Under the experimental conditions, the oxidation of sulphanilamide by the sodium vanadate proceeds according to the equation,

\[(H_2NO_3S)C_6H_4(NH_2) + 6 NaVO_3 + 18 HCl \longrightarrow (H_2NO_3S)C_6H_4(NO_3) + 6 VOCl_2 + 6 NaCl + 10 H_2O\]

To an aliquot volume of sulphanilamide (containing 22-30 mg of sulphanilamide), 25 ml of concentrated hydrochloric acid, 5 ml of orthophosphoric acid and 10 ml of sodium vanadate (0.2 M) are added and the volume made up to 50 ml. The solution is kept at room temperature for 45 minutes and then titrated with standard solution of ferrous ammonium sulphate solution using N-phenyl anthranilic acid as indicator. The results obtained (after applying suitable blank correction) are found to have an accuracy better than 0.5%.

Acetanilide which is the starting material for the preparation of sulphanilamide does not interfere in the procedure. Acetate, perchlorate and sulphate ions also do not interfere. Further work regarding the determination of other sulphurids is in progress.

Department of Chemistry, C. S. Prakasa Sastry.
College of Science and R. Ramakrishna.
Technology,
Andhra University,
Visakhapatnam 530 003, (A.P.),
November 21, 1975.

METAL CHLATES OF Cu^{2+}, Ni^{2+}, Co^{2+} AND VO^{2+}, A SPECTROPHOTOMETRIC STUDY USING SALICYLALDEHYDE-4-p-METHOXYPHENYL-3-THIOSEMICARBAZONE AS A LIGAND

The spectrophotometric reports that salicylaldehyde-4-p-methoxy-phenyl-3-thiosemicarbazone (SMPT) forms coloured chelates with Cu^{2+}, Ni^{2+}, Co^{2+} and VO^{2+}. Cu^{2+}, Ni^{2+} and VO^{2+} form 1:1 (metal: ligand) chelate while Co^{2+} forms 1:2 chelate with this reagent. Effect of pH on chelate and stability constants of chelates has been investigated.

EXPERIMENTAL

The ligand salicylaldehyde-4-p-methoxy-phenyl-3-thiosemicarbazone was synthesized and crystallized to get an analytically pure sample (m.p. 210°C). All the chemicals except the ligand were of BDH analytical grade.

The solution of ligand was prepared by dissolving required amount of ligand in absolute alcohol. The solutions of metal ions were prepared by dissolving their nitrates (BDH Analar grade) except for VO^{2+} for which VO(SO_4)_2 was used. The concentration of metal ions were checked by standard gravimetric and volumetric methods. All the measurements were carried out on Bosch and Lomb Spectronic 20 spectrophotometer. pH of the solutions were checked by Philips pH meter.

RESULTS AND DISCUSSIONS

Effect of pH on the formation of the chelates.—The chelates of the metal ions studied with SMPT are formed within a limited range of pH. The results are included in Table I.

### Table I

<table>
<thead>
<tr>
<th>Chelate</th>
<th>pH range of stability</th>
<th>λ max of chelate (nm)</th>
<th>Studied at pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (II) SMPT</td>
<td>4.0-7.0</td>
<td>390</td>
<td>4.33</td>
</tr>
<tr>
<td>Ni (II) SMPT</td>
<td>4.5-8.2</td>
<td>420</td>
<td>6.99</td>
</tr>
<tr>
<td>Co (II) SMPT</td>
<td>5.0-8.0</td>
<td>395</td>
<td>6.12</td>
</tr>
<tr>
<td>VO (II) SMPT</td>
<td>4.0-6.0</td>
<td>395</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Nature of the complexes formed.—Mixtures containing metal and ligand in the ratio of 1:1, 1:2 and 1:3 were prepared in 50% (v/v) absolute alcohol. The absorbance measurements were taken from 370 nm to 600 nm. All showed only one λ max as shown in Table I.

Composition of the chelates.—The composition of the metal chelates have been determined spectrophotometrically using the method of continuous variation slope ratio and molar ratio methods. In all the systems studied, the composition of the complex has been found 1:1 (metal: ligand) except for Co^{2+} which forms 1:2.

The stability constants have been determined by the method of Dey and Banerjee and the mole ratio method at 30°C ± 1°C. The results are given in Table II.

### Table II

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Composition</th>
<th>Stability constant mole ratio</th>
<th>Stability constant Dey and Banerjee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (II) SMPT</td>
<td>1:1</td>
<td>2.0 \times 10^6</td>
<td>1.0 \times 10^6</td>
</tr>
<tr>
<td>Ni (II) SMPT</td>
<td>1:1</td>
<td>2.2 \times 10^6</td>
<td>1.6 \times 10^6</td>
</tr>
<tr>
<td>VO (II) SMPT</td>
<td>1:1</td>
<td>2.0 \times 10^6</td>
<td>1.2 \times 10^6</td>
</tr>
<tr>
<td>Co (II) SMPT</td>
<td>1:2</td>
<td>5.1 \times 10^{11}</td>
<td>2.7 \times 10^{11}</td>
</tr>
</tbody>
</table>

The authors are thankful to Dr. K. A. Bhaker for providing laboratory facilities and to CSIR, New
Delhi and Gujarat State for the award of scholarship to Y. N. B. and K. K. P. respectively.

University Department
of Chemistry
Saurashtra University,
Bhavnagar,

Y. N. BHATT
K. K. PATEL
K. J. SHA
R. S. PATEL

February 19, 1976.


AMPEROMETRIC DETERMINATION OF THIAMINE (VITAMIN B₁₂) USING POTASSIUM HEXACYANOFERRATE (III)

Introduction

Thiamine has been estimated by polarographic, chromatographic, colorimetric, physico-chemical, enzymatic and microbiological methods. All these methods are either time consuming and tedious and have low accuracy. Thiamine is known to undergo oxidation when treated with alkaline hexacyanoferrate (III) (pH around 12) to give thiochrome. Preliminary studies show that one mole of thiamine is oxidized by two moles of hexacyanoferrate (III) according to the following equation:

2K₃Fe(CN)₆ + CH₃CNH₂N⁺CH₃ → KOH → 2H⁺

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{S} & \quad \text{S} \\
\text{CH₃CNH₂N⁺CH₃} & \quad \text{CH₃CNH₂N⁺CH₃} \\
\text{THIAMINE} & \quad \text{THIOCHROME}
\end{align*}
\]

Experimental

Solutions were prepared using AnalaR grade (BDH) chemicals. Ferricyanide solution was standardized by the potassium iodide method.

Each multivitamin tablet had 0.3 mg of thiamine along with other vitamins and minerals and 10 ml of Elixir Eupeptide syrup contained 0.3 mg of thiamine. Amperometric titrations were carried out with a manual Toshiba (India) polarograph (CLO-2) using a Pye scalamp galvanometer and a dropping mercury electrode (capillary characteristic: 1.5 mg/s). LiCl as supporting electrolyte. The effective concentration of LiCl should be between 1.0 M and 1.5 M.

Procedure

0.5 ml of thiamine solution (concentration between 0.0113 to 0.000113 M) was placed in the polarographic cell. To this was added 5.0 ml of 0.05 M KOH and 10 ml of 2.0 M LiCl and the solution was deaerated by bubbling purified hydrogen. It was then titrated amperometrically against 0.1 to 0.001 M K₃Fe(CN)₆ at -0.35 V.

Table 1

<table>
<thead>
<tr>
<th>Thiamine mg/100 ml</th>
<th>Taken</th>
<th>Found</th>
<th>Accuracy %</th>
<th>Precision %</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>301.01</td>
<td>0.3</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>29.88</td>
<td>0.4</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>19.85</td>
<td>0.7</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10.15</td>
<td>1.5</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.07</td>
<td>1.4</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.94</td>
<td>2.0</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.95</td>
<td>2.5</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

Thiamine in multivitamin tablets

| Glaxo | 2.4 | 2.36 | 1.5 | 2.5 |
| Squibb | 2.4 | 2.35 | 2.1 | 2.4 |

Thiamine in Elixir Eupeptide

| 2.4 | 2.37 | 1.2 | 2.5 |

* Based on the results of triplicate analysis.

For the estimation of thiamine in multivitamin tablets, the powder of two tablets was shaken up with 10 ml of double distilled water and filtered. The filtrate was diluted to 25 ml and 2.0 ml of this solution