PART II
EXPERIMENTAL
CHAPTER 1

PREPARATION OF THE REAGENT AND SOLUTIONS
PREPARATION OF SOLUTIONS

1. Preparation of the resacetophenoneoxime: The ketoxime was prepared from the ketone by the general procedure recommended by Vogel\(^1\). The ketone was prepared from the condensation reaction of acetic acid and resorcinol.

(a) Resacetophenone \((\mathbf{2,4-}-(\mathbf{OH})_2 \text{ - acetophenone})\)

This compound was prepared by the following procedure recommended by Day and Sitaraman\(^2\). 15 gms of \textit{glacial} acetic acid were taken in a 250 ml beaker and 15 gms of anhydrous zinc chloride were dissolved in it by heating. Resorcinol (10 gm) was then added to the above mixture and heated to 142\(^\circ\)C until the syrupy liquid was obtained. It was later treated with a mixture of 40 cc of concentrated hydrochloric acid and 40 cc water. Resacetophenone crystals obtained were recrystallised from hot water. White crystalline needles with melting point 143\(^\circ\)C were obtained.

(b) Resacetophenoneoxime \((\mathbf{2,4-}-(\mathbf{OH})_2 \text{ - acetophenoneoxime})\)

This reagent was prepared from resacetophenone by the general procedure recommended by Vogel (loc. cit.).
100 ml of 10% solution of sodium hydroxide, 50 ml of 50% solution of hydroxylamine hydrochloride and 10 gms of racacetophenone were taken in a one litre round bottomed flask. Sufficient quantity of alcohol was added to it to get a homogeneous solution. The solution in the flask was then refluxed for about 30 minutes. The reaction mixture was poured into ice cold water with brisk stirring when crystals of the oxime separated. The crystals were separated through filtration and recrystallised from hot aqueous alcohol. Colourless crystalline needles melting at 199-200°C were obtained.

2. Methanol: Pro analysis (E. Merck) sample was distilled and the fraction boiling between 63.5° and 64.5°C was collected.

3. n-Butanol: AR (REH) sample was distilled and the fraction boiling between 116° and 117°C was collected.

The polarographic purity of the above solvents was ascertained by the absence of polarographic reduction wave in the potential range of study (0.0 to -2.0 volts vs. Hg pool).

Physical constants of methanol and n-butanol:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>B.P.</th>
<th>Density</th>
<th>Viscosity</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>gm/ml</td>
<td>C. poises</td>
<td>N.V.</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.5°</td>
<td>0.79/25°C</td>
<td>0.55/25°C</td>
<td>32.63/25°C</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>117.7°</td>
<td>0.80/30°C</td>
<td>2.27/30°C</td>
<td>17.10/25°C</td>
</tr>
</tbody>
</table>
4. Titanium(IV) sulphate: About 2.04 grams of AnalR (BDH) potassium titanium oxalate and 4 grams of AnalR (BDH) ammonium sulphate were mixed in 50 ml of AnalR concentrated sulphuric acid. The mixture was carefully boiled for 10 minutes, cooled and poured into 375 ml of conductivity water and diluted to 500 ml in a volumetric flask. Titanium solution was standardized gravimetrically as titanium oxide$^3$.

5. Vanadium(IV) sulphate: About 5.00 grams of pro analysis sample (E. Merck, Germany), of sodium mono vanadate was dissolved in 100 ml of hot conductivity water. 14 ml of concentrated sulphuric acid were added into the same to maintain acidity of the solution at 2 M. 50 ml of water were added and $SO_2$ was passed until the colour of the solution was turned bright and deep blue. Carbon dioxide gas was then flushed to remove the excess of dissolved sulphur dioxide (until it was free from the smell of sulphur dioxide gas). It was then made upto 250 ml. The solution was standardized with a standard solution of potassium permanganate$^4$.

6. Ammonium meta vanadate: Ammonium meta vanadate (0.1 M) solution was prepared by dissolving 2.925 grams of ammonium meta vanadate (Reidel, Budapest, Hungary) in 200 ml hot conductivity water. The solution was cooled, made upto 250 ml and standardized with standard ferrous ammonium sulphate$^5$ solution.
7. Chromium(III) chloride: A stock solution was prepared by dissolving 6.6 grams (Fisher Analyzed Reagent, J.T. Baker Chemical Co., Phillipsburg, N.J.) of chromium chloride hexahydrate in conductivity water and the solution was made up to the mark in a 250 ml standard flask. It is standardized with standard ferrous ammonium sulphate solution.

8. Manganese(II) sulphate: 4.325 grams of (Pro analysi, Reidel, De Haen AG SEELZE-Hannover) manganese sulphate monohydrate were dissolved (MnSO₄·H₂O) in conductivity water and the solution was made up to 250 ml in a standard flask. The solution was standardized after proper dilution colorimetrically.

9. Ferric ammonium sulphate: Approximately 0.25 M solution was prepared in 2 N sulphuric acid by dissolving requisite quantity of ferric ammonium sulphate in water. The solution was standardized volumetrically against standard potassium dichromate solution.

10. Cobaltous chloride: Cobalt(II) chloride (0.1 M) solution was prepared by dissolving 5.95 gms of cobaltous chloride hexahydrate (AnalaR, BDH) in conductivity water. The solution was made up to the mark in 250 ml standard flask. The solution was standardized volumetrically using oxine.

11. Ferric chloride: Approximately 1.0 M solution was prepared by dissolving ferric chloride (BDH) in water containing
small quantity of HCl. The solution was standardized
with standard potassium dichromate solution and diluted to
get 0.1 M stock solution.

12. Zinc Sulphate: 0.1 M solution was prepared by dissolving
7.189 gms of zinc sulphate (AR, BDH) in conductivity water
and making up the solution to 250 ml.

nickel sulphate, hexa hydrate (AnalaR, Hopkin and Williams Ltd.,
England) was dissolved in water and the solution was made upto
the mark in a 250 ml standard flask. The solution was
standardized gravimetrically with dimethyl glyoxime.

14. Sodium perchlorate: 1.0 M stock solution of sodium
perchlorate mono hydrate was prepared by dissolving 14.05 gms
of the sample (Furias, P.a., Fluka, A.G. Bush, E.G.) in
conductivity water and making up the solution to 100 ml. The
solution did not give polarographic wave in the potential range
of study (0.0 to +2.0 volts vs Hg pool).

15. Sodium acetate: 1.0 M solution was prepared by
dissolving 13.61 gms of sodium acetate trihydrate (GR, pro analysi,
Sarabhai M. Chemicals) in conductivity water and making up
the solution to 100 ml in a standard flask. It was diluted
to give a stock solution of 0.1 M. The purity of the solution
was ascertained by the absence of any polarographic wave in
the potential range of study (0.0 to -2.0 V vs Hg pool).
16. Acetic acid:– 1 M solution of acetic acid was prepared by suitably diluting glacial (AnalaR, BDH) acetic acid with conductivity water. The solution was standardized with standard sodium hydroxide.

17. Sodium hydroxide:– The solution was made by dissolving required amount of sodium hydroxide pellets (AnalaR, BDH) in carbon dioxide free conductivity water. The solution was standardized against standard oxalic acid.

18. Oxalic acid:– 0.1 M stock solution was prepared by dissolving 3.15 gms of (AnalaR, BDH) oxalic acid dihydrate in conductivity water and making up the solution to 250 ml in a standard flask.

19. Hydrochloric acid:– 2 M hydrochloric acid was made by suitably diluting concentrated hydrochloric acid (AnalaR, BDH) with conductivity water. The solution was standardized with standard sodium carbonate solution.

20. Sodium carbonate:– 0.1 M solution was prepared by dissolving 1.06 gms of (GR, pro analysis, C. Merck, Germany) anhydrous sodium carbonate in conductivity water and making up to the mark in 100 ml standard flask.

21. Ammonium hydroxide:– 1 M ammonium hydroxide solution was made by suitably diluting liquid ammonia (AnalaR, BDH) with conductivity water. The solution was standardized with standard hydrochloric acid using methyl red as indicator.
22. Ammonium chloride: 3.3725 gms of ammonium chloride (AnalaR, BDH) were dissolved in conductivity water and the solution was made upto 250 ml in a standard flask.

23. Resacet-phononoxime solution: A standard solution of 0.1 N of the reagent solution was prepared by dissolving 1.67 gms of the pure crystalline colourless sample in 50 per cent aqueous alcohol in 100 ml standard flask.

24. Magnesium sulphate: A saturated solution of magnesium sulphate solution was prepared using AnalaR (BDH) sample of the salt in conductivity water.

25. Pyridine: AnalaR BDH pyridine was used.

26. Oxine solution: 2% solution of 8-hydroxyquinoline was prepared by dissolving the required amount of it in conductivity water.

27. Sodium fluoride: 3.36 gms of sodium fluoride (Baker and Adamson) was dissolved in conductivity water and the solution was made upto the mark in a 100 ml standard flask.

28. Nitric acid: 2 N nitric acid was prepared from (An, BDH) nitric acid.

29. Mercury: AnalaR mercury was purified chemically by the procedure described in Vogel and was vacuum distilled.

30. Triscotylamine: Pure triscotylamine (Koch-Light Laboratories, Ltd., England) was used.
31. Potassium dichromate: 0.1 N stock solution of it was prepared by dissolving 0.49 gms of (Anal. Re.) potassium dichromate in conductivity water and making up the solution to 100 ml in a standard flask.

32. Gelatin solution: 0.2% aqueous solution of gelatin was prepared by dissolving 0.2 gms in 100 ml of warm water.

33. Buffer systems are prepared from the following solutions:

<table>
<thead>
<tr>
<th>pH</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0 to 6.0</td>
<td>Sodium acetate (0.2 N) and acetic acid (0.2M).</td>
</tr>
<tr>
<td>8.0 to 9.0</td>
<td>Ammonium chloride (2 N) and ammonium hydroxide (2 N).</td>
</tr>
<tr>
<td>10.0</td>
<td>Sodium hydroxide solution (0.01 M)</td>
</tr>
</tbody>
</table>
REFERENCES


