Trace analysis of platinum in sand sample: A voltammetric approach

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Received 26 March 1997: revised 14 January 1998

An accurate and convenient analytical procedure has been developed for the trace determination of metal ions using voltammetric method. Direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) have been successfully applied for the simultaneous determination of various metal ions in the sand sample. 0.1 M ammonium tartrate and 0.001% gelatin were used as supporting electrolyte and maximum suppressor respectively, at pH 9.00±0.02. The observed voltammetric results have been compared with those observed using AAS method.

Voltammetric methods, have been widely used for the trace analysis of substances of natural \(^1\) and other origins \(^2\). The present note reports the analysis of sand sample obtained from Tapkara village of Raigarh district in Madhya Pradesh, for its trace metals content using direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV).

Experimental

Six sand samples were collected from a forest, 17 km north-east of Tapkara village of Raigarh district Chhatisgarh region of M.P. India. Polarographic measurements were made on an Elico (India) pulse polarograph model CL-90 coupled with a model L.R-108 X-Y polarocard. The electrode system consisting of a dropping mercury electrode (DME) as working electrode, a coiled platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode was used. The instrumental parameters employed were as follows: initial applied voltage 0.0 V vs SCE, sensitivity 10 \(\mu\)A, height of Hg column 140.0 cm, time constant 5.0 ms, pulse amplitude 50 mV, drop time 1 sec., scan rate 12 mV s\(^{-1}\), acquisition fast, IR compensation 5.0 and charging current compensation 3.5. A glassy carbon fibre electrode (NF 12. Sigiti Electitiogitit, UK) was used for DPASV and pH measurements were made on an Elico digital pH meter model LI-120. All the chemicals used were of AR grade (BDH). Stock solutions of ammonium tartrate (1M), Pt, Cu, Pb, Cd, Ni, Zn, Fe, Cr, Ru, and Os (0.01M) and EDTA (disodium salt) (0.01M) were prepared by dissolving the requisite amounts, in doubly distilled water. Gelatin solution (0.01%) was prepared in hot distilled water. The solutions were standardised by known methods and diluted as required.\(^7\) For preparation of sample, 1.0g of finely pulverised sand sample was dissolved in 10 ml of hydrofluoric acid and the final volume was made up to 100 ml with distilled water.

Procedure

To 10 ml of sample solution, 10 ml of 1.0M ammonium tartrate (supporting electrolyte) and 10 ml of 0.01% gelatin (maximum suppressor in polarographic cell) were added and the final volume was made up to 100 ml with distilled water. The pH of the test solution was adjusted to 9.0±0.02 using ammonium hydroxide. The analyte was placed in a polarographic cell. Pure nitrogen gas was bubbled through the test solution for 15 min and the pH of the test solution was checked before recording polarograms/voltammograms.

Results and discussion

Fig.1a, 1b and 1c show DC, DP polarograms and DPAS voltammogram of the sand sample respectively. in 0.1 M ammonium tartrate and 0.001% gelatin at pH 9.00±0.02. The DC and DP polarograms (using dropping mercury electrode) of the sample showed nine distinct polarographic waves with \(E_{1/2}/E_p\) values equal to -0.38V/-0.4V, -0.53V/-0.58V, -0.68V/-0.69V, -0.84V/-0.87V, -0.99V/-1.06V, -1.16V/-1.18V, -1.26V/-1.30V, -1.42V/-1.44V and -1.59V/-1.64V vs SCE. However, on replacing DME with a glassy carbon fibre electrode in addition to the above nine a tenth wave/peak with \(E_{1/2}/E_p\) = +0.05V vs SCE was observed while the DPAS voltammetric peaks with \(E_p\) values equal to +0.05V, -0.32V, -0.53V, -0.75V, -0.9V, -1.08V, -1.22V, -1.4V and -1.52V vs SCE corresponding to Pt(IV), Cu(II), Pb(II), Cd(II), Cr(II), Ni(II), Zn(II), Fe(II), Cr(III) and Ru(IV)/Os(VIII)\(^8\). These differences in peak poten-
Table 1 — Comparison of AAS and voltammetric trace analysis data on the sand sample*

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Amount found in μg × 10⁻²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(VI)</td>
<td>3.9</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>15.1</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>496.2</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>5.1</td>
</tr>
<tr>
<td>Cr(II)</td>
<td>5.0</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>15.0</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>8.3</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>7.8</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>466.0</td>
</tr>
<tr>
<td>Ru(IV)</td>
<td>2.9</td>
</tr>
<tr>
<td>Os(VIII)</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>AAS</td>
</tr>
<tr>
<td></td>
<td>Voltammetry</td>
</tr>
<tr>
<td>Pt(VI)</td>
<td>4.0</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>15.0</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>497.0</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>5.2</td>
</tr>
<tr>
<td>Cr(II)</td>
<td>5.1</td>
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<tr>
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<tr>
<td>Zn(II)</td>
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<tr>
<td>Fe(III)</td>
<td>467.0</td>
</tr>
<tr>
<td>Ru(IV)</td>
<td>3.1</td>
</tr>
<tr>
<td>Os(VIII)</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Average of six samples

tial values in DPP and DPASV modes may be due to increasing ease of reduction on carbon fibre electrode, which in turn shifts the peak potentials to more positive values.

The presence of the metal ions in the sample was confirmed by adding a definite quantity of standard solution of each metal ion to the analyte and recording the polarograms/voltammograms, which results in increase in the wave/peak height of each metal ion signal without any change in $E_{1/2}$ values. Some synthetic samples with varying concentrations of above mentioned metal ions, were prepared and their polarogram/voltammogram were recorded under identical experimental conditions. The results show no change in $E_{1/2}$ values (Fig. 1e).

Analysis of ruthenium and osmium

The polarographic wave with $E_{1/2}$ values equal to -1.59V/1.6V vs SCE created some confusion as to whether it was due to Ru or Os, because its $E_{1/2}$ was -1.59V. According to literature the $E_{1/2}$ is between the $E_{1/2}$ values for Ru and Os. To overcome this problem, differential complexation with EDTA was carried out. On recording the polarogram of EDTA-complexed sample solution, a single peak splitted into two with $E_{1/2}$ values equal to -1.56V and -1.71V, indicating the presence of both i.e. Ru and Os in the sample (Fig. 1d). Ru-EDTA and Os-EDTA complexes in the ratio 1:1 were prepared separately and their polarograms were recorded. They produced well-defined peaks with same $E_{1/2}$ values. After confirming the presence of Ru and Os
in the sample, their quantitative analysis was carried out.

DCP, DPP and DPASV were used for the simultaneous quantitative analysis of Pt, Cu, Pb, Cd, Cr, Ni, Zn, Fe, Ru and Os in the sample at pH 9.00±0.02. Spiked samples were prepared to evaluate the concentration of each metal ion. The results indicate that the percentage recovery was over 99% for all the metal ions, with high accuracy and precision of determination.

Table I shows the final analysis results of the sample. The results were compared with those obtained using AAS method and were found to be in excellent agreement. However, the proposed voltammetric procedure was found to be highly useful for the determination of species in different oxidation states in the sample for example, Cr(II) and Cr(III) in the present case, which is otherwise not possible using AAS method. The comparative and statistical data proves the superiority of the voltammetric method for such an analysis over the other methods.

References