Quantitative estimation of $K_2Cr_2O_7$ salt using iodo-potentiometric technique of analysis

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ABSTRACT

In the present paper, quantitative estimation of an analyte solution of potassium dichromate is carried out using iodo-potentiometric technique, a method in which both potentiometric and iodometric titration results are obtained simultaneously in a two -in - one potentiometric cell. The basic principle involved is the reduction of Cr^{6+} (oxidizing cation) of $K_2Cr_2O_7$ to Cr^{3+} state by I^- (reducing agent). The free I_2 liberated is titrated with standard sodium thiosulphate using iodo-potentiometric technique; and the end points of both and volumetric (iodometric) titrations are obtained in a two-in-one cell set up. Interestingly, 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, measured are again found to have a linear relationship with the concentrations (N) of the $K_2Cr_2O_7$ samples taken. The titre volumes standard sodium thiosulphate (v_1 and v_2,ml) of both potentiometric and iodometric methods are identical. In the light of the above relationships observed, quantitative the estimation of $K_2Cr_2O_7$ is possible by considering the redox chemistry of Chromium(Cr^{6+}) and I^- in terms of their standard reduction potentials. An excellent conformity of results are observed for potentiometric, iodometric and volumetric (oxidometry) titration data for the estimation of $K_2Cr_2O_7$ analyte.

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INTRODUCTION

Aqueous salt solutions containing cations of higher oxidation state, like Ce^{4+}, Cr^{6+}, Fe^{3+}, and others are being reduced to lower oxidation state by iodide (I^-) ions quantitatively in acidic medium; and the redox reactions that takes place are spontaneous and raid. Such reactions are feasible because the reduction potentials (1.44V, 1.33V and 0.771V respectively) of these cations (oxidizing agents) are higher than the I^- (reducing agent) ion. Numerous reliable procedures have been used for redox volumetric titrations[1-4] for quantitative chemical analysis. Among these, iodometry is one of the easiest, most rapid and accurate methods for the determination of a relatively small amount of oxidizing agent. The molar reduction potential (E^0) of the reaction $I_2 + 2e \rightarrow 2I^-$ is 0.535volts, and therefore, it would appear that iodide, (I^-) might be used for reducing a considerable a number of compounds which are positive to it in potential series. Iodide (I^-) ion is, therefore,

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reducing agent that many oxidizing agents can react completely with the iodide ion resulting in many useful iodometric processes.

The usual procedure[1] 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 redox reaction taking place between iodine and thiosulphate is the basis principle of all iodometric processes.

The iodine –thiosulphate reaction is quite fast and the equilibrium is far to the product side. This reaction may be represented as

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + 2S_4O_6^{2-} ; E^0 = 0.09V \tag{1}$$
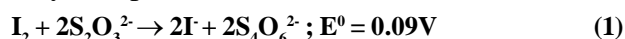
The amount of iodine liberated in the reaction between iodide(I^-) and an oxidizing agent (equation 2) is a measure of the quantity of oxidizing agent (Cr^{6+}) present in the analyte solution.

$$Cr_2O_7^{2-} + 6I^- \rightarrow 2Cr^{3+} + 3I_2 ; E^0 = 1.33V \tag{2}$$
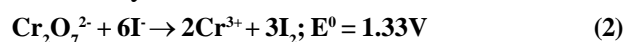
The amount of standard sodium thiosulphate required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent (Cr^{6+}) as shown in equation (2).

In the present investigation, we have used iodo-potentiometric, a two- in- one method ;wherein, the analyte potential (E_M) is noted when all the 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, using fresh starch as an indicator. The process of measurement of potentials are repeated for different concentrations of analyte solutions at pH =1.0. If the redox reaction between Cr^{6+} and I^- is stoichiometrically feasible and fast in acid medium, then, the measured potentials (E_M) for equation (2) may change linearly with different concentrations of Cr^{6+} solutions at pH =1.0; and again, it may be expected that, potentials (E_M) to change linearly with volume of standard sodium thiosulphate (V_1 and V_2 ml) obtained from potentiometric and iodometric titrations for different molar concentrations cerium.

EXPERIMENTAL

Preparation of different $K_2Cr_2O_7$ sample solutions

$K_2Cr_2O_7$ [Fischer scientific, Qualigen fine chemicals, assay: 99.5%, Mol Weight:294.185] of different concentrations are taken for iodo-potentiometric investigations.. In the present investigation, the following concentrations $K_2Cr_2O_7$ [TABLE 1] are prepared for the quantitative estimation of $K_2Cr_2O_7$ (Cr^{6+} state) and its percentage in each sample solution.

Requisite quantities of $K_2Cr_2O_7$ crystals are weighed accurately and transferred into different 250ml volumetric flasks. It is dissolved in requisite amount of distilled water and the clear solution is made up to 250ml mark.

TABLE 1 : Weight of $K_2Cr_2O_7$ sample

S.No	Weight of $K_2Cr_2O_7$ sample
1	1.0133
2	0.9695
3	0.8353
4	0.7457
5	0.6240
6	0.5186
7	0.4396
8	0.3309
9	0.2570
10	0.1100

Preparation of standard sodium thiosulphate solution

7.6749g of $Na_2S_2O_3$ crystals weighed and transferred to 1litre standard flask and dissolved with distilled water and made up to the mark, shaken thoroughly and used for titration. The Normaility of the $Na_2S_2O_3$ solution used for the investigation is 0.1237.

Preparation of standard ferrous ammonium sulphate

9.7913g of analar ferrous ammonium sulphate (FAS) crystals are transferred to 250ml standard flask. 10-15 ml of dilute sulphuric acid is introduced into it to keep acidic to avoid hydrolysis of the sample. The solution is made up to 250 ml and shaken for uniform concentration. The molarity of the prepared sample is 0.09986.

Electrochemical cell set up iodo-potentiometric studies

Potentiometry is an important electrochemical technique used for quantitative chemical analysis in analytical chemistry. In redox potentiometry, potential of an

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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 25^0C is given by

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

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 0.2volts.

The electrochemical set up desired for the investigation is

$Hg/Hg_2Cl_2/KCl(Satd)//Redox$ 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, 0.2422volts.

Procedures

Iodo-potentiometric titration

The potentiometric titration is carried out in a cell as shown in the Figure 1.

(i) 25 ml of $K_2Cr_2O_7$ solution is pipette out into the glass cell. Requisite quantity of dilute sulphuric acid is added to maintain pH =1.0. 6ml of 10% KI solution is added. After I_2 is liberated in a cell, the equilibrium potential (E_M) of the solution 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 color of the solution in the cell is straw yellow, 1 ml of freshly prepared starch is added. The color changes to blue due to starch iodine complex. 2 ml of NH_4CNS is also added to release the iodine that is bound to the starch –iodine complex. At this stage, standard sodium thiosulphate is added from the burette drop by drop till the blue color disappears permanently. This is the end point of both volumetric and potentiometric ti-
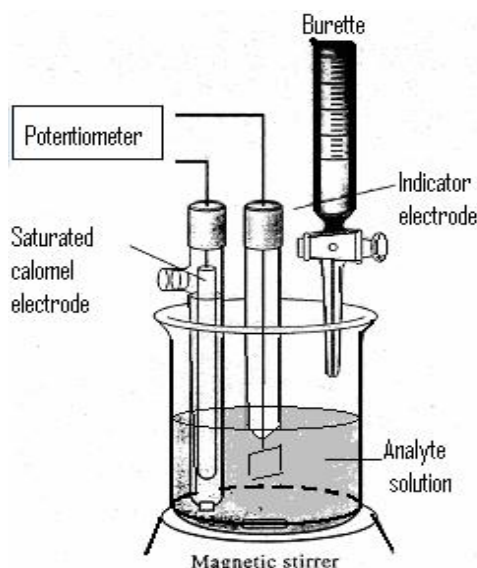

Figure 1 : A two in one cell set up for iodo- potentiometric titrations.

trations of this redox reaction. The volume of standard thiosulphate consumed (V_1ml) and the potential at the end point (E_{EP}) are recorded. The potentiometric titration of different molar concentrations of $K_2Cr_2O_7$ are shown in Figure 2 and potentials E_M (millivolts) are given in TABLE 2.

Iodometric titration

25 ml of $K_2Cr_2O_7$ solution is pipette out into the glass cell. The pH of the solution is maintained at 1.0 by adding requisite quantity of dilute sulphuric acid . 6ml of 10% KI solution is added. The liberated I_2 is titrated against standard sodium thiosulphate solution till the solution turns straw yellow. 2-3ml of NH_4CNS is added and then, 1-2 ml of freshly prepared starch is added. Titration is continued till the disappearance of blue color of the starch –iodine complex. Volume of sodium thiosulphate consumed (V_2, ml) at the end point is recorded. Investigations are repeated for different concentrations of $K_2Cr_2O_7$ and the data is tabulated in TABLE 3.

Volumetric titration

25 ml of $K_2Cr_2O_7$ solution is pipette out into a conical flask. 15ml of dilute H_2SO_4 is added. 2-3 drops of Ferrion indicator is added. Titrated with standard Ferrous ammonium sulphate ¯brownish red color. Volume of standard FAS consumed, (V_3 ml), are noted for different concentration $K_2Cr_2O_7$ solutions and are given in TABLE 4.
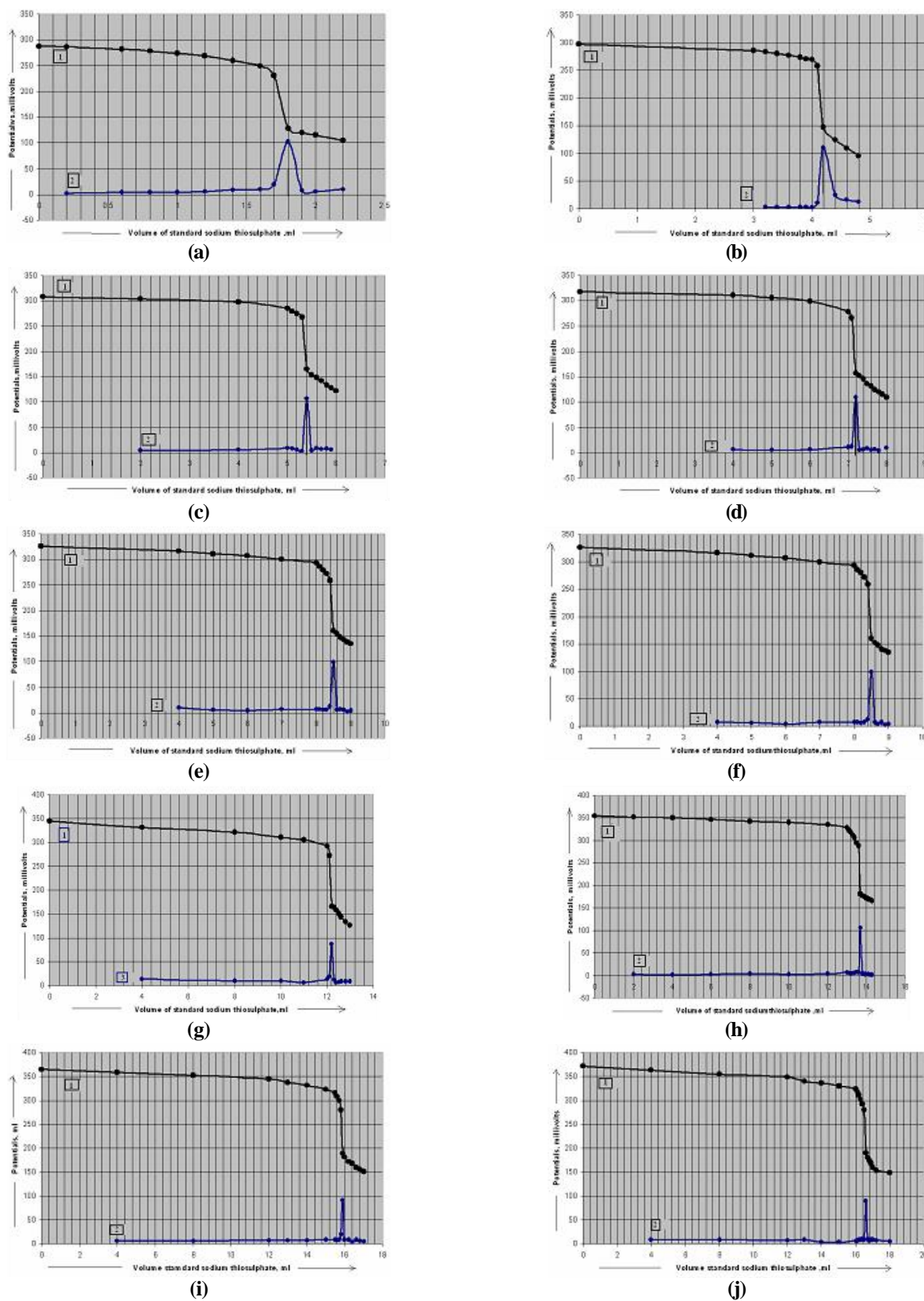
Figure 2 : Potentiometric titrations of K$_2$Cr$_2$O$_7$ solution of concentration (1) (a) 0.08213N (b) 0.07818N (c) 0.06779N (d) 0.06036 (e) 0.05047N (f) 0.04206 N (g) 0.03562N (h) 0.267220. (i) 0.02079N (j) 0.00890N (2) Differential plots of the titrations.

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TABLE 2 : Data of the results of potentiometric titrations

Sl. No	Weight of $K_2Cr_2O_7$ g/250ml	Potentials E_M Millivolts	Volume of 0.1237N sodium thiosulphate consumed from differential plot Figure 1, ml	Estimated normality of $K_2Cr_2O_7$ solution N	Estimated weight of $K_2Cr_2O_7$ /250 ml by potentiometric Analysis	Estimated percentage of Potassium dichromate %
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	1.0133	368	16.6	0.08213	1.0063	99.31
2	0.9695	364	15.8	0.07818	0.9580	98.80
3	0.8353	355	13.7	0.06779	0.8306	99.43
4	0.7457	345	12.2	0.06036	0.7395	99.17
5	0.6240	336	10.2	0.05047	0.6184	99.10
6	0.5186	326	8.5	0.04206	0.5153	99.37
7	0.4396	318	7.2	0.03562	0.4365	99.30
8	0.3309	308	5.4	0.26722	0.3274	98.94
9	0.2570	302	4.2	0.02079	0.2546	99.08
10	0.1100	288	1.8	0.00890	0.1091	99.02

Average = 99.17%

TABLE 3 : Data of the results of iodometric titrations of $K_2Cr_2O_7$

Sl. No	Weight of $K_2Cr_2O_7$ g/250ml	Volume of 0.1237N sodium thiosulphate consumed from iodometric Ml	Estimated normality of $K_2Cr_2O_7$ solution N	Estimated weight of $K_2Cr_2O_7$ /250 ml By volumetric Analysis	Estimated percentage of Potassium dichromate %
(1)	(2)	(3)	(4)	(5)	(6)
1	1.0133	16.6	0.08213	1.0063	99.31
2	0.9695	15.9	0.07867	0.9640	99.42
3	0.8353	13.7	0.06779	0.8306	99.43
4	0.7457	12.2	0.06036	0.7395	99.17
5	0.6240	10.2	0.05047	0.6184	99.10
6	0.5186	8.5	0.04206	0.5153	99.37
7	0.4396	7.2	0.03562	0.4364	99.30
8	0.3309	5.4	0.02672	0.3274	98.94
9	0.2570	4.2	0.02068	0.2534	98.60
10	0.1100	1.8	0.008906	0.1091	99.20

Average : 99.18%

TABLE 4 : Data of the results of volumetric titration of $K_2Cr_2O_7$ Vs Standard FAS solution

Sl. No	Weight of $K_2Cr_2O_7$ g/250ml	Volume of 0.09986N Ferrous ammonium sulphate, M	Estimated normality of $K_2Cr_2O_7$ solution N	Estimated weight of $K_2Cr_2O_7$ /250 ml by volumetric Analysis	Estimated percentage of Potassium dichromate %
(1)	(2)	(3)	(4)	(5)	(6)
1	1.0133	20.6	0.08228	1.0081	99.49
2	0.9695	19.6	0.07829	0.9593	98.95
3	0.8353	16.9	0.06751	0.8271	99.02
4	0.7457	15.1	0.06032	0.7390	99.10
5	0.6240	12.6	0.05033	0.6167	98.83
6	0.5186	10.5	0.04192	0.3139	99.09
7	0.4396	8.9	0.03555	0.4356	99.10
8	0.3309	6.7	0.02676	0.3279	99.10
9	0.2570	5.2	0.02077	0.2545	99.02
10	0.1100	2.2	0.00880	0.1078	98.02

Average : 99.01%

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RESULTS AND DISCUSSION

The estimation of either $K_2Cr_2O_7$ or I_2 can be carried out by considering the general procedure described elsewhere[1-4] iodometrically using volumetric method.

Recently, Palanna and his co-workers[5-7] have estimated few oxidizing cations like Ce^{4+}, Cr^{6+}, Fe^{3+} using iodo-potentiometric technique of analysis .$K_2Cr_2O_7$ is a strong oxidizing agent ($E^o = 1.33V$) and oxidizes many reducing agents, especially, iodide (I^-) ions ($E^o = 0.535V$) rapidly and quantitatively to release free iodine. The more positive the E^0 value of the oxidizing agent, the stronger the oxidizing power and the weaker is its conjugate ions as an reducing agent.The redox reaction taking place between Cr^{6+} (of $K_2Cr_2O_7$) and I^- ions are the basis for iodo-potentiometric chemical analysis. The potential change of the reaction [Equation (2)] is attributed due to

$$Cr_2O_7^{2-} + 6I^- \rightarrow 2Cr^{3+} + 3I_2;$$
$$E_M = [\,1.33 - 0.535\,] = 0.795 volts$$
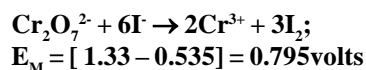
at standard conditions.

The equililibrium constant K, is given by

$$K = \exp \frac{2 \times 96485 \times 0.795}{8.3145 \times 298.15}$$

$$K = 7.52 \times 10^{25}$$

The potential of the reaction, E^0 is positive and 'K' for the above reaction is high; and therefore, the reaction proceeds favourably to the right, as predicted from the difference of their standard reduction potential values for feasibility of the reaction. The above redox reaction is carried out at pH about 0.9. The potential, E_M at non standard conditions of investigation can be obtained from equation (2).

$$E_M = [1.33 - 0.535] - \log_{10} \frac{[Cr^{3+}]^2\ [I^-]^2}{[Cr^{6+}]^2\ [I_2]} \qquad (3)$$

and which is dependent on the concentration of potassium dichromate taken for investigation at $pH = 0.9$.

The estimation of few metal cations of higher oxidation states and standard reduction potentials are reported earlier[10-] using iodo-potentiometric technique. In the present paper, the same procedure has been adopted for the estimation of potassium dichromate (Cr^{6+}) using iodo-potentiometric method.

The results of the potentiometric analysis based on the iodometric basic principles are shown in Figure 2. The potentiometric curves (Figure 2) illustrates the following aspects: i) the potential,(E_M), at point marked 'A' accounts for equation (3), and thereafter, the potential slowly decreases with the addition of small increments of standard sodium thiosulphate (Curve AB) which is due to the consumption of iodine with sodium thiosulphate [Equation (1)]. Thereafter, the potential decreases abruptly to C (BC) indicating the end point of potentiometric titration. CD describes the potential change due to the addition of excess of sodium thiosulphate. The Figure 2, curve (2), indicates the differential [∂^2E/∂^2V] plots of potentiometric titrations of potassium dichromate against a standard sodium thiosulphate. The end points of potentiometric titrations for different concentrations of $K_2Cr_2O_7$ solutions are noted from these differential plots which are tabulated in column (4) of TABLE 2.The estimated weight of $K_2Cr_2O_7$ /250ml is calculated and are given in column (6). It found that chemical assay of $K_2Cr_2O_7$ by potentiometric method is 99.17%.

The end points (V_2 ml) obtained from iodometric titrations of $K_2Cr_2O_7$ for different concentrations are given in TABLE 3, column (3). The estimated weight of $K_2Cr_2O_7$ /250ml are shown in column (5) and the estimated percentage of $K_2Cr_2O_7$ is 99.18, which is very close to the result obtained from potentiometric method.

To confirm the above results, we have carried out the volumetric titration of $K_2Cr_2O_7$ against standard ferrous ammonium sulphate solution using ferroin indicator. The estimated weights of $K_2Cr_2O_7$/ 250ml are given in TABLE 4, column (5) and the average percentage of $K_2Cr_2O_7$ on analysis is found to be 99.01.

To analyse the unknown concentration of $K_2Cr_2O_7$, the following steps have to be followed:

i) Note the potential, E_M of the solution (at Point 'A') potentiometricallymaintaing the same conditions of redox reaction; that is., The potential E_M of unknown is 350 mV.

ii) From linear calibration potentials,E_M, Vs volume of $Na_2S_2O_3$ plot, find out the corresponding volume required (Vml) for potential 350 mV. The volume of sodium thiosulphate required for consumption is

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13.1 ml from Figure 3, which is equivalent to a concentration of 0.06482N (or 0.7942g/250ml) of $K_2Cr_2O_7$.
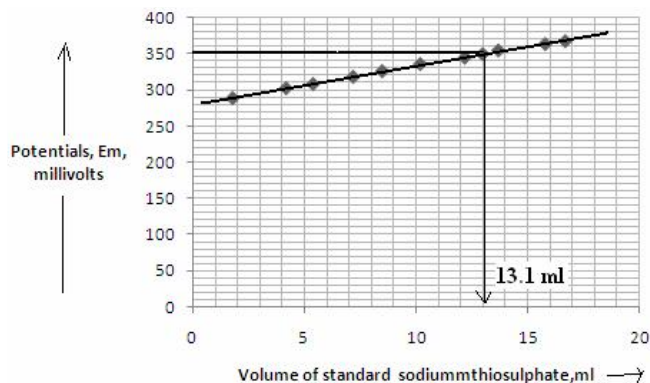

Figure 3 : A caliberation plot of potentials, E_M, against volume of standard sodium thiosulphate, ml

The assay of quantitative analysis obtained from the three methods of analysis are in excellent agreement with each other and the results point out that iodo-potentiometric method of combined analysis is also a useful tool to analyse quantitatively such compounds.

ACKNOWLEDGEMENTS

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