the presence of coordinated water\textsuperscript{4,5}. Evidences in favour of bonding sites have been further substantiated by the observations of ν(M-N) and ν(M-O) around 330 and 450 cm\textsuperscript{-1} respectively in the far IR spectra.

In the electronic spectra of nickel complexes three bands appear at 8·5 (7), 13·5 (7-2) and 24·6 \textsuperscript{(17)} kK, assignable\textsuperscript{6}, to \(\bar{A}_{2\varepsilon} \rightarrow \bar{T}_{2\varepsilon} (F)\), \(\bar{A}_{2\varepsilon} \rightarrow \bar{A}_{1\varepsilon} (F)\) and \(\bar{A}_{2\varepsilon} \rightarrow \bar{T}_{1\varepsilon} (F)\) transitions respectively. A comparison of the bands with those obtained in the reflectance spectrum indicates a possible dissociation in solution and presumably a distorted octahedral configuration is expected for this compound. Cobalt complex exhibit three absorption bands at 21 (19), 19-1 (32), 7-8 (8 kK attributable to \(\bar{T}_{1\varepsilon} (F) \rightarrow \bar{A}_{2\varepsilon} (P)\), \(\bar{T}_{1\varepsilon} \rightarrow \bar{A}_{2\varepsilon} (F)\) and \(\bar{T}_{2\varepsilon} \rightarrow \bar{A}_{2\varepsilon} (F)\) transitions respectively. Molar absorbivity values and calculation of \(\bar{D} \) and \(\bar{S}\) indicate a spin-free octahedral configuration for this complex.

One broad band is observed in the case of copper complex around 17-0 (30) kK. The complex presumably has a planar configuration.

From the analysis, conductance and IR spectral studies \(\text{Zn(II)}, \text{Cd(II)}\) and \(\text{Hg(II)}\) complexes are found to be four-coordinated having a tetrahedral environment around the metal ions.

References


Detection & Determination of Piperidine & Piperazine Using Chloranil as a Reagent

U. Muralikrishna \\& N. Someswara Rao

Department of Chemistry, Andhra University
Waltair 530003

\textit{Received 1 March 1978; accepted 14 April 1978}

Spot detection and determination of microgram quantities of piperidine and piperazine using chloranil as reagent in chloroform are reported. The procedures now developed are based on the spectral characteristics of the charge transfer complexes formed, and have the advantages of being simple, rapid and sensitive.

Piperidine and piperazine interact with chloranil with the production of blue coloured charge-transfer complexes at relatively low concentrations of the donors, showing maximum absorption at 590 and 575 nm respectively. This property has been utilized in working out a procedure for the spot detection and determination of these two compounds.

Stock solutions of piperidine and piperazine (Fluka, purum) were prepared by dissolving 0·1 g of each in chloroform (25 ml) a saturated solution of chloranil (E. Merck, GR) in chloroform was prepared and filtered to get a clear solution.

Absorption measurements were made with a Unicam SP-700 ultraviolet-visible recording spectrophotometer at room temperature (25°) using matched silica cells of 1 cm path length. The spectra of the mixtures of piperidine-chloranil and piperazine chloranil in chloroform were scanned against reagent as blank. However, it may be noted that chloranil in chloroform has no absorption in this region. The characteristic new band for piperidine-chloranil is at 590 nm and for piperazine-chloranil is at 575 nm.

**Procedure for the spot detection** — Test solution (0-1 ml) was taken in the cavity of a spot plate and mixed with chloranil solution (0-1 ml) and diluted with chloroform to 0·3 ml. The solution is thoroughly mixed when a blue colour slowly developed within 10 min.

From such a study, the identification and dilution limits are: For piperidine: 1-0 μg, and 1·5·0 × 10\textsuperscript{-4} respectively and for piperazine 5-0 μg, and 1·2·0 × 10\textsuperscript{-4} respectively.

The method for the detection of piperazine was applied with success in the case of some pharmaceutical preparations piperazine phosphate and piperazine citrate after extracting piperazine into chloroform layer from alkali solution of piperazine salts. The properly diluted solution gave the test.

**Procedure for the determination** — To suitable aliquots of the nitrogen bases from the stock solutions was added chloranil solution (1 ml) and the contents made up to 10 ml by adding chloroform. The absorbance of the piperidine solution was measured at 590 nm and that of piperazine at 575 nm after 10 min. A calibration curve was drawn from the known results. The sample solution was then treated with an excess of the reagent (1 ml of chloranil) and its absorbance measured against the reagent blank in just the same manner as described for standard solutions. The amount of the unknown base was then read off from the calibration plot. The results are presented in Table 1.

**Table 1 — Determination of Piperidine and Piperazine**

<table>
<thead>
<tr>
<th>Taken</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piperidine</td>
<td></td>
</tr>
<tr>
<td>4·55</td>
<td>4·40</td>
</tr>
<tr>
<td>9·05</td>
<td>9·05</td>
</tr>
<tr>
<td>11·40</td>
<td>11·35</td>
</tr>
<tr>
<td>18·50</td>
<td>22·50</td>
</tr>
<tr>
<td>42·65</td>
<td>42·60</td>
</tr>
<tr>
<td>63·35</td>
<td>63·20</td>
</tr>
<tr>
<td>Piperazine</td>
<td></td>
</tr>
<tr>
<td>11·25</td>
<td>11·10</td>
</tr>
<tr>
<td>20·50</td>
<td>20·50</td>
</tr>
<tr>
<td>42·65</td>
<td>42·60</td>
</tr>
<tr>
<td>66·00</td>
<td>66·00</td>
</tr>
<tr>
<td>83·95</td>
<td>82·80</td>
</tr>
</tbody>
</table>

**NOTES**

<table>
<thead>
<tr>
<th>Conc. (μg/ml) contained in final solution</th>
<th>Appr. range of Beer's law (μg/ml)</th>
</tr>
</thead>
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<td></td>
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</table>
The coloured solution are stable for two days, in the solution after keeping properly seated tubes.

We are grateful to the CSIR, New Delhi, for the award of a junior research fellowship to one of us (N.S.R.).

References

Solvent Extraction of Cu(II) Using 4-Isonitroso-3-methyl-1-phenyl-5-pyrazolone
H. C. Arora & R. K. Taluk
Department of Atomic Energy, Atomic Minerals Division, New Delhi 110022

Received 9 February 1978; accepted 25 May 1978

Solvent extraction behaviour of Cu(II) using 4-isonitroso-3-methyl-1-phenyl-5-pyrazolone (HIMPP) in benzene as extracting agent has been studied. Composition of the extracted complex has been determined. Interference due to a number of foreign elements has also been tested.

In an earlier investigation, Arora et al. studied the solid metal complexes of 4-isonitroso-3-methyl-1-phenyl-5-pyrazolone (HIMPP). Presently we report the use of this ligand for the solvent extraction of Cu(II). Interferences due to most of foreign elements likely to be present in alloys, ores and industrial materials have been found to be negligible.

The ligand was prepared as described earlier and its purity checked; m.p. 160°. It is soluble in benzene, alcohol and chloroform. Stock solution of copper (II) was prepared by dissolving known weight of pure metallic copper in dilute (1:1) nitric acid. The solution was evaporated to dryness and finally made up to a known volume with 0.1 N hydrochloric acid. Stock solution was diluted suitably to obtain Cu(II) solution containing copper equal to 10 μg per ml. Procedure — An aliquot of 1.6×10⁻⁴ M copper solution (5 ml) and buffer solution (5 ml) were mixed and distilled water (10 ml) added to it. The mixture was shaken with a solution of HIMPP (20 ml) in benzene (6.16×10⁻⁴ M) for 5 min at 25±1°. The two phases were allowed to separate. The amount of Cu(II) extracted into organic phase and that left unextracted into aqueous phase was determined spectrophotometrically using sodium diethyl dithiocarbamate reagent. Copper present in the organic phase was stripped with 1.25 HCl (20 ml) prior to its determination. The distribution coefficients (D) were calculated as usual. In all the experiments the equilibrium pH was measured. In the same fashion experiments were conducted at constant pH 4.9 by varying the ligand concentration from 0.3 to 2 mM, keeping the copper concentration constant. It was observed that Cu(II) is almost completely extracted above pH 5.6 with 6.16×10⁻⁴ M HIMPP in benzene. The slope of the plots of log D vs pH and of log D vs log [HIMPP] is two in each case indicating that two moles of hydrogen ions are liberated in the extraction process and two moles of ligand are involved in complex formation. Hence the extraction process may be represented by the equation Cu²⁺ + 2HIMPP ⇌ Cu(IMPP)₂ + 2H⁺. The composition of the extracted complex is thus 1:2 (Cu-HIMPP).

In order to test the applicability of the method for the extraction of copper present in ores, alloys and industrial materials, etc. a number of interferences were examined by adding them to the aqueous solution containing 50 μg of Cu(II) and subjecting them to the general procedure maintaining the pH 5.4 and concentration of HIMPP 2.46×10⁻⁴ M in each case. In some cases tartaric acid was successfully used to prevent hydroxide formation. The results indicate that barring Al(III) and Sn(IV), none of the foreign cations added (1 mg each) hinders the complete extraction of Cu(II). The organic phase in each case was back washed with 1.25 HCl solution and analysed for Cu(II) and also for interfering elements, if any. It was observed that Ni(II), Be(II), Mg(II), Ca(II), Mn(II), Fe(III), Al(III), Th(IV), Sn(IV), Ti(IV), V(V) and U(VI) are not at all extracted along with Cu(II) whereas citrate, oxalate and ethylenediaminetetraacetate anions seriously interfere. Phosphate and sulphate anions at 100 mg level are without any effect on the extraction of Cu(II).

References

o-Mercaptoacetamidobenzoic Acid as a Gravimetric Reagent for Zr(IV)
M. Padmini & Geetha Parameswara
Department of Chemistry, University of Calicut, Calicut 673635

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Gravimetric determination of zirconium in pure salts as well as in zircon has been carried out using o-mercaptoacetamidobenzoic acid (o-MAB). The results obtained are comparable to those obtained with mandelic acid. The solid complex has been isolated and its IR data reported.

Several organic reagents have been tried for the gravimetric determination of zirconium in its salts, alloys and ores. Since zirconium has a less tendency to form stable complexes with sulfur donor ligands it was of interest to see if o-mercaptoacetamidobenzoic acid (o-MAB), which has a —COOH group, besides —SH and —N donor sites, will form a complex with zirconium. It was found that zirconium forms a very stable complex with o-MAB and this can successfully be used for