APPENDIX B

Preparation of reagents

Determination of zinc using Erichrome Black T as indicator

Reagents: EDTA Solution: (0.1 M)

Dissolve 37.23 g of AR grade disodium dihydrogen ethylenediamine tetra acetate dihydrate in water and dilute to 1 litre in a volumetric flask with double distilled or deionised water. Use of metal ion indicator in an EDTA filtration may be written as:

\[ M-In + EDTA \rightarrow M-EDTA + In \]

Reaction will proceed if the metal indicator complex M-In is less stable than the metal EDTA Complex M-EDTA. The former dissociates to a limited extent and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M-In to leave the free indicator.

In the pH range 7-11, Erichrome Black T exhibits – blue colour, many metal ions form red complexes.

Metal ion indicators like EDTA are chelating agents and the dyestuff molecular possesses several ligand atoms suitably disposed for coordination with a metal atom. They can also take up protons which also produces a colour change. Metal ion indicators are also pH indicators.

Erichrome Black T. Indicator

This substance is sodium 1-(1-hydroxy-2-naphthylazo) 5-nitro-2-naphthol-4-sulphonate (I) it is also known as Solochrome Black T or WDFA and is No. 203. A red brown product and consequently the indicator is rarely applied in the EDTA titration of solutions more acidic than pH = 6.5. The sulphonic acid group gives up its proton long before the pH range of 7-12, which is of immediate interest for metal ion indicator use. Below pH=5.5, the solution of Erichrome Black T is red, between 7 and 11 it is
blue and above pH of 11.5, it is yellowish orange. In the pH range 7-11, the addition of metallic salts produces a brilliant change in colour from blue to red. To maintain the pH constant (ca-10), a buffer mixture is added and most of the above metals must be kept in solution with the aid of a weak complexing reagent such as ammonia.

The indicator solution is prepared by dissolving 0.2 g of the dyestuff in 15 ml of triethanolamine with the addition of 5 ml of absolute ethanol to reduce viscosity, the reagent is stable for several months. A 0.4% solution of the pure dyestuff in methanol remains serviceable for at least a month.

**Zinc-ion Solution : (0.1 M) (Standard Solution)**

Dissolve about 1.63 g, accurately weighed of AR zinc shots or pellets in hydrochloric acid nearly neutralize the resulting solution with ca 1 M Sodium hydroxide, and dilute to 250 ml in a volumetric flask with distilled water.

**Buffer Solution : (pH =10)**

Add 142 ml of concentrated ammonia solution (Sp. gr. 0.88-0.90) to 17.5 g of AR grade ammonium chloride, and dilute to 250 ml with distilled water.

**Procedure :**

Dilute 250 ml of the zinc-ion solution to 100 ml with distilled water, add 2.0 ml of buffer solution and a few drops of the indicator. Titrate with the EDTA solution until the colour changes from wine red to blue.

1 ml of 0.1 M EDTA = 6.538 mg Zn

**Polarographic determination of zinc**

Zinc from the solution was determined using ELICO Polarograph model CL-25D as per the protocol supplied by the manufacturer ELICO,
India. The typical representative polarographic analysis for standard and the test samples is presented here as chart.

**Determination of copper as diethyldithiocarbamate complex**

Sodium diethyldithiocarbamate (A) reacts with a slightly acidic or ammonical solution of copper(+2) in a low concentration to produce a brown colloidal suspension of the cupric diethyldithiocarbamate. The suspension may be extracted with an organic solvent (chloroform, carbon tetrachloride or N. butyl acetate) or 435 nm (carbon tetrachloride or chloroform).

Many of the heavy metals give slightly soluble products (some white, some coloured) with the reagents, most of which are soluble in the organic solvents mentioned. The selectivity of the reagent may be improved by use of masking agents, like EDTA.

The reagent decomposes rapidly in solutions of low pH.

**Procedure:**

Dissolve 0.0393 g AR grade cupric sulphate pentahydrate in 1 litre of water in a volumetric flask. Pipette 10.0 ml of this solution (containing about 100 μg Cu) into a beaker, add 5.0 ml of 25% aqueous citric acid solution, render slightly alkaline with dilute ammonia solution and boil off the excess of ammonia, alternatively adjust to pH 8.5 using a pH meter. Add 15.0 ml of 4% EDTA solution and cool to room temperature. Transfer to a separating funnel, add 10 ml of 0.2% aqueous sodium diethyldithiocarbamate solution and shake for 45 seconds. A yellow brown colour develops in the solution. Pipette 20 ml of n-butyl acetate into the funnel and shake for 30 seconds. The organic layer acquires a yellow colour, cool, shake for 15 seconds and allow the phases to separate. Remove the lower aqueous layer, add 20 ml of 5% (v/v) sulphuric acid, shake for 15 seconds, cool and separate the organic phase. Determine the optical density at 560 nm. All the copper is removed in one extraction.
Chart: Polarographic chart for zinc extraction.

Standard: 1000 µg, Span: 150 mV/min, Sensitivity: 0.2 µA/div

Test
Atomic Adsorption Spectrophotometric analysis of metals

Copper and zinc were analyzed by using Atomic absorption Spectrophotometer model Varian AA-175 by standard procedures.

Determination of ferrous iron

Standard ferrous solution:

Weigh out accurately about 14.0 g of ferrous sulphate crystals, dissolve in 450 ml of 5% (v/v) sulphuric acid in a 500 ml volumetric flask and make up to the mark with distilled water. Shake well, titrate 25.0 ml with the standard 0.1 N potassium dichromate using Diphenylamine – as internal indicator.

Standard 0.1 N Potassium dichromate

Weigh accurately 4.9 g of potassium dichromate and transfer the salt quantitatively to a 1 litre measuring flask. Dissolve salt in the flask in water and make up to the mark, shake well.

Calculate exact normality by dividing the actual weight of the potassium dichromate employed by the theoretical weight for 1 litre of normal solution (49.035 g). An exactly 0.1 N solution may be prepared by weighing out 4.904 g of the salt an dissolving in water and diluting to 1 litre in a volumetric flask.

Diphenylamine Indicator: (1%)

Weigh 1.0 g diphenylamine indicator and dissolve in 100 ml of concentrated sulphuric acid.

Procedure:

Use 3 drops of indicator, add 200 ml of 2.5% (v/v) sulphuric acid followed by 5 ml of 85% orthophosphoric acid and titrate slowly, whilst stirring constantly with the standard dichromate until the solution assumes...
a bluish green or greenish blue tint near the end point. Continue the titration, adding the dichromate solution dropwise and maintaining an interval of a few seconds between each drop, until the addition of one drop causes the formation of an intense purple or violet blue colouration, which remains permanent after shaking and is unaffected on the further addition of the dichromate. Carry out two or at the most three titrations, this should agree within 0.1 ml.

Use of phosphoric acid lowers the oxidation potential of the ferric-ferrous system by forming a complex Fe(HPO₄)⁺ with the ferric ions so that the equivalence potentials coincides more nearly with that of the indicator.

The action of diphenylamine as an indicator depends upon its oxidation first into colourless diphenylbenzidine, which is the real indicator and is reversibly further oxidized to diphenylbenzidine violet.

Diphenylbenzidine violet undergoes further oxidation if allowed to stand with excess of dichromate solution, the excess oxidation is irreversible and red or yellow products of unknown composition are produced.

\[
1 \text{ml } 0.1 \text{ N } \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 5.585 \text{ mg } \text{Fe}^{2+}
\]

**Reduction of ferric to ferrous iron**

Iron often occurs in the ferric state or as a mixture of ferrous and ferric iron in ores and other materials. For the volumetric determination of iron, the ferric iron must be first quantitatively reduced to the ferrous state. The following method was applied in our studies.

**Reduction with stannous chloride solution**

Many iron ores are brought into solution with concentrated hydrochloric acid. In such case, the reducing agent frequently employed is stannous chloride:

\[
2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}
\]
5-6 N hydrochloric acid is used to dissolve the iron, which is reduced by adding concentrated stannous chloride solution dropwise from a burette, with stirring until the yellow colour of the solution is nearly disappeared. The reduction is then completed by diluting the concentrated solution of stannous chloride with 2 volumes of dilute hydrochloric acid and until the liquid has a faint green colour, quite free from any tinge of yellow. The solution is then rapidly cooled under the tap to about 20° C, with protection from the air, and the slight excess of stannous chloride present removed by adding 10 ml of a saturated solution (ca 5%) of mercuric chloride rapidly in one portion and with thorough mixing.

A slight milky white precipitate of mercurous chloride should be obtained:

\[ 2\text{HgCl}_2 + \text{Sn}^{2+} \rightarrow \text{Hg}_2\text{Cl}_2 + \text{Sn}^{4+} + 2\text{Cl}^- \]

The oxidizing agent has no appreciable effect upon the small amount of mercurous chloride in suspension. If a heavy precipitate forms or a grey or black precipitate is obtained, too much stannous chloride has been used, the results are inaccurate and the reduction must be repeated.

After addition of the mercuric chloride solution, the whole is allowed to stand for 5 minutes and volume made with water which is then titrated using 0.1 N potassium dichromate.

**Stannous chloride (Tin Chloride) solution**

The concentrated solution of stannous chloride is prepared by dissolving 12 g of pure tin or 30 g of AR grade crystallized stannous chloride (SnCl₂·2H₂O) in 100 ml concentrated hydrochloric acid and diluting to 200 ml with water.

**Digestion of ore**

Weight out accurately 0.5-1.0 g of the finely powdered (-325 #) ore sample into a 250 ml beaker, add 10-15 ml of concentrated nitric acid, and
heat until the ore is well disintegrated and all the metals come in the solution. Evaporate to a volume of 5 ml (e.g. on an electric hot plate). Add 10 ml of concentrated hydrochloric acid and 10 ml of 1:1 sulphuric acid and evaporate to dense white fumes. Filter off the residues using Whatman filter paper-No. 42 and with the filtrate collected make final volume of 250 ml using distilled water in a volumetric flask. Cool it.

From the filtrate remove sample and to this solution add ammonia solution to precipitate all the iron, this mixture is then filtered and from the filtrate, copper and zinc are analyzed.

**Determination of Lead**

Samples were digested as mentioned above. The solution was cooled and filtered, leach residues were washed with 10% sulphuric acid and then by distilled water. Along with filter paper residues were transferred to 250 ml beaker. 10-20 ml 25% CH₃COONH₄ (ammonium acetate) and about 100 ml of distilled water was added. System was heated and titrated against standard ammonium molybdate using freshly prepared tannic acid as an external indicator to a faint yellow colour of the indicator drop.

\[
7\text{Pb(CH}_3\text{COO)}^2 + (\text{NH}_4)_6\text{Mo}_7\text{O}_{24}^4 + 4 \text{H}_2\text{O} \rightarrow 7\text{PbMoO}_4 + 6 \text{NH}_4\text{(CH}_3\text{COO)} + 8\text{CH}_3\text{COOH}
\]

**Reagents**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>CH₃COONH₄ (ammonium acetate)</td>
<td>25%</td>
</tr>
<tr>
<td>(NH₄)₆Mo₇O₂₄ (ammonium molybdate)</td>
<td>1 ml = 5 mg Pb (4.261 g.l⁻¹)</td>
</tr>
<tr>
<td>(CH₃COO)₂Pb</td>
<td>1 ml = 5 mg Pb (4.575 g.l⁻¹)</td>
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<tr>
<td>Tannic acid</td>
<td>0.5% in distilled water (prepare fresh).</td>
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