Estimation of Fe₂O₃ in Haematite Ore of Hospet by Iodo-Potentiometric Technique

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A successful attempt is made to estimate ferric oxide (Fe_2O_3) in haematite, an iron ore obtained from Hospet mining area (Karnataka) by iodo-potentiometric method. Both iodometric and potentiometric investigations are carried out in a single two-in-one cell to obtain the data related for the estimation of Fe_2O_3 in haematite ore. A quantitative relationship is observed between the potentials, E_M and the volumes of standard sodium thiosulphate consumed (at the end point) in potentiometric and volumetric titrations. These potentials, E_M, are again found to have a linear relationship with the weight of the ore sample taken. The titre volumes (v_1 and v_2 mL) of both potentiometric and iodometric methods are identical. Interestingly, the estimation of Fe_2O_3 in haematite ore is possible in the light of the above relationships observed. An excellent conformity of results are observed for potentiometric, iodometric and volumetric (Sn reduction method) titration data for the estimation of the percentage of Fe_2O_3 in haematite ore.

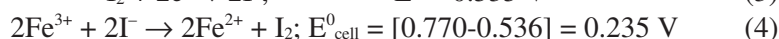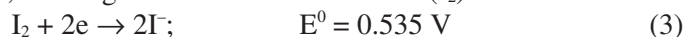**Key Words: Estimate, Haematite, Mining, Iodometric, Potentiometric, Quantitative, Ferric oxide.**

INTRODUCTION

The molar potential (E^0) of the reaction $2I^- \rightarrow I_2 + 2e$ is -0.535 volts and therefore, it would appear that iodine might be used as an oxidizing agent for considerable number of compounds which are positive to it in the table of standard reduction potentials. Similarly, iodide (I^-) ion might be used for reducing a considerable number of compounds which are negative to it in that series. Iodide ion is, therefore, a strong reducing agent ($E^0 = 0.535$ volts) that many agents can react completely with the iodide ion resulting in many useful iodometric processes. The usual procedure involves the addition of excess of a soluble iodide to the oxidizing agent to be determined, whereby an equivalent amount of iodine is set free. This is then titrated with a standard sodium thiosulphate. The iodine-thiosulphate reaction is quite fast and the equilibrium is far to the product side. This reaction may be represented as:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + 2S_4O_6^{2-}; \quad E^0 = 0.09 \text{ V} \tag{1}$$

The feasibility of analyte redox reaction in potentiometry is dependent on the standard reduction potentials value of iron ($E^0 = 0.77$ V) and the iodide (0.535 V). The reduction reaction of Fe^{3+} in the presence of I^- can occur, possibly, as:

$$Fe^{3+} + e \rightarrow Fe^{2+}; \qquad E^0 = 0.771 \text{ V} \qquad (2)$$
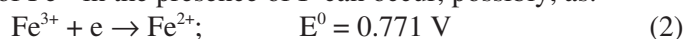
And simultaneously, iodide gets oxidized to free iodine (I_2).

$$I_2 + 2e \rightarrow 2I^-; \qquad E^0 = 0.535 \text{ V} \qquad (3)$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2; E^0_{cell} = [0.770\text{-}0.536] = 0.235 \text{ V} \qquad (4)$$

By virtue of the difference of potential values of reaction, the reaction occurs spontaneously between the analyte (Fe^{3+}) and iodide ions and the redox reaction is feasible, rapid and quantitative in acid medium.

Potentiometry is one of the most frequently used analytic technique for chemical analysis because of its flexibility and versatility. It is, therefore, evident that the above redox reaction can be conveniently considered for the estimation of iron by potentiometric method. When requisite amount of KI solution is added to a solution containing Fe^{3+} ions, it oxidizes iodide (I^-) ions and thus, I_2 is liberated. The basic principle of the above redox reaction between Fe^{3+} and I^- can be used to determine quantitatively the amount of ferric oxide (Fe_2O_3) present in haematite ore in acidic (pH = 1.0) solution.

In the present investigation, we have adopted iodo-potentiometric, a two-in-one method; wherein, the analyte potential (E_M) is noted when all the quantitative I_2 is set free after the redox reaction. The liberated iodine is, then, titrated against standard sodium thiosulphate solution observing the changes of potentials during the titration process, simultaneously, using fresh starch as an indicator. The process of measurement of potentials are repeated for different concentrations of analyte solutions at pH = 1.0.

The redox reaction taking place between iodine and thiosulphate is:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
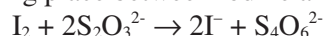
The amount of iodine liberated in the reaction between iodide (I^-) and an oxidizing agent (eqn. 4) is a measure of the quantity of oxidizing agent (Fe^{3+}) present in the analyte solution. The amount of standard sodium thiosulphate required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent (Fe^{3+}) as shown in eqn. 4. If the redox reaction between Fe^{3+} and I^- is stoichiometrically feasible and fast in acid medium, then, the measured potentials (E_M) changes linearly with different molar concentrations of Fe^{3+} solutions at pH = 1.0 and again, it can be expected that, potentials (E_M) to change linearly with volume of standard sodium thiosulphate consumed (v_1 and v_2 mL) of potentiometric and iodometric titrations for different molar concentrations iron, which is obtained from haematite ore.

EXPERIMENTAL

Preparation of different iron solutions from haematite ore: The process of the dissolution haematite ore sample (obtained from Hospet, Karnataka) is made by

adding 20-25 mL of concentrated HCl acid into a weighed sample (Table-1) of the ore in a 250 mL beaker and heated for 15 min. After cooling, 50 mL of dil. HCl is added and boiled for 40 min. Cooled and filtered off to remove the undissolved materials of the ore. The filterate containing ferric iron is collected and transferred to 250 mL volumetric flask and made up to the mark by adding distilled water.

TABLE-1
DIFFERENT SAMPLES OF ORE

Sample No	Weight of haematite taken (g)
1	1.0043
2	0.9097
3	0.7326
4	0.6306
5	0.5286
6	0.4604
7	0.3068

Preparation of standard sodium thiosulphate solution: 57.825 g of $Na_2S_2O_3$ crystals are weighed and transferred to 1 L standard flask and dissolved with distilled water and made up to the mark, shaken thoroughly and used for titration. The molarity of the $Na_2S_2O_3$ solution used for the investigation is 0.233.

Preparation of standard $K_2Cr_2O_7$ solution: 2.455 g of $K_2Cr_2O_7$ crystals are weighed and transferred to a 500 mL volumetric flask. The sample crystals are dissolved in distilled water and made up to the mark, shaken for homogeneity. The strength of the $K_2Cr_2O_7$ solution is 0.0900 N.

Electrochemical cell set up iodo-potentiometric studies: Owing to its simplicity and versatility, potentiometric technique is used frequently as a tool for quantitative analysis in analytical chemistry. It is an electrochemical technique which measure or monitor electrode potential utilizing electro chemical concept. In redox potentio-*metry, potential of an indicator electrode in equilibrium with redox ions to be determined is measured. Such redox titrations involve the transfer of electrons from the substance being oxidized to the substance being reduced.

Oxidized form + n electrons → reduced form

For such reactions, the potential (E) acquired by the indicator electrode at 25 ºC is given as:

$$E = E^0 + \frac{0.0591}{n} \log_{10} \frac{[Ox]}{[Red]}$$

The potential is controlled by the ratio of these concentration terms. It is possible to titrate two substances by the same titrant provided the standard potentials of the substances being titrated and their oxidation or reduction products, differ by about 0.2 volts.

The electrochemical set up desired for the investigation is:

Hg/Hg$_2$Cl$_2$/KCl(satd)   //   Analyte solution/Pt

(reference electrode)   (indicator electrode)
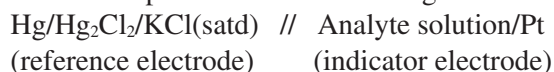
The emf of the cell, E$_{cell}$ = [E$_{Indi}$ - E$_{ref}$]

= E$_{Indi}$ - 0.2422

Therefore, E$_{Indi}$ = E$_{cell}$ + 0.2422

where, E$_{ref}$ is a saturated calomel electrode of constant potential, 0.2422 volts.

Procedures

Iodo-potentiometric titration: The iodo-potentiometric titration is carried out in a cell as shown in the Fig. 1.
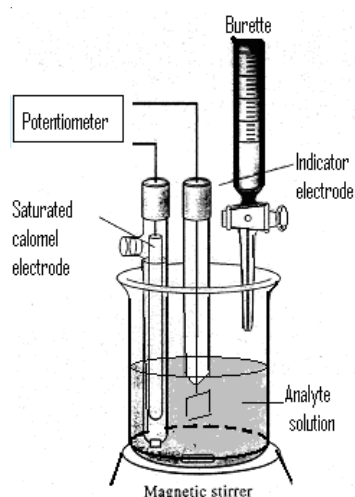

Fig. 1. A two in one cell set up for iodo-potentiometric titrations

25 mL of The prepared ferric chloride solution is pipette out into the glass cell. pH = 1 is maintained by adding requisite quantity of 1:1 HCl acid. 6 mL of 10 % KI solution is added. After I$_2$ is liberated in a cell, the equilibrium potential (E$_M$) is noted. Potential variations are noted for each addition (an increment of 0.2 mL) of standard sodium thiosulphate. A magnetic stirrer is used continuously to swirl the solution during titration. When the colour of the solution in the cell is straw yellow, 1-2 mL of freshly prepared starch is added. The colour changes to blue due to starch iodine complex. Standard sodium thiosulphate is added from the burette drop by drop till the blue colour disappears permanently. This is the end point of both volumetric and potentiometric titrations of this redox reaction. The volume of standard thiosulphate consumed and the potential at the end point (E$_{EP}$) are recorded. The end point volumes (v$_1$) of standard sodium thiosulphate consumed for potentiometric titrations are obtained from differential plots (Fig. 2). The potentiometric titrations of different molar concentrations of iron solutions are shown in the Fig. 2 and the potentials E$_M$ (mV) are given in Table-2.
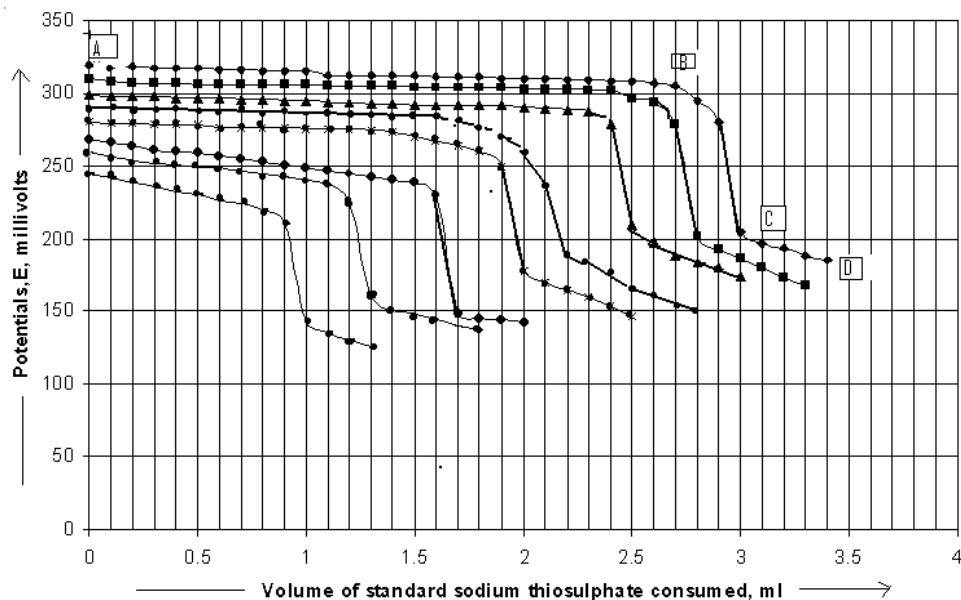
Fig. 2. Iodo-potentiometric titration curves for iron solution of haematite ore

Iodometric titration: 25 mL of prepared ferric chloride solution is pipette out into the glass beaker cell. pH of the solution is maintained at 1.0 by adding requisite quantity of 1:1 HCl acid. 6 mL of 10 % KI solution is added. The liberated I$_2$ is titrated against standard sodium thiosulphate solution till the solution turns straw yellow and then, 1-2 mL of freshly prepared starch solution is added. Titration is continued till the disappearance of blue colour of the starch-iodine complex. Volume of sodium thiosulphate consumed (v$_2$, mL) at the end point is noted. Investigations are repeated for different molar concentrations of feric chloride obtained from ore and the data are tabulated in Table-3.

TABLE-2
POTENTIOMETRIC TITRATION DATA OF Fe$_2$O$_3$ IN HAEMATITE

Weight of Haematite taken (g)/250 mL	Potentials (E$_M$) (mV)	Potentiometric titration volume of Na$_2$S$_2$O$_3$ (V$_1$ mL)	Estimated weight of Fe$_2$O$_3$ from potentiometric titration (g)/250 mL	Percentage of Fe$_2$O$_3$ in Haematite
1.0043	320	3.0	0.5732	57.01
0.9097	310	2.8	0.5350	58.81
0.8000 (calcd.)	**299***	**2.5***	**0.4776***	**59.19***
0.7326	291	2.2	0.4203	57.40
0.6306	280	2.0	0.3821	60.59
0.5286	268	1.7	0.3248	61.44
0.4604	260	1.4	0.2675	58.10
0.3068	245	1.0	0.1910	62.27

*E$_M$ of unknown solution.   Average: **59.35** %.

Estimation of iron by stannous chloride reduction method: 25 mL of Ferric chloride solution obtained from the same ore is pipette out into a conical flask. 15 mL of dilute HCl is added. The solution is boiled for *ca.* 5-10 min. It is reduced with drop by drop addition of $SnCl_2$ solution in hot condition till colourless. An excess of 1-2 drops of $SnCl_2$ is added. 2 mL of mercuric chloride is added to get a silky white precipitate. Few drops of ferroin indicator is added. It is then, titrated with standard $K_2Cr_2O_7$ solution with continuous swirling. At the end point, the colour of the solution changed to brownish red colour. Volumes of standard $K_2Cr_2O_7$ solution consumed, (v_3 mL), are noted for different molar concentration iron solutions and are given in Table-4.

TABLE-3
VOLUMETRIC TITRATION DATA OF Fe_2O_3 IN HAEMATITE

| Weight of haematite taken, g/250 mL	Volumetric titration, volume of $Na_2S_2O_3$ (v_2 mL)	Estimated weight of Fe_2O_3 from potentiometric titration, (g)/250 mL	Percentage of Fe_2O_3 in haematite
1.0043	3.1	0.5923	58.98
0.9097	2.8	0.5350	58.81
0.8000*(Table-1)	**2.5***	**0.4776***	**59.19***
0.7326	2.3	0.4203	57.40
0.6306	1.9	0.3631	57.57
0.5286	1.6	0.3057	57.83
0.4604	1.4	0.2675	58.10
0.3068	1.0	0.1910	62.27

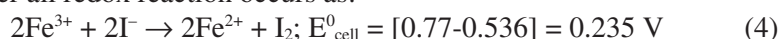*E_M (Unknown)   Average: **58.77** %.

RESULTS AND DISCUSSION

Generally, iron in iron salts and ore samples are estimated by well known conventional volumetric and spectrophotometric methods[1-9]. However, Palanna *et al.*[10-12] have reported a successful technique for the estimated copper and cerium in their salt solutions. Here, we are reporting the investigation of iron in haematite ore sample by considering the basic principles of iodometry using a iodo-potentiometric technique in which quantitative information's of both volumetric and potentiometric data are obtained. The method is comparable to any other conventional methods of estimation of iron.

The feasibility of redox reaction between iron in Fe^{3+} state and iodide (I^-) can be assessed from (eqns. 2 and 3) as follows:

$$2Fe^{3+} + 2e \rightarrow 2Fe^{2+}; E^0 = 0.771 \text{ V}$$
$$I_2 + 2e \rightarrow 2I^- ; E^0 = 0.535 \text{ V}$$
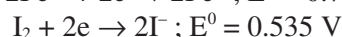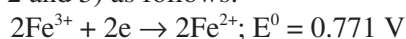
And the over all redox reaction occurs as:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2; E^0_{cell} = [0.77-0.536] = 0.235 \text{ V} \qquad (4)$$

at standard conditions.

For non-standard conditions, it is described as:

$$E_M = E^0_{cell} - \frac{0.0591}{2} \log 10 \frac{[Fe^{2+}]^2[I_2]}{[Fe^{3+}][I^-]^2} \tag{5}$$

The E$^0_{cell}$ is positive (0.235 V) and hence, as expected the redox reaction is rapid and spontaneous and proceeds more towards the right side.

The equilibrium constant, K, for the above (eqn. 4) reaction can be calculated from the relation, nF (E^0) = RT ln K.

Therefore,

$$K = \exp\frac{nF(E^0)}{RT};$$

$$K = \exp\frac{2 \times 96485 \times 0.235}{8.3145 \times 298.15}$$

$$K = 9.3 \times 10^3$$

which is equivalent to $\dfrac{[Fe^{2+}]^2[I_2]}{[Fe^{3+}]^2[I^-]^2}$

The equilibrium constant, K = 9.3 ×10^3 is fairly high and hence the reaction is feasible for iodo-potentiometric method.

The potentiometric and volumetric titrations are based on the reaction between sodium thiosulphate and iodine; and the potential changes during titration process is due to the following reactions.

$$I_2 + 2e \rightarrow 2I^-; \qquad\qquad E^0 = 0.535 \text{ V} \tag{6}$$

$$S_4O_6^{2-} + 2e \rightarrow 2S_2O_3^{2-}; \qquad E^0 = 0.090 \text{ V} \tag{7}$$

The overall redox reaction is:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}; \qquad E^0 = 0.45 \text{ V} \tag{8}$$

The potentiometric titration data obtained from the investigation of iron in haematite ore are given in Table-2.

After the completion of the redox reaction (eqn. 4), the potentials (E$_M$) for different iron solutions are recorded in column (2) of Table-2 and the their corresponding end points (v$_1$ mL) of potentiometric titration are noted in column (3). Fig. 2 indicates iodo-potentiometric titrations curves against standard Na$_2$S$_2$O$_3$ solution for different iron solutions (Table-1) obtained from the haematite ore.

The volumes (v$_1$ mL) of standard sodium thiosulphate consumed for different titrations for the different weights of ore samples are in column (3) and the corresponding titration curves are shown in Fig. 3. In Fig. 2, point marked 'A' indicates the potential, E$_M$ of the solution after completion of redox reaction of eqn. 4, while 'AB' shows the potential changes after the addition of each increment of sodium thiosulphate to the analyte solution. The sharp decrease of potential from B to C indicates the end point of titration ;and thereafter, the potential variation (C to D) may be ascribed due to the addition of excess thiosulphate into the analyte solution.
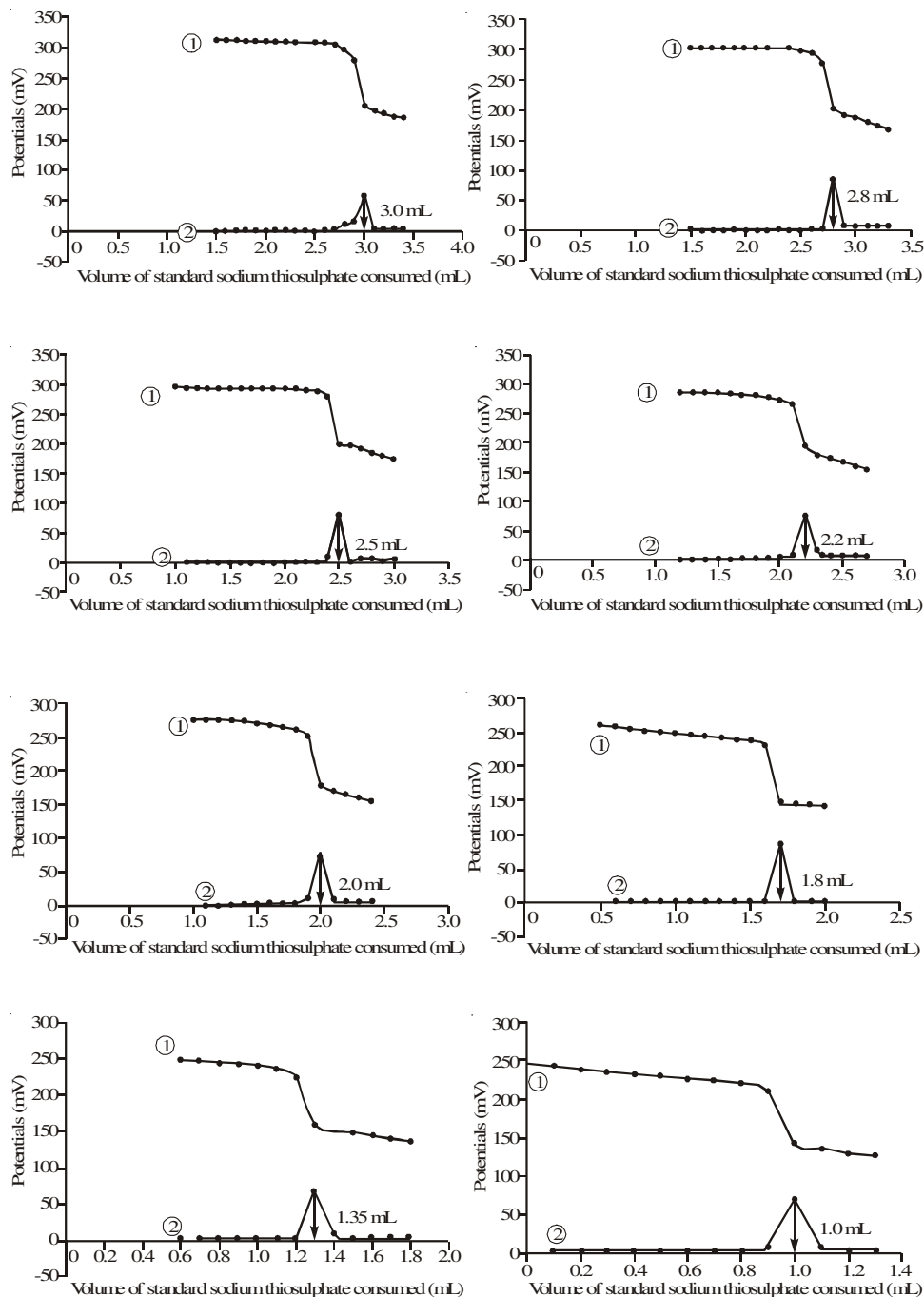
Fig. 3.   Potentiometric titrations (1) E *vs.* volume of sodium thiosulphate, mL
          (2) differential plots, $(\partial^2 E/\partial^2 V)$ *vs.* volume of sodium thiosulphate, mL

The end points of potentiometric titration can also be obtained from the differential plots (∂^2E/∂^2V) as shown in the Fig. 3 (2). The percentage of Fe_2O_3 in haematite obtained from the potentiometric titration is presented in Table-2, column (5). The average percentage of Fe_2O_3 in haematite is found to be 59.35.

The volumetric titrations (iodometric) data are given in Table-3 and the end points of titrations are presented in column (2) for different weights of the haematite ore taken.

The volume of standard sodium thiosulphate consumed at the end points of volumetric (iodometric) titrations are tabulated in column (2) of Table-3. The weight of ferric oxide in haematite estimated by volumetric method is given in column (3) and the assessment of their percentage in the ore samples are indicated in column (4). By volumetric method, the average percentage of Fe_2O_3 in haematite is 58.77 %. In addition, we have investigated the percentage of Fe_2O_3 in haematite by $SnCl_2$ reduction method as shown in Table-4.

TABLE-4
DATA OF Fe_2O_3 IN HAEMATITE BY $SnCl_2$ REDUCTION METHOD

Weight of haematite taken, g/250 mL	Volumetric titration, volume of $K_2Cr_2O_7$ (v_3 mL)	Estimated weight of Fe_2O_3 from $SnCl_2$ reduction method, (g)/250 mL	Percentage of Fe_2O_3 in haematite
1.0043	4.0	0.5839	58.14
0.9097	3.6	0.5255	57.76
0.8000*(Table-1)	**3.2***	**0.4671***	**57.88***
0.7326	2.9	0.4233	57.78
0.6306	2.6	0.3795	58.32
0.5286	2.2	0.3212	60.75
0.4604	1.9	0.2774	60.24
0.3068	1.2	0.1752	57.09

*E_M (UnKnown)   Average: **58.50** %.

The data of the estimation of Fe_2O_3 in haematite ore by stannous chloride reduction method (volumetric) is given in column (2) of Table-4 and their corresponding estimated weights of Fe_2O_3 in haematite is presented in column (3). The percentage of Fe_2O_3 in haematite ore is shown in column (4). The average percentage of Fe_2O_3 in haematite is observed to be 58.50 %.

In the present paper, it can be clearly shown that the potentials (E_M) for different iron solutions (Table-1) are related linearly to the titre values (v_1 or v_2) of potentio-metric/volumetric methods (Tables 2 and 3). Interestingly, one of the notable findings of investigation is that these potentials (E_M) bear a linear relationship with volume of $Na_2S_2O_3$ (v_1 or v_2 mL) consumed, as well with weight of haematite ore as shown in Figs. [4(a) and 4(b)].
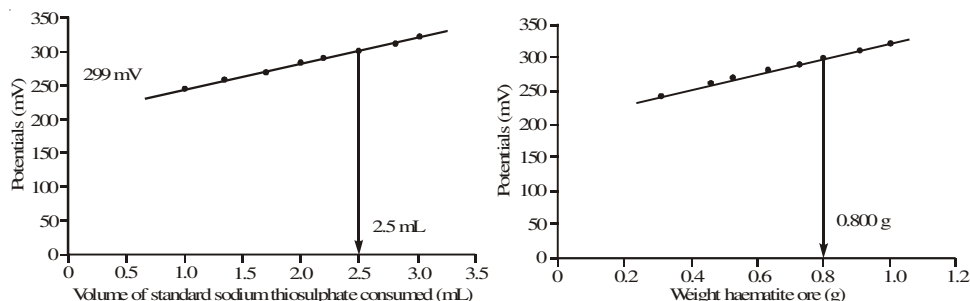
Fig. 4.   Determination of amount of Fe_2O_3 in haematite - (a) Potentials (E_M) *vs.* volume of
$Na_2S_2O_3$ (v_1 or v_2 mL), (b) potentials (E_M) *vs.* weight of haematite ore taken

If the potential E_M of unknown iron solution of haematite is measured (*e.g.*, 299 mV), then the corresponding standard sodium thiosulphate volume required for the end point can be noted from linear plot (Fig. 4(a)), that is., 2.5 mL. On calculation, this amounts to 0.4776 g/250 mL of Fe_2O_3 in haematite. The second Fig. 4(b) accounts for the weight of haematite (0.8000 g/250 mL) for 299 mV (unknown). With these results of analysis, one can find out the percentage (59.19 %) of Fe_2O_3 in Haematite. This two-in-one iodo-potentiometric method conforms the results of both potentiometric as well as the volumetric (iodometric) methods. The comparative statement of the results of analysis for Fe_2O_3 in haematite obtained from the three methods are tabulated in Table-5.

TABLE-5
COMPARATIVE STATEMENT OF DATA ANALYSIS OF Fe_2O_3 IN
HAEMATITE BY DIFFERENT METHODS OF ANALYSIS

Weight of haematite taken, (g)/250 mL	Percentage of Fe_2O_3 in haematite (Table-2)	Percentage of Fe_2O_3 in haematite (Table-3)	Percentage of Fe_2O_3 in haematite (Table-4)
1.0043	57.01	58.98	58.14
0.9097	58.81	58.81	57.76
0.8070	59.19	59.19	57.88
0.7326	57.40	57.40	57.78
0.6306	60.59	57.57	58.32
0.5286	61.44	57.83	60.75
0.4604	58.10	58.10	60.24
0.3068	62.27	62.27	57.09

The data of the results of investigation of Fe_2O_3 in haematite are in agreement with each other highlighting the importance of this novel iodo-potentiometric technique as one of the methods of quantitative chemical analysis.

ACKNOWLEDGEMENTS

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