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Iodo-potentiometric method of estimation of ceric salts in the presence of iron (Fe^{3+}) by masking iron with fluoride (F^-) ions

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ABSTRACT

Iodo-potentiometric method, a versatile technique in which both iodometric and potentiometric results can be obtained in a two-in- one cell for the estimation of an oxidizing cation in analyte solution. It is observed that the Fe^{3+} ions present in ceric solutions can be masked completely at $\text{pH} = 1.0$ as FeF_6^{-3} by adding requisite amount of NH_4HF_2 . 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 molar concentrations of the analyte samples taken. The titre volumes of standard sodium thiosulphate (v_1 and v_2 , ml) of both potentiometric and iodometric methods are identical. Interestingly, the estimation of ceric (Ce^{4+}) is possible in the light of the above relationships observed. An excellent conformity of results are observed for potentiometric, iodometric and volumetric (cerimetric) titration data for the estimation of cerium in cerium salt solutions containing another oxidizing agent like Fe^{3+} ions.

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KEYWORDS

Iodometric;
Potentiometric;
Analyte;
Complexing;
Auantitative;
Potentials;
Oxidizing.

INTRODUCTION

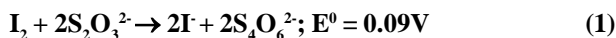
The molar reduction potential (E^0) of the reaction $\text{I}_2 + 2e \rightarrow 2\text{I}^-$ is 0.535volts, and therefore, it would appear that iodide, (I^-) might be used for reducing a considerable a number of compounds which are positive to it in potential series. Iodide (I^-) ion is, therefore, a strong enough reducing agent that many oxidizing agents can react completely with the iodide ion resulting in many useful iodometric processes. Quadrivalent cerium is a strong and powerful oxidizing agent in molar sulphuric acid solutions. The use of acidified solutions of ceric salts as volumetric oxidizing agents was suggested long ago^[1-5], but only a few decades back, the applications

of ceric sulphate been systematically studied by Atanasiu^[1-2], young^[3], Berry^[4], and Furman and co-workers^[5]. Early potentiometric studies on cerium salts by conventional technique were done by Someya^[6,7]. Ceric sulphate cannot be used in faintly acid or neutral solutions because slightly soluble basic ceric salts are formed. Perceric salts are formed by the action of air on cerous salts in alkaline media. Therefore, it is desirable that acid concentrations of greater than 1M should be used, if ceric sulphate is used as oxidizing agent for any investigations.

The usual procedure^[9-11] involves the addition of excess of a soluble iodide to the oxidizing agent to be determined, whereby an equivalent amount of iodine is

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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



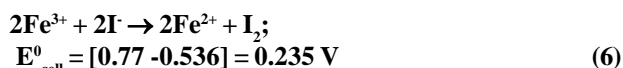
The feasibility of analyte redox reaction in potentiometry is dependent on the standard reduction potentials values of Ce^{4+} ($E^0 = 1.44\text{V}$), Fe^{3+} ($E^0 = 0.77\text{V}$) and the I^- (0.535V). The following reduction reactions can take place in highly acidic solution ($\text{pH} = 1.0$) in the presence of I^- ions,



And simultaneously, iodide gets oxidized to free iodine (I_2).



And, the possible redox reactions that can occur are as



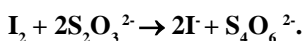
By virtue of the difference of reduction potential values of reaction, the reaction between the analyte containing both Fe^{3+} and Ce^{4+} and the iodide ions occurs spontaneously to the right; and therefore, the redox reaction is feasible, rapid and quantitative in acid medium.

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 cerium and iron by potentiometric method. When requisite amount of KI solution is added to a solution containing Ce^{4+} and Fe^{3+} ions, both oxidize iodide (I^-) ions and thus, I_2 is liberated. The basic principle of the above redox reaction between Ce^{4+} and I^- ions can be used to determine quantitatively the amount of cerium in the presence of Fe^{3+} in acidic ($\text{pH} = 1.0$) solution, if, Fe^{3+} ions are masked completely as complex ions, FeF_6^{-3} .

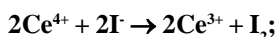
In the present investigation, we have used iodo-potentiometric, a two- in- one method ;wherein, the analyte potential (E_M) is noted when all the I_2 is set free after the redox reaction. The liberated Iodine is, then, titrated against standard sodium thiosulphate solution observing the changes of potentials 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 $\text{pH} = 1.0$.

The redox reaction taking place between iodine and thiosulphate is the basis principle of all iodometric processes.



The amount of iodine liberated in the reaction between iodide(I^-) and an oxidizing agent (equation 5) is a measure of the quantity of oxidizing agent (Ce^{4+}) present in the analyte solution [If Fe^{3+} ions are masked] .



The amount of standard sodium thiosulphate required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent (Ce^{4+}) as shown in equation (6). If the redox reaction between Ce^{4+} and I^- is stoichiometrically feasible and fast in acid medium, then, the measured potentials (E_M) for equation (5) may change linearly with different molar concentrations of Ce^{4+} solutions at $\text{pH} = 1.0$; 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 ceric ammonium sulphate solutions

Ceric ammonium sulphate [Fischer scientific, Qualigen fine chemicals, assay: 95%, Mol Weight:632.56] is taken for iodo-potentiometric investigations for different molar concentrations cerium.

In the present investigation, the following molar concentrations ceric ammonium sulphate salt [TABLE 1] are prepared for the quantitative estimation of cerium

TABLE 1 : Weight of sample (C. A. S)

S.No	Weight of the ceric ammonium sulphate (C.A.S)
1	15.810
2	12.566
3	9.406
4	6.305
5	3.141
6	1.660

and its percentage in each sample solution.

Requisite quantities of ceric ammonium sulphate crystals are weighed accurately and transferred into different 250ml standard flasks. The samples are dissolved in 1:1 conc H_2SO_4 and the clear solution is made up to 250ml mark with dil H_2SO_4 .

Preparation of 0.1N $FeCl_3$ solution

About 16.22g of $FeCl_3$ is dissolved in 1:1 HCl, shaken thoroughly for homogeneity and made up to 1000ml. The strength of the solution is about 0.1M.

Preparation of standard sodium thiosulphate solution

About 57.825g 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 molarity of the $Na_2S_2O_3$ solution used for the investigation is 0.2457.

For cerimetric titration: Preparation of standard ferrous ammonium sulphate

9.8850g 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 0.1012.

Electrochemical cell set up iodo-potentiometric studies

Potentiometry is an important tool used for quantitative analysis in analytical chemistry. 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 \rightarrow reduced form

For such reactions, the potential (E) acquired by the indicator electrode at 25°C 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/Hg₂Cl₂/KCl(Satd)//Redoxanalyte 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.

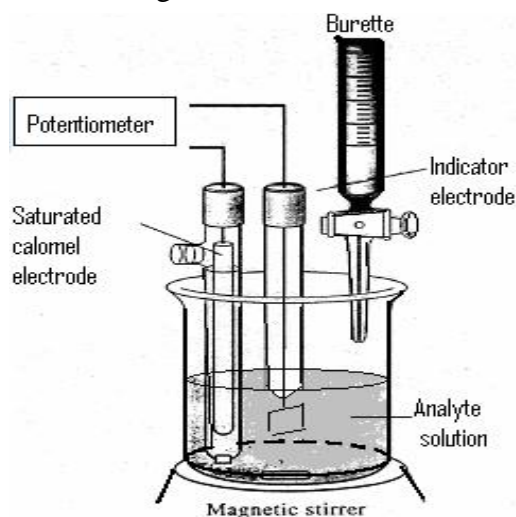


Figure 1 : A two in one cell set up for iodo- potentiometric titrations.

(i) 25 ml of ceric ammonium sulphate solution is pipette out into the glass cell.

Requisite quantity of 1:1 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

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from the burette drop by drop till the blue color disappears permanently. This is the end point of both volumetric and potentiometric titrations of this redox reaction. The volume of standard thiosulphate consumed (V_1 , ml) and the potential at the end point (E_{EP}) are recorded. The potentiometric titration of different molar concentrations of ceric ammonium sulphate are shown in Figure 2 and potentials E_M (millivolts) are given in TABLE 2.

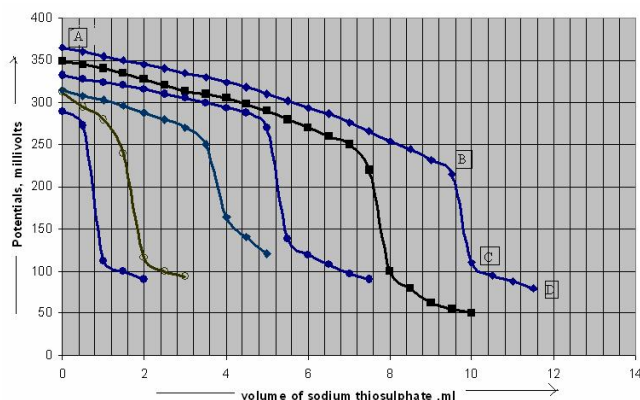


Figure 2 : Potentiometric titration curves of ceric ammonium sulphate at pH=1=0.

TABLE 2 : Potentiometric data of ceric ammonium sulphate of different molar solutions

Weight of the ceric amm sulphate (g/ 250ml)	Potentials, millivolts Equation (7) (E_M)*	Volume of sodium 0.2457M thiosulphate from potentiometric end points before and after masking, (V_1 ml)	Estimated Molar concentration of ceric Amm sulphate, (M)	Estimated weight of ceric Amm. sulphate. (g/250ml)	Percentage of ceric amm sulphate. (%)
(1)	(2)	(3)	(4)	(5)	(6)
15.810	365	9.8	0.0963	15.229	96.3
12.566	348	7.8	0.0766	12.1228	96.47
9.406	332	5.8	0.0570	9.0143	95.83
6.305	315	3.9	0.03833	6.0614	96.13
3.141	298	1.9	0.01866	2.953	94.01
1.660	289	1.0	0.009828	1.5542	93.62

(E_M)* denotes potentials respective molar concentrations. Average = 95.39

The investigation is similarly carried out for ceric ammonium sulphate solutions containing iron which is masked by fluoride as complex ions.

Iodometric titration

(i) 25 ml of ceric ammonium sulphate solution is pipette out into the glass cell. pH of the solution is maintained at 1.0 by adding requisite quantity of 1:1 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 molar concentrations of ceric ammonium sulphate and the data is tabulated in TABLE 3.

TABLE 3 : Volumetric data of ceric ammonium sulphate of different molar solutions

Weight of the ceric amm sulphate (g/ 250ml)	Volume of sodium 0.2457M thiosulphate from Volumetric end points. (V_2 ml)	Estimated Molar concentration of ceric Amm sulphate, (M)	Estimated weight of ceric Amm . sulphate. (g/250ml)	Percentage of ceric amm sulphate. (%)
(1)	(2)	(3)	(4)	(5)
15.810	9.8	0.0963	15.229	96.3
12.566	7.8	0.0766	12.1228	96.47
9.406	5.6	0.0541	8.5490	90.88
6.305	3.8	0.03735	5.906	93.67
3.141	1.9	0.01866	2.953	94.01
1.660	1.0	0.009828	1.5542	93.62

Average = 94.11 %

(ii) 25ml of ceric ammonium sulphate solution is pipetted out and add 2ml of about 0.1M $FeCl_3$ in to it. To mask the Fe^{3+} , 5ml of 0.5M NH_4HF_2 is added, shaken well and titrated as explained above. The titrations are carried out for other concentrations of ceric salt containing iron.

Cerimetric titration

25 ml of Ceric ammonium sulphate is pipette out into a conical flask. 15ml of 1:1 H_2SO_4 is added. 2-3 drops of Ferrion indicator is added. Titrated with standard Ferrous ammonium sulphate solution with continuous swirling. At the end point, the color of the solution changed to brownish red color. Volume of standard FAS consumed, (V_3 ml), are noted for different molar concentration ceric salt solutions and are given in TABLE 4.

TABLE 4 : Estimation of cerium by cerimetric titration

Weight of the ceric amm sulphate (g/ 250ml)	Volume of Ferrous amm sulphate 0.1012M from volumetric end points. (V_3 ml)	Estimated Molar concentration of ceric Amm sulphate, (M)	Estimated weight of ceric Amm . sulphate. (g/250ml)	Percentage of ceric amm sulphate. (%)
(1)	(2)	(3)	(4)	(5)
15.810	22.8	0.09229	14.856	93.96
12.566	18.6	0.07529	12.1185	96.90
9.406	^	0.06048	8.7957	93.51
6.305	9.4	0.03805	6.1244	97.12
3.141	4.6	0.02061	2.997	95.44
1.660	2.3	0.009310	1.4985	93.90

Average = 95.14 %

RESULTS AND DISCUSSION

Cerium in 4+ oxidation state in analyte solution behaves as a strong and powerful oxidizing agent in highly acidic medium. The redox reaction taking place between Ce^{4+} and I^- ions is feasible because of its high value of reduction potential ($E^0_{Ce^{4+}/Ce^{3+}} = 1.44\text{volts}$)^[8] at $1N H_2SO_4$ solution. In addition, the works of Atanasu^[1,2] and young^[3], Berry^[4] and Furman^[5] indicated that cerium (Ce^{4+}) have wonderful applications in analytical Chemistry. Ceric salts when dissolved in faintly acidic or neutral condition forms a slightly soluble basic salts and hence, cannot be used. In 1928, Someya^[6,7] carried out potentiometric studies by conventional method for cerium. After a break of few decades of initial research investigations of cerium as oxidizing agent and their applications, Anandamurthy and Palanna^[12-14] and other coworkers^[14], have reported a novel technique for the quantitative estimation of copper, iron and cerium by iodo-potentiometric method. The redox reactions involved in such cases are rapid and quantitative in acidic solution ($pH = 1.0$); and hence, can be exploited to carry out investigations to estimate metal cations of higher reduction potentials (oxidizing agents) through iodo-potentiometric method, a novel technique through which one can obtain both volumetric as well the potentiometric data. Ce^{4+} (1.44V) and Fe^{3+} (0.77V) ions have higher reduction potentials than iodide (0.535V) and hence, both the cations oxidize iodide to free I_2 . Therefore, it clear that Ce^{4+} cannot be estimated quantitatively in the presence Fe^{3+} state, if both these ions are present in an analyte solution.

In order to get rid off this type of problem in quantitative estimation, we have used Fluoride ion (F^-) as a complexing agent, which quantitatively removes ferric iron as a Complex, FeF_6^{-3} . When KI is added to cerium salt solution containing iron (in Fe^{3+} state) at $pH = 1.0$, both the below mentioned reactions takes place simultaneously releasing iodine since both the reactions are feasible to the right.



equation (5)



equation (6)

The feasibility of the above reactions also can be highlighted in terms of the values of Potentials (E) and

the equilibrium constant (K) at standard conditions as shown

For cerium, it is

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

$$K = \exp \frac{2 \times 96485 \times 0.905}{8.3145 \times 298.15}$$

$$K = \exp (70.44)$$

$$K = 3.90 \times 10^{30}$$

The equilibrium constant, K, for reduction of cerium Ce^{4+} to Ce^{3+} is 3.90×10^{30} .

For iron, it is,

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

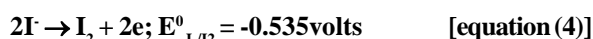
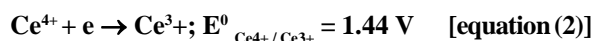
$$K = \exp \frac{2 \times 96485 \times 0.235}{8.3145 \times 298.15}$$

$$K = \exp (18.29)$$

$$K = 8.77 \times 10^7$$

The equilibrium constant, K, for the reduction reaction of Fe^{3+} to Fe^{2+} is 8.77×10^7 which is also fairly high and takes place in the forward direction.

If Fe^{3+} is masked in analyte solution as FeF_6^- , then Ce^{4+} ions can only interact with KI and liberate free iodine equivalent to the amount of ce^{4+} present in analyte solution.



The Ce^{4+} ions gets reduced to Ce^{3+} ions, whereas Iodide(I^-) ions gets oxidized quantitatively to free I_2 . In Figure 2, the potentiometric titration curves of ceric ammonium sulphate solution (in the absence of iron salt) for different molar concentrations are shown.

2 ml of 0.1M $FeCl_3$ (Fe^{3+}) is introduced into different concentrations of ceric ammonium sulphate solutions. The ferric iron of the solutions are then masked by adding 2 - 3ml of 0.5M NH_4HF_2 and it is titrated using two-in-one cell as shown in the Figure 1 with standard sodium thiosulphate taken in the burette. The potentiometric titration curves obtained for iron masked ceric ammonium sulphate solutions and for pure ceric salt solutions are depicted in curves 1 and curve 2 respectively in Figure 3. The differential ($\partial^2E/$

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∂^2V) titration plots are shown curve 3 of Figure 3. The end points of potentiometric titration in each case is identical to that obtained for analyte solution without Fe^{3+} ions for a particular molar concentration. However, it can be noticed that the overall potentials

(E_M) of analyte solutions containing iron is higher than the one observed for pure ceric ammonium sulphate solutions due to complexation of iron as FeF^{-3} ; and however, the titration behaviour is similar as indicated in (1) and (2) of Figure 3.

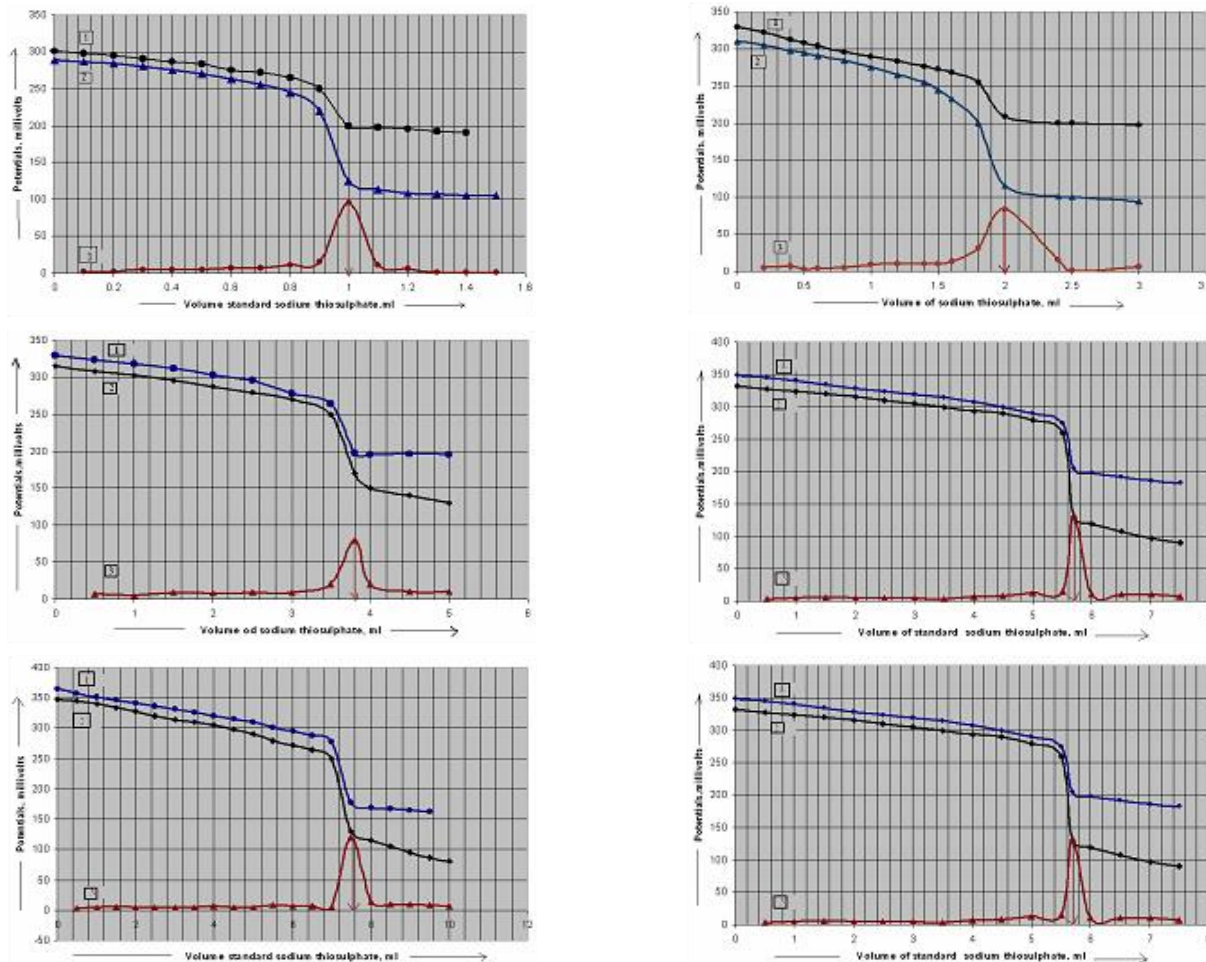


Figure 3 : Potentiometric titrations of (1) iron masked analyte solutions (b) pure ceric ammonium sulphate solutions and (3) differential $[\partial^2E/\partial^2V]$ plots for both titrations.

The data of the results of potentiometric studies of both pure ceric ammonium sulphate and Fe^{3+} masked solutions are tabulated in TABLE 2. In Figure 3, point marked 'A' indicates the potentials, E_M , for both pure ceric ammonium sulphate and Fe^{3+} masked analyte solutions, which is given as

$$E_M = [1.44 - 0.535] - \frac{0.0591}{2} \log_{10} \frac{[Ce^{3+}]^2 [I^-]^2}{[Ce^{4+}]^2 [I_2]} \quad (7)$$

AB shows the changes of potentials during the titrations iodine against standard sodium thiosulphate, Equation (5). BC is the indication of the potential changes nearer end point. CD is the potentials due to the addition

of excess sodium thiosulphate solution to the analyte. From curve 3 of Figure 3, the end points potentiometric titrations are obtained from the differential potential (∂^2E/∂^2V) plots for analyte and the masked solutions. The Fe^{3+} ions are completely masked by fluoride ions as stable complex ions and it is remarkable to note that the end points for both potentiometric titrations are identical (V_1 ml) for a particular molar concentration. The iodometric titration data obtained (V_2 ml) for both the above solutions are tabulated in TABLE 3.

To confirm the results of potentiometric and iodometric titrations, we have also estimated the ceric in ceric ammonium salt and iron masked analyte solu-

tions by cerimetric titrations and the data of the results are given in TABLE 4. It can be remarked that the estimated amounts cerium ammonium sulphate from all the methods of estimation are nearly identical (TABLES 2-4). It is observed that the potentials, E_M , of the analyte (after masking Fe^{3+} also) varies linearly with the molar concentration of ceric salt solutions. This linear calibration plot E_M versus volume of standard sodium thiosulphate (V ml) is shown in Figure 4. The concentration of the unknown cerium(Ce^{4+}) solution (in the absence Fe^{3+} ions) can be obtained from the above linear plot. The measured cell potential, E_M , is 338mV after masking ferric iron with fluoride ions for unknown analyte. The estimated concentration of unknown solution is 0.05M, which corresponds to a volume of 4.6 ml (Figure 4) of 0.02457M sodium thiosulphate. The estimated weight of ceric ammonium sulphate and the one that is masked for iron are identical, which points out that iodo-potentiometric technique also can be successfully used for the estimation.

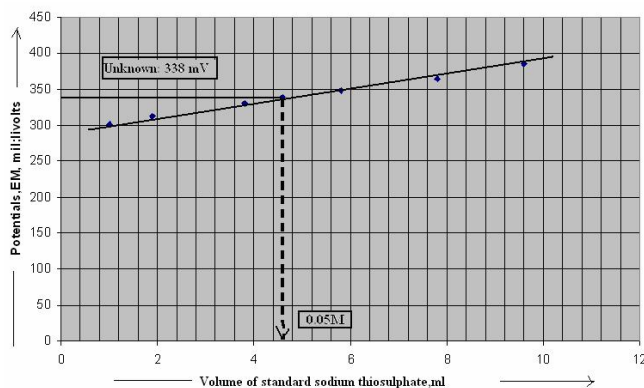


Figure 4 : Determination of molar concentration of unknown ceric ammonium sulphate solution from calibration plot of E_M (after masking) Vs Volume of sodium thiosulphate, ml.

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