Iodo-Potentiometric Technique for the Estimation of Potassium Permanganate

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Potasium permanganate is estimated quantitatively by carrying out iodo-potentiometric method. The uniqueness of the procedure is that both iodometric and potentiometric results are obtained in two-in-one cell. A quantitative relationship is noticed between the potentials, E_M and the volumes of standard sodium thiosulphate (V_1 and V_2, mL) consumed in potentiometric and volumetric titrations for all concentrations. The potentials, E_M, are found, again, to have a linear relationship with the concentration of $KMnO_4$ sample taken. The titre volumes of both potentiometric and iodometric methods (V_1 and V_2, mL) are identical. It is quite interesting to note that estimation of $KMnO_4$ is possible in the light of the above facts. An excellent conformity of results are observed for potentiometric, iodometric and volumetric (using FAS and oxalate methods chemical analysis) titration data for the estimation of the percentage of $KMnO_4$ sample.

Key Words: Iodometric, Potentiometric, Quantitative, Potassium permanganate.

INTRODUCTION

Manganese occurs naturally in the form of a large number of ores and depending upon the application, the ore is evaluated for its manganese dioxide content. Pyrolusite ore is the main source of manganese. Manganese is used principally in the manufacture of iron and steel. Manganese can exist in different oxidative states; the most manganese compounds are those that contain Mn(II), Mn(IV) or Mn(VII). Manganese dioxide and other manganese compounds are used in products such as batteries, glass and fireworks. Potassium permanganate is used as an oxidant in volumetric chemical analysis, for cleaning, bleaching and disinfection purposes. Therefore, prime importance is given for a precise and rapid technique of chemical analysis for salts/products containing manganese.

Trace amounts of manganese ions also play important roles in a wide spectrum of areas. Manganese is an essential micronutrient for organisms and plants. However, it is toxic at higher levels and chronic manganese poisoning affects the central nervous system[1]. The determination of manganese content is becoming increasingly important because of the increased interest in industrial products, environmental and biological samples.

Several techniques are known to determine manganese in samples. Neutron activation analysis (NAA), electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry, electro-thermal atomic absorption spectrometry (ETAAS), molecular absorption spectrophotometry (UV-vis), atomic emission spectrometry with inductively-coupled plasma excitation (ICP-AES), X-ray fluorescence and voltametry[2] are commonly used depending on the amount of manganese in samples. A significant number of methods were proposed for determination of manganese in different samples based on its catalytic action on the oxidation of organic compounds with inorganic oxidants[3,4]. However, molecular absorption spectrophotometry[5-9] is a very attractive tool for the analysis of samples due to its operational simplicity, low cost, high selectivity and automation potential.

In the present paper, the iodo-potentiometric technique is being used for the estimation of $KMnO_4$. Though, trace and high concentration of manganese can be determined by various techniques. In the present paper, we present an affordable, precise, convenient and rapid technique of chemical analysis of manganese in $KMnO_4$, an iodo-potentiometric electroanalytical method, which gives results of both iodometric and potentiometric analysis.

EXPERIMENTAL

Preparation of different $KMnO_4$ solutions: A known weight of $KMnO_4$ sample is taken for investigation. It completely dissolved by swirling in distilled water and made up to 250 mL in a volumetric flask. Similarly, $KMnO_4$ solutions of different concentration are prepared as given in column (1) of Table-1.

Preparation of standard sodium thiosulphate solution: 57.825 g of $Na_2S_2O_3$ crystals are weighed and transferred to 1 dm³ standard flask and dissolved with distilled water and

TABLE-1
IODO-POTENTIOMETRIC TITRATIONS-PERCENTAGE OF KMnO₄ FROM IODO-POTENTIOMETRY

Weight of KMnO₄ taken, (g)/250mL	Potentials (mV) E_M	Volume of 0.1100 N sodium thiosulphate consumed, (EP) = V_1 mL	Estimated concentration of KMnO₄ (N)	Estimated weight of KMnO₄ g/250 mL	Percentage of KMnO₄
0.7851	423	22.2	0.09937	0.76880	98.3
0.6851	403	19.3	0.08672	0.76120	97.9
0.6208	394	17.6	0.07858	0.61670	98.5
0.5485	382	15.6	0.06943	0.53880	98.8
0.4560	369	12.9	0.05772	0.44750	98.3
0.3817	356	10.8	0.04831	0.37500	98.3
0.2933	345	8.3	0.03712	0.28680	98.4
0.2167	332	6.1	0.02743	0.21110	97.3
0.1370	321	3.9	0.01734	0.13540	98.9
0.0781	312	2.2	0.00988	0.07562	97.9

Average: 98.27 %.

made up to the mark, shaken thoroughly and used for titration. The normality of the $Na_2S_2O_3$ solution used for the investigation is 0.1100.

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 potentiometry, 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.
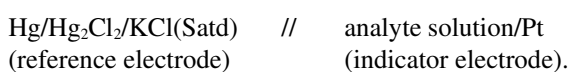
Oxidized form + n electrons → reduced form

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

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

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 V.

The electrochemical set up desired for the investigation is

Hg/Hg₂Cl₂/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} = saturated calomel electrode of constant potential, 0.2422 V.

Procedures

25 mL of KMnO₄ solution is pipetted out into the glass cell as shown in Fig. 1. The pH of the solution is maintained at 1.0. 6-8 mL of 10 % KI is added. The equilibrium potential (E_M) of the solution is noted after quantitative release of iodine. The potentials are monitored for each addition (an increment of 0.2 mL) of standard sodium thiosulphate solution from the burette. A magnetic stirrer is used to swirl continuously the solution during titration. When the colour of the solution is straw yellow in the cell, 1-2 mL of freshly prepared starch is added. The colour changes to blue due to starch-iodine complex.

Standard sodium thiosulphate is added further from the burette drop by drop till the blue colour disappears permanently. This is the end point of both volumetric and potentiometric titrations. The volume of standard thiosulphate consumed and the potential at the end point (E_{EP}) are also recorded. The end point of titre volumes (V_1 mL) of standard sodium thiosulphate consumed for potentiometric titrations are noted (Table-1).

Iodometric titration: 25 mL of the KMnO₄ solution is pipette out into the cell. The pH of the solution is maintained at 1.0 by adding requisite amount of dilute H₂SO₄. 6-8 mL of 10 % KI solution is added. The liberated I₂ 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. The colour changes to blue due to starch-iodine complex. Titration is continued till the disappearance of blue colour. Volume of sodium thiosulphate consumed (V_2, mL) at the end point is noted. Investigations are carried out for different amounts of KMnO₄ and the results obtained are tabulated in Table -2.

TABLE-2
IODOMETRIC TITRATIONS-ESTIMATED PERCENTAGE OF KMnO₄ IN THE SAMPLE

Weight of KMnO₄ g/250 mL	Volume of 0.1100 N Na₂S₂O₃ consumed, V_2 mL	Estimated normality of KMnO₄, (N)	Estimated weight of KMnO₄, g/250 mL	Percentage of KMnO₄
0.7851	22.2	0.09937	0.7717	98.3
0.6851	19.3	0.08672	0.6709	97.9
0.6208	17.6	0.07858	0.6118	98.5
0.5485	15.6	0.06943	0.5423	98.8
0.4560	12.9	0.05772	0.4484	98.3
0.3817	10.8	0.04831	0.3754	98.3
0.2933	8.3	0.03712	0.2885	98.4
0.2167	6.1	0.02743	0.2155	97.3
0.1370	3.9	0.01734	0.1356	98.9
0.0781	2.2	0.00988	0.7647	97.9

Average: 98.15 %.

Estimation of KMnO₄ by using ferrous ammonium sulphate: 25 mL of the prepared KMnO₄ solution is pipette out in a conical flask. 1-2 test tube of dilute sulphuric acid is added. Titrated against standard ferrous ammonium sulphate solution (FAS). The disappearance of the pink colour when the last drop of FAS added, is the end point of titration. The volume FAS consumed at the end point is noted as 'V₃', mL

(Table-3). Volume of FAS consumed for titrations for other concentrations are also noted.

TABLE-3
ESTIMATION OF KMnO$_4$ USING STANDARD
FERROUS AMMONIUM SULPHATE

Weight of KMnO$_4$ g/250 mL	Volume of 0.09972 N FAS solution consumed, V$_3$, mL	Estimated normality of KMnO$_4$ (N)	Estimated weight of KMnO$_4$. g/250 mL	Percentage of KMnO$_4$
0.7851	24.3	0.09732	0.7688	98.0
0.6851	21.2	0.08496	0.6712	98.0
0.6208	19.4	0.07806	0.6167	98.4
0.5485	17.1	0.06821	0.5388	98.2
0.4560	14.2	0.05664	0.4475	98.2
0.3817	12.9	0.04747	0.37.50	98.2
0.2933	9.1	0.03630	0.2868	97.8
0.2167	6.7	0.02672	0.2111	97.4
0.1370	4.2	0.01715	0.1354	98.9
0.0781	2.4	0.00957	0.0756	97.7

**Estimation of KMnO$_4$ by using sodium oxalate method:** 25 mL of the prepared standard sodium oxalate solution is pipette out in to a conical flask. 1-2 test tube full of dilute sulphuric acid is added. The solution is heated to 70-80 ℃ and titrated against KMnO$_4$. The end point is the appearance of permanent pink colour. Volume of KMnO$_4$ consumed for the titration is noted as 'V$_4$', mL. The data obtained is tabulated in Table-4.

TABLE-4
ESTIMATION OF KMnO$_4$ BY OXALATE METHOD

Weight of KMnO$_4$, g/250 mL	Volume of 0.09849 N Na$_2$C$_2$O$_4$ consumed, V$_4$, mL	Estimated normality of KMnO$_4$ (N)	Estimated weight of KMnO$_4$ g/250 mL	Percentage of KMnO$_4$
0.7845	10.1	0.09510	0.7704	98.2
0.6182	12.8	0.07690	0.6079	98.3
0.4560	17.4	0.05660	0.4472	98.1
0.3867	20.6	0.04781	0.3777	97.7
0.2933	27.1	0.03632	0.2869	97.8
0.2165	36.4	0.02706	0.2138	98.7

RESULTS AND DISCUSSION

Mn(VII) state in KMnO$_4$ behaves as an oxidizing agent by virtue of its higher reduction potential (E^0 = 1.51 V) than I$^-$ ions (E^0 = 0.535 V). The redox reaction between Mn(VII) and I$^-$ is feasible and occurs spontaneously liberating free iodine (forms I$_3^-$ in the presence of excess KI), which is titrated against sodium thiosulphate and is the basis for iodo-potentiometrical chemical analysis, which provide results from both volumetric and the potentiometric analysis.

When requisite amount of KI is added to KMnO$_4$ solution in acidic condition, iodine is liberated spontaneously (eqn. 1).

$$(E_M)\ldots 2Mn^{7+} + 10I^- \rightarrow 2Mn^{2+} + 5I_2 \qquad (1)$$
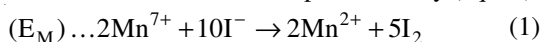
The potential developed (E$_M$) for each solution is attributed due to the presence of their respective concentrations of Mn(II) and I$_2$ present in solution after redox reaction, which is, in fact, proportional to the quantity of Mn(VII) taken as shown in Table-1.

Therefore, $E_M = [E^0_{Mn^{7+}/Mn^{2+}} - E^0_{I^-/I_2}] = [1.51 - 0.535]$ = 0.975 V at standard conditions.

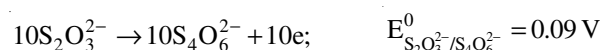The equilibrium constant K of the reaction is given by

$$K = \exp \frac{2 \times 96485 \times 0.975}{8.3145 \times 298.1}$$

The over all potential of the reaction, E^0 (0.975 V), is positive and 'K' for the above reaction is high and therefore, the reaction proceeds favourably to the right, as predicted from their standard reduction potential values for feasibility of the reaction. The potential, E$_M$, at non-standard conditions of investigation for different concentrations of analyte depends on the ionic concentrations of manganese at the experimental conditions as described in eqn. 2.

$$E_M = [1.51 - 0.535] - \frac{0.0591}{2} \log \frac{[Mn^{2+}]^2[I^-]^{10}}{[Mn^{7+}]^2[I_2]^5} \quad (2)$$

The eqn. 5 accounts for the variation of potential values, when liberated I$_2$ is titrated against standard sodium thiosulphate solution using freshly prepared starch as indicator.

The potential (E$_{Ep}$) at the end point of reaction is attributed due to the following redox reactions for standard conditions and 1 M concentrations.

$$5I_2 + 10e \rightarrow 10I^-; \qquad E^0_{I_2/I^-} = +0.535 \text{ V} \qquad (3)$$

$$10S_2O_3^{2-} \rightarrow 10S_4O_6^{2-} + 10e; \qquad E^0_{S_2O_3^{2-}/S_4O_6^{2-}} = 0.09 \text{ V}$$

The iodine-thiosulphate redox reaction for 1 M solutions can be depicted as

$$5I_2 + 10S_2O_3^{2-} \rightarrow 10S_4O_6^{2-};$$
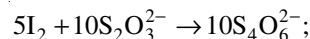
$$E_{EP} = [0.535 - 0.09] = 0.446 \text{ V} \qquad (4)$$

During the process of titration, I$_2$ gets reduced to I$^-$ ions and the thiosulphate changes to tetrathionate ions. For non-standard conditions of investigation, the potential, E, changes with the decreasing concentration of iodine (I$_2$) and as well, with decreasing amounts of manganese analyte solutions.

The iodo-potentiometric titration curves for different weights [Table-1, column (1)] of manganese samples are shown in the Fig. 2(1) and 2(2). The observed potentials (E$_M$) for corresponding concentrations of manganese(VII) are given in (column 2). Point marked at 'A' in the potentiometric titration curves [Fig. 2(1)] indicate the potentials (E$_M$) due to the presence of free I$_2$ and Mn(II) (quantitatively converted from Mn(VII) state in analyte solution) after redox reaction. At the end point (EP) of titration, the potential (E$_{EP}$) refers to a situation where all the liberated iodine is consumed completely ([I$_2$] = 0) by standard sodium thiosulphate solution. The decrease in potential values in the potentiometric curve (ABCD), Fig. 2(1), marked from A-C indicates that iodine is consumed continueously with the addition of sodium thiosulphate during the potentiometric titration and from A-C indicates that the iodine (I$_2$) concentration decreases with its continuous consumption with the addition of standard sodium thiosulphate (eqn. 4). Simultaneously, the concentration of S$_2$O$_4^{2-}$ increases due to the oxidation of S$_2$O$_3^{2-}$ by iodine during the titration.

The potential, E, variation from A-C in the curve is accounted for by the eqn. 5.

$$E_{A-D} = 0.446 - \frac{0.0591}{2} \log_{10} \frac{[I^-]^2 [S_4O_6^{2-}]}{[I_2][S_2O_3^{2-}]} \tag{5}$$

The potential change (mV) after the end point (EP) is depicted in curve as C-D, which is due to the presence of excess titrant, $S_2O_3^{2-}$ along with Mn(II) and $S_4O_6^{2-}$ ions. The similar trend and behaviour is observed for other concentrations in potentiometric titrations, but the end points are different depending on the molar concentration (g/250 mL) of manganese solutions.

The differential $(\partial^2 E)/(\partial^2 V)$ plots of potentiometric titrations of different concentrations of manganese solutions are shown in Fig. 2(2). The end point of potentiometric titrations (EP) are noted from these differential plots. The potentials, E_M, (column 2) and the end points (V_2 mL) (column 3) of potentiometric titrations are tabulated in Table-1.

A linear plot is obtained when potentials, E_M, are plotted against the volumes (V_1 and V_2 mL) of standard sodium thiosulphate consumed (Tables 1-3) for both potentiometric and iodometric methods. The column (2) of Table-1 indicates potential (E_M) measured at the conditions referred to (eqn. 1) and is found to vary linearly with different concentrations of manganese solutions.

A useful link of information is obtained from these results to estimate manganese in $KMnO_4$ as Mn(VII), potentiometrically. Knowing the volume of sodium thiosulphate consumed (V, mL) for unknown $KMnO_4$ solution, the amount of $KMnO_4$ and its percentage is determined with usual calculation. There is an excellent agreement of results obtained from the investigations of potentiometric, iodometric and oxalate methods analysis (Tables 1-4) indicating the usefulness of the novel iodo-potentiometric, an electroanalytical technique, for the estimation of $KMnO_4$.

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