Role of some complexing agents during electrodeposition of tellurium

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The uses of electrodeposition processes for the production of tellurium as a pure metal from different baths containing tellurous acid with some suitable additives have been investigated. The quantity and quality of the deposited metal are found to be dependent on the type of the baths used. The effects of different parameters such as kind and concentration of acids, current density, temperature, electrode type (platinum and graphite) and metal to complexing agent concentration ratio on the cathodic efficiency and on the quality of deposit have been discussed. The interfering effect of some cations and anions has also been studied. Spectrophotometric, AAS and X-ray analyses revealed the purity of separated deposit to be 99.9%. An analytical application for preconcentration and separation of tellurium from its natural ores and alloys using the proposed electrolytic method is found to be satisfactory.

Tellurium is widely used in photography for toning prints especially silver prints. More than 90% of tellurium is used in iron and steel production and alloys. Small amount of TeO₂ is used in tinting glass and tellurium compounds find some use as catalyst. Tellurium compounds are used as fungicide. Tellurium compounds have also been used in making many dye stuffs. Various methods of preconcentration (e.g. freeze drying, extraction, sorption, ion exchange and flotation) were applied for the separation of trace amounts of elements.

The electrodeposition of tellurium from different baths in aqueous and non-aqueous solutions of tellurium ions and TeCl₄ on platinum-sheet and copper-sheet, in both acidic and basic baths were described.

The aim of the present work is to prepare highly pure tellurium in high yield by electrodeposition from baths containing H₂TeO₃ acidic solution in presence of complexing or reducing agents and to develop a simple and rapid electrolytic separation process for tellurium in synthetic and natural samples followed by the analysis of deposited tellurium by AAS and UV spectrophotometric methods.

Experimental Procedure

The experimental procedure is the same as described earlier. A Perkin-Elmer model lambda 3B UV/Vis spectrophotometer was also used for comparing the determined results with the AAS method. The current density applied for all baths was 0.1 A dm⁻². The electrodeposition of tellurium concerned was carried out for 10 min and the current efficiency was calculated from the weight of deposit. Other conditions are shown in Table 1. The tellurium deposit was dissolved in 5 mL concentrated nitric acid and made up to 25 mL by twice distilled water and was analysed using the AAS and UV spectrophotometric methods. Moreover, the deposited metal was subjected to X-ray diffraction measurements using the method described in literature and PW 1840 (Philips), PW Generator, 2θ range (10-100), Kα, λ = 1.542 Å and Cu-filter were used.

Results and Discussion

Cathodic deposition of tellurium — Many experiments were carried out in order to determine the optimum conditions necessary for the cathodic deposition of tellurium using different complexing agents at different acid concentrations, applied voltages, current densities, and types of electrode. The more convenient baths are shown in Table 1. The results of chemical analysis revealed that the purity of tellurium was 99.9%. The chemical analysis also indicate that no TeO₂ was deposited at the cathode.

Effect of different baths — Table 1 shows the effect of different baths on both quality and quantity (cathodic current efficiency, %) of tellurium
**Table 1** - Suitable baths for electrolytic production of tellurium from H₂TeO₄ (Each bath was prepared by mixing 2.5 mL 0.05 M H₂TeO₄ and appropriate amount of different additives, completed with bidistilled water to 25 mL current density 0.1 A dm⁻² under a potential difference 2.5 V; duration of deposition = 10 min using Pt-electrode at 25°C.

<table>
<thead>
<tr>
<th>No</th>
<th>Bath</th>
<th>Additive</th>
<th>Cathodic current efficiency %</th>
<th>Quality of deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic acid</td>
<td>5 mL acetic acid + 1.4 mL, 18 M H₂SO₄ acid</td>
<td>85.5</td>
<td>two layers, lower is silvery and the upper is gray</td>
</tr>
<tr>
<td>2</td>
<td>N,N-diethylaniline</td>
<td>2.5 mL ethanol + 37.3 mg/L N,N-diethylaniline</td>
<td>84.0</td>
<td>black-compact-adherent-fine crystals</td>
</tr>
<tr>
<td>3</td>
<td>Phenylisothiocyanate</td>
<td>2.5 mL ethanol + 33.8 mg/L phenylisothiocyanate + 2.5 mL 10.4 M HNO₃ acid</td>
<td>83.5</td>
<td>black-compact-adherent-fine crystals</td>
</tr>
<tr>
<td>4</td>
<td>Salicylaldehyde</td>
<td>2.5 mL ethanol + 30.5 mg/L salicylaldehyde 0.7 mL, 18 M H₂SO₄ acid</td>
<td>82.0</td>
<td>two layers, lower is silvery and the upper is black</td>
</tr>
<tr>
<td>5</td>
<td>Aniline</td>
<td>2.5 mL ethanol + 100 mg/L aniline + 2.5 mL, 10.4 M HNO₃ acid</td>
<td>80.5</td>
<td>brown-fine crystals-adherent</td>
</tr>
<tr>
<td>6</td>
<td>Diacetylbenzene</td>
<td>40.5 mg diacetyl benzene + 2.5 mL 10.4 M HNO₃</td>
<td>79.1</td>
<td>black-fine crystals-adherent</td>
</tr>
<tr>
<td>7</td>
<td>Benzylamine</td>
<td>26.8 mg/L benzylamine + 2.5 mL 10.4 M HNO₃</td>
<td>78.8</td>
<td>two layers, lower is silvery, the upper is black</td>
</tr>
<tr>
<td>8</td>
<td>1,5-diphenyl carbazide</td>
<td>2.5 mL ethanol + 6.06 mg/L 1,5-diphenyl carbazide + 1.2 mL 18 M H₂SO₄ acid</td>
<td>78.5</td>
<td>black-fine crystals-compact-adherent</td>
</tr>
<tr>
<td>9</td>
<td>Thiourea</td>
<td>19 mg thiourea 2.5 mL, 10.9 M H₃PO₄ acid</td>
<td>75.5</td>
<td>gray-small particles-adherent</td>
</tr>
<tr>
<td>10</td>
<td>Amm-formate</td>
<td>16 mg Amm. formate 2.5 mL, 10.4 M HNO₃</td>
<td>74.0</td>
<td>two layers, lower is silvery and the upper is black</td>
</tr>
<tr>
<td>11</td>
<td>Thiosulphate</td>
<td>39.5 mg sodium thiosulphate + 2.5 mL 10.4 M HNO₃</td>
<td>73.0</td>
<td>brownish black-fine crystals-compact</td>
</tr>
<tr>
<td>12</td>
<td>Rubeanic acid</td>
<td>2.5 mL ethanol + 30 mg/L rubeanic acid + 1.4 mL, 18 M H₂SO₄ acid</td>
<td>70.5</td>
<td>brownish black-fine crystals-adherent-compact</td>
</tr>
<tr>
<td>13</td>
<td>Malonic acid</td>
<td>2.5 mL ethanol + 26 mg malonic acid + 2.5 mL, 10.4 M HNO₃ acid</td>
<td>69.1</td>
<td>two layers, lower is silvery, and the upper is black</td>
</tr>
<tr>
<td>14</td>
<td>Thiophenol</td>
<td>2.5 mL ethanol + 27.9 mg thiophenol + 2.5 mL, 10.4 M HNO₃ acid</td>
<td>68.2</td>
<td>brownish black, fine crystals-adherent</td>
</tr>
<tr>
<td>15</td>
<td>1-Pyrrolidine dithiocarboxylic acid</td>
<td>2.5 mL ethanol + 41 mg 1-pyrrolidine-dithiocarboxylic acid + 2.5 mL, 10.4 M HNO₃ acid</td>
<td>66.2</td>
<td>brownish-fine crystals-adherent compact</td>
</tr>
<tr>
<td>16</td>
<td>Amm tetramethylene dithiocarbamate</td>
<td>2.5 mL ethanol + 41 mg Amm. tetramethylene dithiocarbamate</td>
<td>65.5</td>
<td>brownish-black-fine crystals-adherent-compact</td>
</tr>
</tbody>
</table>

From the obtained results, it can be concluded that the baths can be arranged according to current efficiency (Table 1). It was found that the highest cathodic current efficiency is 85.5% in case of acetic acid bath and the minimum value is 65.5% in case of ammonium tetramethylene dithiocarbamate in acidic medium.

**Polarization curve**—The polarization curves for electrodeposition of tellurium from its baths have four distinct branches. It can be concluded that the steps of cathodic polarization potentials are dependent upon the type of complexes species. Tellurium metal was deposited at + 400 to + 25 mV using different baths.

**Effect of type and acid concentration on current efficiency**—This study was done by changing the type of acid (H₂SO₄, H₃PO₄ and HNO₃) and its concentration (0.1-8 mol dm⁻³). Good deposit was formed in case of low acids concentrations (0.1-1.0 mol dm⁻³) with a current efficiency ≥ 50% using salicylaldehyde bath (Fig. 1).

**Effect of current density**—The effect of current
Effect of concentration of complexing agent on current efficiency of tellurium deposit on platinum cathode, (1) 1,5-diphenylcarbazide, (2) salicylaldehyde, (3) thiourea and (4) aniline current, density 0.2 A/dm² and T = 25°C.

Fig. 3 – Effect of concentration of complexing agent on current efficiency of tellurium deposit on platinum cathode, (1) 1,5-diphenylcarbazide, (2) salicylaldehyde, (3) thiourea and (4) aniline current, density 0.2 A/dm² and T = 25°C.

Effect of temperature – It was found that by increasing the temperature of the baths from 25 to 80°C, the deposition of tellurium increases (1,5-diphenyl carbazide). This was attributed to the acceleration of deposition, ionic migration of the complex species and the fast evolution of hydrogen gas at cathode surface. Above a temperature of 60°C slight decrease in current efficiency was observed. This latter effect may be due to a non-adherent and randomly oriented deposit of tellurium on the surface of cathode.

Analytical determination of tellurium deposit – The spectrophotometric determination of tellurium ion was done using thiourea in a medium of 1 mol dm⁻³ sulphuric acid (λ_max = 315 nm)²⁴. The concentration range, linear regression coefficient, molar absorptivity and detection limit were found to be 2-20×10⁻³ mM, 0.9998, 2.9×10⁴ dm³ mol⁻¹ cm⁻¹ and 2×10⁻⁴ mM respectively. The relative standard deviation as calculated from the range method²⁷ was found to be 0.2-2%. The second method used for the determination of the deposited tellurium was by AAS (cf. experimental procedure). The concentration range, linear regression and slope of the obtained calibration curve were found to be 1-30 µg mL⁻¹, 0.9999 and 3.6×10³, respectively.

Interfering effect of foreign species – The analytical separation procedures for tellurium were done in presence of different anions and cations which...
Table 2 - Analytical results for the determination of tellurium from different samples, acetic acid bath current density 0.1 A dm⁻², T = 30°C and duration time = 30 min, n = 5

| Sample No. | Sample and description | Method, Te (%) | |  |  | Two-tailed F-test |
|------------|------------------------|----------------|---|---|------------------|
|            | AASM, x₁, % | SM, x₂, % | |  | |               |
| 1          | (Te, 40% and Bi, 60%) | 39.8 | 0.1 | 0.3 | 39.7 | 0.1 | 0.3 | 1.581 | 1.00 |
| 2          | (Te, 10% and Bi, 90%) | 9.9 | 0.1 | 1.0 | 9.8 | 0.1 | 1.0 | 1.581 | 1.00 |
| 3          | (Te, 50%, S, 10% and Bi, 40%) | 49.7 | 0.2 | 0.4 | 49.5 | 0.2 | 0.4 | 1.581 | 1.00 |
| 4          | (Te, 5% and Pb, 95%) | 5.1 | 0.1 | 2.0 | 4.9 | 0.1 | 2.0 | 3.162 | 1.00 |
| 5          | (Te, 10% and Hg, 90%) | 9.8 | 0.1 | 1.0 | 9.9 | 0.1 | 1.0 | 1.581 | 1.00 |
| 6          | (Te, 5%, Au, 5% and Ag, 20%) | 4.9 | 0.1 | 1.0 | 4.8 | 0.1 | 2.1 | 1.581 | 1.00 |
| 7          | (Te, 5%, Sc, 10% and Na₂SiO₃, 85%) | 5.1 | 0.1 | 2.0 | 4.9 | 0.1 | 2.0 | 3.162 | 1.00 |
| 8          | (Te, 40%, Sb, 20%, Bi, 10% and Na₂SiO₃, 30%) | 40.1 | 0.1 | 0.3 | 40.2 | 0.2 | 0.5 | 1.000 | 0.25 |
| 9          | (Te, 20%, Fe, 70% and S, 10%) | 19.8 | 0.1 | 0.5 | 19.6 | 0.2 | 1.0 | 2.000 | 0.25 |
| 10         | (Te, 3%, Al, 90% and Cu, 7%) | 3.0 | 0.2 | 6.7 | 2.9 | 0.1 | 3.4 | 1.000 | 4.00 |
| 11         | (Te, 10%, Ni, 80% and Hg, 10%) | 10.1 | 0.2 | 2.0 | 10.3 | 1.1 | 1.0 | 2.000 | 4.00 |
| 12         | (Tellurobismithite, Bi₂Te₃) | 44.5 | 0.1 | 0.2 | 44.3 | 0.2 | 0.5 | 2.000 | 0.25 |
| 13         | (Tetradymite, Bi₂Te₂S) | 48.1 | 0.2 | 0.4 | 48.4 | 0.3 | 0.6 | 1.860 | 0.44 |
| 14         | (Montanite, Bi₂Te₂(OH)₄) | 55.5 | 0.1 | 0.2 | 55.8 | 0.2 | 0.4 | 3.000 | 0.25 |
| 15         | (Durdenite, Fe₂(TeO₃)₄·H₂O) | 51.6 | 0.2 | 0.3 | 51.3 | 0.3 | 0.6 | 2.121 | 0.11 |
| 16         | (Tetradymite, Bi₂Te₂S) | 30.1 | 0.2 | 0.7 | 30.4 | 0.3 | 1.0 | 1.860 | 0.44 |
| 17         | (Sylvanite, (Ag, Au)Te) | 43.5 | 0.3 | 0.7 | 43.2 | 0.4 | 0.9 | 1.342 | 0.56 |
| 18         | (Altaite, Pb, Te) | 36.0 | 0.2 | 0.6 | 35.7 | 0.3 | 0.8 | 1.860 | 0.44 |
| 19         | (Bismuth glance, Bi₂Te₂) | 46.2 | 0.3 | 0.7 | 46.5 | 0.2 | 0.4 | 1.860 | 2.25 |
| 20         | (Hessite, Ag, Te) | 61.0 | 0.4 | 0.7 | 60.6 | 0.3 | 0.5 | 1.789 | 1.78 |

Notes:
(i) \(|t| = \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} \) for the comparison of the experimental means of both AASM and SM for \(P=0.05\) and \(n=10\) for the two methods (8 degrees of freedom) equal 2.300.
(ii) \(F_{0.05, 10} = 9.605\) two-tailed test.
(iii) \(s_p\) is the pooled estimate of standard deviation = \(\sqrt{s_1^2(n_1-1) + s_2^2(n_2-1)}/(n_1 + n_2 - 2)\).

are the most element present in the tellurium ores and minerals. Some of the studied ions have buffering effect and also high conductance in solution, e.g., Ba²⁺. This ion increase recovery percentage up to 112%. Other ions have moderate effect on recovery, e.g., Zn²⁺, Cd²⁺ and Au¹⁺. \(\text{MnO}_2\), \(\text{Cr}_2\text{O}_7^{2-}\) and \(\text{CrO}_4^{2-}\) have strong action on decreasing recovery, % of tellurium. This is due to the strong oxidizing power of such ions to \(\text{Te}^{4+}\) into the higher oxidation state (\(\text{Te}^{6+}\)) which is difficult to reduce to the metallic state on cathode. For iodide ion the lower recovery, % value
(2%) is due to the formation of the highly stable red complex Te\text{2}\textsuperscript{-} which is more difficult to be cathodically reduced\textsuperscript{28}. The lower R % in case of sulphide ion is due to the formation of the sparingly soluble brown-precipitate of TeS\text{2} \textsuperscript{(Ref. 28)}.

Analytical application for the separation of tellurium—The experiment was carried out by taking 0.5 g of sample and 6 mL of a mixture of concentrated HCl and HNO\text{3} (equal volume) in 100 mL-beaker. The whole solution was evaporated till near dryness, then cooled and 1 mL of concentrated H\text{2}SO\text{4} was added followed by the addition of 10 mL KI (10%) and 0.5 g thiourea. To the latter solution 10 mL of 5% SnCl\text{2} was added following by filtration for the formed precipitate. The precipitated tellurium metal was dissolved in hot 1:1 (v/v) nitric acid and diluted to 25 mL using doubly distilled water. The formed solution was subjected to electrodeposition in order to get the pure metal on the cathode under the investigated optimum conditions. The analytical results for the determination of tellurium metal in series of synthetic samples and natural ores containing tellurium with another metals are shown in Table 2.

Comparison between the experimental means of the atomic absorption spectrometric method (AASM) and spectrophotometric method (SM) was done using the null hypothesis of $I$ for $P=0.05$ and $n=5$ (Ref. 27). From Table 2, it is found that for all the synthetic samples (1-11) with the exception of samples (4) and (7) which have $|t|=3.162$, the null hypothesis of $|t|$ is between (1.000-2.000). This means that $|t| \leq 2$ for all the referred samples. This also proves that the observed experimental values of $|t|$ of such samples are approximately equal or less than the tabulated value ($|t|=2.300$), so the null hypothesis is retained. So, it is concluded that both methods for all samples with the exception of samples (4) and (7) (in which the null hypothesis is rejected) have right means or accepted recoveries. From Table 2, it is also found that for all real naturally occurring samples (12-20) with the exception of sample (14) which has $|t|=3.00$, the null hypothesis of $|t|$ is between (1.79-2.12) which shows that $|t| < 2.30$. This proves that the observed experimental values of $|t|$ of such samples are less than the tabulated value ($|t|=2.30$), so the null hypothesis is retained. These can be explained for the real ores determinations as mentioned earlier.

Comparison between the standard deviations of the two investigated methods to estimate random errors of the two sets of data was done using two tailed F-test\textsuperscript{27}. From Table 2, it is clear that all the experimental $F_{4,4}$ values are between 0.11-4.00 for all the experimentally determined synthetic and natural ore samples. These values are less than the tabulated value of $F_{4,4}$ for $P=0.05$ (9.605). This means that there is no significant difference between the two investigated variances (standard deviations) at the 5% level for both AASM and SM or the two methods have the same precision. Also, all samples for both methods are not subjected to any random errors. From the analytical results it is clear that the separation of tellurium by the suggested electrodeposition method in ores and synthetic samples are simple, reliable and can be applied successfully with good accuracy and precision.

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