ttance of the extracts of metal complexes was within ±2%.

Determination of osmium in osmiridium — Synthetic mixtures of platinum metals corresponding to the composition of osmiridium were prepared and osmium content determined following the standard procedure. The results are quite satisfactory and the reagent can be used with good accuracy.

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References

The metal ion solutions were prepared from AR metal sulphates with the exception of silver for which nitrate was used. BDH reagent grade tri-n-butyl phosphate and benzene were used as such. 110mAg, 115mCd, 203Hg and 204TI radio isotopes (Bhabha Atomic Research Centre, Bombay) were used for the distribution studies.

The aqueous phase consisted of metal ion solution (1.0 × 10^{-4}M) labelled with the radioactive tracer in an appropriate concentration of ammonium thiocyanate. Initial pH of the aqueous phase was adjusted with perchloric acid and sodium hydroxide. The organic phase consisted of appropriate concentration of TBP in benzene. Equal volumes of both the phases were mixed together and equilibrated for 5 min. After clear separation of the two phases, the pH of the aqueous phase was measured. Suitable aliquots of each phase were assayed for their activity. The gamma activity of 110mAg, and 203Hg was counted on a well-type NaI(Tl) scintillation counter while in the case of 115mCd and 204TI, beta counting was done on a G. M. counter.

All the distribution studies were performed at room temperature (25 ± 3°C).

The effect of pH on the extraction of cadmium(II) was studied at 1.0M ammonium thiocyanate with 1.0M TBP in benzene. It was observed that the extraction is almost independent of pH in the range 3-6, and pH 5 was chosen for the aqueous phase.

The effect of varying [Cd(II)] on its distribution ratio was studied at constant ammonium thiocyanate (1.0M) and TBP (2.0M) concentrations. The distribution ratio was practically independent of [Cd(II)] in the range 10^{-8}−10^{-3}M. The distribution ratios were within ±5% of the average value, indicating that, probably, no polymeric species were getting extracted into the organic phase.

The effect of varying ammonium thiocyanate concentration at constant TBP concentration and vice-versa on the extraction of cadmium was studied. The extraction increases with increasing concentration of thiocyanate and plot of log[NH4SCN] versus log D was linear with a slope close to 4. These results suggest that four molecules of TBP are associated with the extracted species.

On the basis of above results, the species being extracted is inferred to be [Cd(SCN)4TBP]^-. Since a non-polar medium has been used for extraction,

Table 1 — Some Metal Ion Separations from NH₄SCN Solutions by TBP in Benzene

<table>
<thead>
<tr>
<th>Metal ions separated</th>
<th>[NH₄SCN]M</th>
<th>Separation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)-Ag(I)</td>
<td>2.0</td>
<td>1.6x10^2</td>
</tr>
<tr>
<td>Cd(II)-TI(III)</td>
<td>0.02-2.0</td>
<td>&gt;10^2</td>
</tr>
<tr>
<td>Hg(II)-Ag(I)</td>
<td>2.0</td>
<td>3.2x10^2</td>
</tr>
<tr>
<td>Hg(II)-TI(III)</td>
<td>0.02-2.0</td>
<td>&gt;10^2</td>
</tr>
</tbody>
</table>
a neutral species in association with some anion is presumed to be formed. The possibility of OH− getting attached with cadmium species is ruled out because the extraction is almost independent of pH. Therefore, it is safe to assume that ClO− is attached since it is present in large excess in the aqueous phase. Thus, the extracted species is Cd(SCN)X.4TBP, where X = ClO−.

The extraction behaviour of silver(I), cadmium (II), mercury(II) and thallium(III) has been studied as a function of ammonium thiocyanate concentration (0.02-2.0 M) at constant TBP concentration (2.0 M) in benzene. The extraction of cadmium(II) and mercury(II) increases with increasing concentration of thiocyanate (Fig. 1) while that of silver(I) shows an opposite trend. Thallium (III) shows negligible extraction over the entire investigated range of thiocyanate concentration. On the basis of extraction data some metal ion separations have been achieved and are listed in Table 1. The metal ions from the organic phase have been conveniently stripped by washing it with distilled water.

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References