Extractive separation of tellurium(IV) with triphenylarsine oxide and tributylphosphine oxide as extractants

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Tellurium(IV) is quantitatively extracted from halide media using triphenylarsine oxide (TPAsO) and tributylphosphine oxide (TBPO) as extractants. The optimum extraction conditions are critically evaluated and discussed. The nature of extracted species is deduced along with the probable mechanism of extraction. The method affords binary separation of tellurium(IV) from associated elements and has been further extended to the analysis of alloy samples.

Tellurium is an industrially important element. It is widely used in thermoelectric couples and cooling machines. Bi₂Te₃ is used in preparation of semiconductors. In ceramic industry tellurium is used for colouring glasses and porcelains. However, tellurium can cause fatal intoxication, headache, epigastric pain and disorder. In view of this, separation and determination of tellurium(IV) from associated elements is desired.

Very few extraction methods are available for tellurium(IV). Among the oxygen containing solvents, use of tributylphosphate, methyl isobutyl ketone, trioctylphosphine oxide and di(2-ethylhexyl) phosphoric acid for the extraction of tellurium(IV) has been critically reviewed by Havezov and Jordanov1 and by Sekine and Hasegawa2. In our laboratory tris(2-ethylhexyl) phosphate3 and triphenylphosphine oxide4 has been extensively used for the extraction studies of tellurium(IV) from halide media. However, no work has been reported on the use of organoarsenic compounds as extractants for tellurium(IV). In the present note we have studied the use of triphenylarsine oxide (TPAsO) and tributylphosphine oxide (TBPO) as extractants for tellurium(IV) from halide media. The method is simple and rapid and facilitates separation of tellurium(IV) from associated elements as well as from commercial samples.

Experimental
Absorbance and pH measurements were made on a Shimadzu UV-vis 160 A spectrophotometer and Control Dynamics digital pH meter with combined glass electrode respectively.

Stock solution of tellurium(IV) was prepared by dissolving sodium tellurite (0.435 g) in distilled water and diluting it to 250 cm³ with distilled water. The solution was standardized gravimetrically3 and diluted further to obtain working solutions. Triphenylarsine oxide (Fluka) dissolved in chloroform and tributylphosphine oxide (Aldrich) dissolved in toluene were used as extractants. A solution of thiourea6 (10%, w/v) was used for the spectrophotometric determination of tellurium(IV). All other reagents used were of AR grade.

General extraction procedure for tellurium
To an aliquot containing 100-200μg of tellurium(IV), enough hydrochloric acid or hydrobromic acid was added such that its concentration was in the range 6.5-8.0 or 2.2-3.0 mol dm⁻³ respectively, in a total volume of 10 cm³. The solution was transferred into a separating funnel and equilibrated for 30 s with 5 cm³ of 5% TPAsO dissolved in chloroform or with 5 cm³ of 3.5% TBPO dissolved in toluene. After phase separation, tellurium(IV) from organic phase was re-extracted with 2x5 cm³ of distilled water and determined spectrophotometrically with thiourea6 at 324.5 nm.

Results and discussion
The conditions for quantitative extraction of tellurium(IV) were established by varying parameters like concentrations of hydrochloric acid (0.5-8.5 mol dm⁻³), hydrobromic acid (0.5-5 mol dm⁻³), TPAsO (1-5% in chloroform) and TBPO (0.5-5% in toluene), diluents and shaking period. It was observed that tellurium(IV) is quantitatively extracted from 6.5-8.0 mol dm⁻³ hydrochloric acid or 2.2-3.0 mol dm⁻³ hydrobromic acid with 5 cm³ of 5% TPAsO dissolved in chloroform or 5 cm³ of 3.5% TBPO dissolved in toluene.

The study showed that shaking period of 30 s is enough for complete transfer of tellurium(IV) into
organic phase for both the systems. Prolonged shaking, however, had no adverse effect on the extraction in either case.

The suitability of various solvents was investigated for the proposed systems. It was observed that for TPAsO system, extraction is quantitative with toluene, xylene, benzene and chloroform but decreased with nitrobenzene and carbon tetrachloride. Chloroform was chosen as the diluent for further studies since TPAsO dissolves more readily in chloroform than in toluene. For TBPO system, it was observed that extraction is quantitative with toluene and xylene only. Further studies were carried out with toluene as it gives better and quick phase separation.

In both the cases it was observed that tellurium(IV) is easily re-extracted with distilled water.

Nature of extracted species

The nature of extracted species was ascertained with log-log plots. The plot of log of distribution ratio versus log of hydrochloric acid concentration (at fixed extractant concentration) gives a straight line with slope of 6.0 indicating 1:6 ratio of metal : chloride. Similarly plot of log of distribution ratio versus log of hydrobromic acid concentration gives a straight line with slope of 6.2 again indicating 1:6 molar ratio of metal : bromide. The plot of log of distribution ratio versus log of TPAsO concentration and TBPO concentration (at fixed halide concentration) gives straight lines with slopes of 3.08 and 1.90 respectively for the two systems. The probable extracted species deduced from the above are \( H_2TeX_6 \), TPA\( _3 \)SO and \( H_2TeX_2 \), TBPO for TPAsO and TBPO systems respectively, where \( X \) indicates chloride or bromide.

In both the cases, extraction occurs by solvation mechanism. The neutral metal halide is solvated by the extractants. The resulting species being more hydrophobic, readily transfers into organic phase.

Effect of diverse ions

Varying amounts of foreign ions were added to study their effect on the extraction and subsequent determination of tellurium(IV) by the proposed method. The tolerance limit was set as the amount of foreign ions causing ± 2% error in the recovery of tellurium(IV). It was observed that for TPAsO system there is no interference from 5000 µg of Ba (II), 4000 µg of Cu (II), 2500 µg each of Ca (II) and Al (III), 2000 µg each of Mg (II), La (III), Th (IV) and thiosulphate, 1500 µg each of Cd (II), Pb (II), Ni (II), Ti (IV) and Zr (IV), 1000 µg each of Zn (II), Co (II), Hf (IV), Ce (IV), V (V), U (VI), Cr (VI), Mo (VI), sulphate and nitrate; 500 µg each of thiourea and tartarate; 200 µg each of Bi (III) and EDTA. Similarly for TBPO system there is no interference from 5000 µg each of Ba (II) and Ca (II); 2500 µg of U (VI); 2000 µg each of Mg (II), Cu (II), Pb (II), Al (III), Th (IV), Ti (IV), Zr (IV), Hf (IV), Ce (IV), Cr (VI), Mo (VI) and nitrate; 1500 µg each of Cd (II), Zn (II) and Ni (II); 1000 µg of sulphate; 500 µg each of EDTA and thiourea; 400 µg of V(V); 200 µg of tartarate; 100 µg each of Bi (III) and thiourea and 50 µg of Co (II).

For both the systems, oxalate and citrate were not tolerated.

Binary separation of tellurium (IV) from copper (II), cadmium (II), lead (II), bismuth (III), gold (III) and selenium (IV)

Under the optimum extraction conditions, the ions such as copper(II), cadmium(II), lead(II), bismuth(III) and selenium(IV) remain in the aqueous phase quantitatively. This facilitates their binary separation from tellurium(IV) by the proposed method. Tellurium(IV) in organic phase is back-extracted with water and determined as described above in the general extraction procedure. The aqueous phase containing the unextracted ions was evaporated to dryness and each

<table>
<thead>
<tr>
<th>Comp., µg</th>
<th>Recovery of Tellurium(IV), %</th>
<th>Recovery of added ions, %</th>
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<tbody>
<tr>
<td></td>
<td>TPASO</td>
<td>TBPO</td>
</tr>
<tr>
<td>Te(IV), 200; Cu(II), 200</td>
<td>99.1</td>
<td>99.3</td>
</tr>
<tr>
<td>Te(IV), 200; Pb(II), 200</td>
<td>99.6</td>
<td>99.2</td>
</tr>
<tr>
<td>Te(IV), 200; Cd(II), 200</td>
<td>99.3</td>
<td>99.7</td>
</tr>
<tr>
<td>Te(IV), 200; Bi(III), 200</td>
<td>99.3</td>
<td>99.3</td>
</tr>
<tr>
<td>Te(IV), 200; Au(III), 200</td>
<td>99.4</td>
<td>99.6</td>
</tr>
<tr>
<td>Te(IV), 200; Se(IV), 200</td>
<td>99.6</td>
<td>99.7</td>
</tr>
</tbody>
</table>

1 Average of triplicate analysis.
Table 2—Analysis of tellurium(IV) in alloy samples

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Comp., %</th>
<th>Tellurium(IV), t mg</th>
<th>Coeff. of var., %</th>
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<tbody>
<tr>
<td></td>
<td>Added</td>
<td>Found</td>
<td>TPAsO TBPO</td>
</tr>
<tr>
<td>Leaded brass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(BCS 385)</td>
<td>2.0</td>
<td>1.97</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.928</td>
</tr>
<tr>
<td>Nimonic 901</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(BCS 387)</td>
<td>2.0</td>
<td>1.98</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.180</td>
</tr>
</tbody>
</table>

*Average of triplicate analysis.

may be determined by standard procedures. Copper(II), cadmium(II) and lead(II) were determined spectrophotometrically by 4-(2-pyridylazo) resorcinol (PAR) while bismuth(III) and selenium(IV) were determined spectrophotometrically with thiourea and 3,3 diaminobenzide respectively.

Binary separation of gold(III) and tellurium(IV) was achieved by selectively extracting gold(III) from 2 mol dm⁻³ hydrochloric acid with 0.5% TBPO dissolved in toluene. Under this condition, tellurium(IV) remains quantitatively in the aqueous phase. The extracted gold(III) was back-extracted with water and determined spectrophotometrically by stannous chloride method while unextracted tellurium(IV) was determined as described in the general extraction procedure. The results of the binary separation analysis are reported in Table 1.

Analysis of alloy samples

The applicability of the proposed methods was verified by analysing standard alloy samples. Since standard alloy samples containing tellurium(IV) are not available, we analysed leaded brass (BCS 385) and Nimonic 901 (BCS 387) to which known amounts of tellurium(IV) were added. Tellurium(IV) was recovered after extraction by the proposed method.

A sample of leaded brass (BCS 385, 50 mg) was dissolved in 3 cm³ of cone nitric acid and evaporated to dryness. The residue was taken up in distilled water and the precipitate of metastannic acid was filtered off. To the filtrate, tellurium(IV) (2 mg) was added and solution was diluted to 25 cm³ with distilled water. An aliquot of 2.5 cm³ containing 200 µg of tellurium(IV) was analysed by the proposed method.

Nimonic 901 (BCS 387, 20 mg) was dissolved in 3 cm³ of aqua-regia. The residue was taken up with water. To this solution, tellurium(IV), (2 mg) was added and solution was diluted to 25 cm³ with distilled water. An aliquot of the diluted solution (2.5 cm³) was analysed by the proposed method. The results of the analysis were reported in Table 2.

Acknowledgement

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References