2). Concentrations:  $[Te(IV)] = 2 \cdot 10^{-6} \text{ mol l}^{-1}$  (1, 2);  $[H_2THG] = 0.2 \text{ mol l}^{-1}$  (1);  $[methylene\ blue] = 5 \cdot 10^{-5} \text{ mol l}^{-1}$  (2). Current range  $1 \times 100$



The electrocapillary curves (Fig. 4) presented for Te(IV)–H<sub>2</sub>Tart–azure I with respect to 0.2 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (curve 1) reveal adsorption of all components of the electrochemical reaction. In H<sub>2</sub>Tart solutions the electrocapillary maximum decreases and moves to negative potentials what is characteristic of anion adsorption (curve 2). As has been shown<sup>17</sup>, H<sub>2</sub>Tart and H<sub>2</sub>THG solutions at pH 1–1.5 contain not only non-dissociated molecules of these acids but also HTart<sup>-</sup> and HTHG<sup>-</sup> anions. Moreover, on the mercury surface can be adsorbed not only the forms prevailing in the solution, but also forms present in small quantities<sup>18</sup>. The curve 2 shows that HTart<sup>-</sup> particles are adsorbed. The electrocapillary curve of azure I (curve 4) is lowered considerably with respect to the supporting electrolyte and its maximum is at the same potential as that of the supporting electrolyte. Its course has been explained in the study of Sn(IV)–H<sub>2</sub>Ox–azure I system<sup>8</sup>. The electrocapillary curve depression is more pronounced in the case of the joint adsorption of H<sub>2</sub>Tart and azure I (curve 5). As for joint adsorption<sup>8</sup> of H<sub>2</sub>Ox and azure I, the dip in the curve 5 indicates formation of an associate-type compound between protonized particles of the dye and HTart<sup>-</sup>. Introduction of Te(IV) in H<sub>2</sub>Tart (curve 3) and in H<sub>2</sub>Tart–azure I (curve 6) solutions causes a greater decrease of the electrocapillary maximum and shifts it to negative potentials. The dip in the curve 3 indicates interaction of tellurium with tartaric acid anions on the electrode surface.

The electrocapillary curves show that the thiazine dye enhances the adsorption of H<sub>2</sub>Tart by additional formation of complexes on the electrode surface. On the

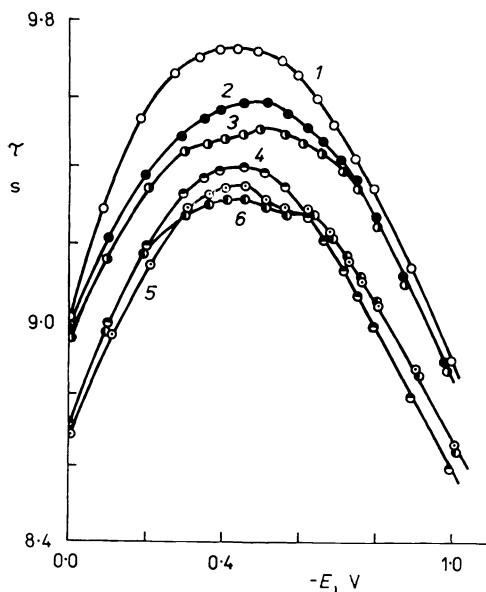


FIG. 4  
Electrocapillary curves. 1 0.2 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>; 2 0.2 mol l<sup>-1</sup> + 0.4 mol l<sup>-1</sup> H<sub>2</sub>Tart; 3 solution 2 + 1 · 10<sup>-6</sup> mol l<sup>-1</sup> Te(IV); 4 0.2 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 1 · 10<sup>-4</sup> mol · l<sup>-1</sup> azure I; 5 solution 4 + 0.4 mol l<sup>-1</sup> H<sub>2</sub>Tart; 6 solution 5 + 1 · 10<sup>-6</sup> mol l<sup>-1</sup> Te(IV)

other hand, joint adsorption of the dye and  $H_2Tart$  can lead to formation of mixed-ligand tellurium complexes. All these factors stimulate an increase of the tellurium analytical signal.

Thiazine dyes (thionine, azure I and methylene blue) promote the process of tellurium electroreduction; upon their addition the summit potential moves from  $-0.87$  V to  $-0.83$  V, the peak height increases up to 4 times and in the limit it becomes equal to the tellurium peak height on the supporting electrolyte of  $0.3 \text{ mol l}^{-1} \text{ HCl} + 0.1 \text{ mol l}^{-1} \text{ KCl} + 1 \cdot 10^{-4} \text{ mol l}^{-1}$  azure I. Figure 1 (curves 3 and 3') and Fig. 2 (curve 3) show linear relation between the peak height of oxalate solutions of thionine and tartaric solutions of azure I containing  $Te(IV)$ , and its concentration ( $5 \cdot 10^{-7}$  to  $4 \cdot 10^{-6} \text{ mol l}^{-1}$ ).

The determination of tellurium in the supporting electrolyte of  $0.4 \text{ mol l}^{-1} H_2Tart$

TABLE I

Tellurium determination in binary mixture;  $0.4 \text{ mol l}^{-1} H_2Tart$ ,  $10^{-4} \text{ mol l}^{-1}$  azure I, pH 1–1.5,  $r = 0.95$

No.	Te taken $\bar{x} \cdot 10^6$ $\text{mol l}^{-1}$	[Bi] · $10^4$ $\text{mol l}^{-1}$	[Pb] · $10^5$ $\text{mol l}^{-1}$	[Cd] · $10^5$ $\text{mol l}^{-1}$	[Fe] · $10^5$ $\text{mol l}^{-1}$	Te found $\bar{x} \cdot 10^6$ $\text{mol l}^{-1}$	<i>n</i>	$S_r$	$\pm \delta$	Ratio Te : Me
1	0.250	—	—	—	—	0.253	6	0.035	0.009	—
2	1.000	—	—	—	—	1.007	6	0.047	0.050	—
3	0.250	—	2.5	—	—	0.252	5	0.022	0.027	1 : 100
4	0.250	—	—	2.5	—	0.251	6	0.026	0.007	1 : 100
5	0.250	—	—	—	5.0	0.253	7	0.017	0.004	1 : 200
6	1.000	2.0	—	—	—	1.000	5	0.042	0.049	1 : 200

TABLE II

Tellurium determination in bismuth of high purity doped by tellurium;  $0.4 \text{ mol l}^{-1} H_2Tart$ ,  $10^{-4} \text{ mol l}^{-1}$  azure I, pH 1–1.5,  $r = 0.95$

No.	Te found $\bar{x}$ , wt. %	<i>n</i>	$S_r$	$\pm \delta$	Te found <sup>a</sup> $\bar{x}$ , wt. %
1	0.152	8	0.030	0.004	0.149
2	0.155	5	0.024	0.005	0.158
3	0.266	6	0.018	0.005	0.266
4	0.145	5	0.022	0.004	0.141

<sup>a</sup> Tellurium determination was carried out by the method described in ref.<sup>1</sup>,  $n = 5$ .

in the presence of  $1 \cdot 10^{-4} \text{ mol l}^{-1}$  azure I features high sensitivity and selectivity. The tellurium determination is not hampered by (multiple excess) Fe(II) (400); Sb(III), Bi(III), Cr(III), Pb(II) (200); Cd(II), Cu(II), Co(II), Mn(II) (100); Ti(IV) (80); Sn(IV) (50); In(III), Ni(II) (40); As (III) (20). Se(IV) impedes the determination. In the optimal condition ( $0.2-0.4 \text{ mol l}^{-1} \text{ H}_2\text{Tart}$ ,  $1 \cdot 10^{-4} \text{ mol l}^{-1}$  azure I, pH 1–1.5) the determination of tellurium has been carried out in binary mixtures Pb–Te (100 : 1), Cd–Te (100 : 1), Fe–Te (200 : 1), Bi–Te (200 : 1).

The results of these determinations and the methodological characteristics are given in Table I. Tellurium determination is usually hampered by elements reduced at more positive potentials (Cd, Pb, Bi, etc.), as they form non-soluble tellurides with tellurium. Table I shows that the use of complexing agents adsorbed on the mercury ( $\text{H}_2\text{Ox}$ ,  $\text{H}_2\text{Tart}$ , etc.) as supporting electrolytes makes it possible to determine tellurium with high precision in the presence of these elements in excess. Table II shows the results of tellurium determination in bismuth of high purity doped by tellurium. Validity of the results obtained was tested by comparison with the results of tellurium determination by the method described in ref.<sup>9</sup>. Table II shows that the results obtained by the two independent methods are in good agreement.

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Translation revised by M. Heyrovský.