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Determination of Cerium in Ceric Ammonium Sulphate by Novel Iodo-Potentiometric Method

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The basic principles of the redox reactions between cerium (Ce^{4+}) and iodide (I^-) ions are being used to estimate quantitatively cerium in ceric ammonium sulphate by both iodometric and potentiometric methods. Precisely, the new iodo-potentiometric technique used in the present paper is a two-in-one method, wherein, both potential and volumetric data are obtained in a single process of titration at strongly acidic ceric solutions at the specified conditions. After the liberation of free iodine by adding 10 % KI to cerium solutions, the potentials (E_M) are noted. These observed potentials (E_M) have a linear relationship with molar concentration (M) of cerium solutions and again, these potentials are also found to vary linearly with iodometric titre (V_1 mL) values of standard sodium thiosulphate for different concentrations of cerium in acidic (pH 1) medium. The potential (E_M) recorded for cerium solution of unknown concentration after the addition of KI is marked in the linear plot of E_M *versus* V_1, mL of sodium thiosulphate and the corresponding volume (V mL) of standard sodium thiosulphate consumed for the liberated iodine is noted. From this, the amount of cerium present in ceric ammonium sulphate and its percentage is determined. The results of potentiometric titration data obtained are in excellent conformity with the obtained data from iodometric and cerimetric methods of estimation of cerium.

Key Words: Redox, Quantitative, Iodometric, Potentiometric, Sodium thiosulphate, Linear and cerimetric.

INTRODUCTION

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], but only a few decades back, the applications of ceric sulphate been systematically studied by Atanasiu[2,3], Willard and Young[4], Berry[5] and Furman and co-workers[6]. Early potentiometric studies on cerium salts by conventional technique were done by Someya[7,8]. 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 more than 1 M should be used, if ceric sulphate is used as oxidizing agent for any investigations.

The normal oxidation potential of cerium measured[9] in 1 M sulphuric acid is -1.44 V at 25 ºC. Iodide ion is a strong reducing agent ($E^0 = 0.535$ V) that many oxidizing agents can react completely with the iodide ion resulting in many useful iodometric processes. The usual procedure involves the addition of an excess of iodide ion to the oxidizing agent analyte which produces iodine, which can be titrated against standard sodium thiosulfate solution. The iodine-thiosulphate reaction is quite fast and the equilibrium is far to the product side. In the determination of cerium using the iodometric/potentiometric methods, the basic reaction considered is represented as:

$$2Ce^{4+} + 2I^{-} \rightarrow 2Ce^{3+} + I_2 \qquad (1)$$

This is a rapid, quantitative reaction in acidic solutions (pH 1). When requisite amount of KI solution is added to a solution containing Ce^{4+} ions, it oxidizes iodide (I^-) ions and thus, I_2 is liberated. The basic principle of the above redox reaction between Ce^{4+} and I^- can be used to determine quantitatively the amount of cerium present in ceric ammonium sulphate in highly acidic (pH 1) solution. In the present investigation, we have adopted iodo-potentiometric , a two in one method; wherein, the established potential (E_M) is measured for cerium solution when stoichiometric amounts of iodine is set free and the liberated iodine is also titrated against standard sodium thiosulphate solution, simultaneously, using fresh starch as an indicator. The process of measurement of potentials are repeated for different concentrations of ceric solutions at pH 1.

The redox reaction between iodine and thiosulphate reaction is as given:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-} \qquad (2)$$

The amount of iodine liberated in the reaction between iodide ion and an oxidizing agent is a measure of the quantity of oxidizing agent originally present in the solution. The amount of standard sodium thiosulphate required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent.

If the redox reaction (1) is feasible stoichiometrically at pH 1, a quantitative linear variation of the measured potentials (E_M) is expected for different molar concentrations cerium solutions at pH 1 and at the same time, potentials to vary linearly with volume of standard sodium thiosulphate consumed (V_1 mL) in iodometric titration for different molar concentrations cerium salt.

EXPERIMENTAL

Preparation of different ceric ammonium sulphate solutions: Ceric ammonium sulphate [Fischer scientific, Qualigen fine chemicals, assay: 95 %, m.w.: 632.56] is taken for iodo-potentiometric investigations for different molar concentrations of cerium. In the present investigation, the following molar concentrations as given in Table-1, column 1, are prepared for the quantitative estimation of cerium and its percentage in each sample solution.

TABLE-1
IODOMETRIC TITRATIONS DATA FOR CERIUM SALT

Molar concentrations of Ceric ammonium sulphate (M) taken	Volume of 0.233 M sodium thiosulphate consumed at the end point, V_1 mL	Estimated molar concentrations of ceric ammonium sulphate (M)	Percentage of cerium in ceric amm. sulphate
0.103800	10.6	0.09879	95.00
0.083000	8.4	0.07828	94.30
0.060970	6.2	0.05778	94.76
0.040500	4.1	0.03821	94.34
0.020400	2.0	0.01957	94.87
0.009876	1.0	0.00932	94.34

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

Preparation of standard sodium thiosulphate solution: 57.825 g of $Na_2S_2O_3$ crystals 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.

For cerimetric titration

Preparation of standard ferrous ammonium sulphate: 9.885 g of AnalaR ferrous ammonium sulphate (FAS) crystals are transferred to 250 mL standard flask. 10-15 mL of dil sulphuric acid is introduced into it to maintain acidic and to prevent hydrolysis of the sample. The solution is made up to 250 mL and shaken for uniform concentration. The molarity of the prepared sample is 0.1008.

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.

$$\text{Oxidized form} + \text{n electrons} \rightarrow \text{reduced form}$$

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

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

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 V.

The electrochemical set up desired for the investigation is

$Hg/Hg_2Cl_2/KCl(satd)//\text{redox analyte solution}/Pt$
(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, 0.2422 V.

Procedures

Iodometric titration: 25 mL of ceric ammonium sulphate solution is pipette out into the glass cell. pH of the solution is maintained at 1 by adding requisite quantity of 1:1 sulphuric 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. 2-3 mL of NH_4CNS is added and then, 1-2 mL of freshly prepared starch is added. Titration is continued till the disappearance of blue colour of the starch-iodine complex. Volume of sodium thiosulphate consumed (V_1, 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-1.

Iodo-potentiometric titration: The potentiometric titration is carried out in a cell as shown in the Fig. 1. 25 mL of ceric ammonium sulphate solution is pipette out into the glass cell. pH 1 is maintained by adding requisite quantity of 1:1 sulphuric 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 mL of freshly prepared starch is added. The colour 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 colour disappears permanently. This is the end point of both volumetric and potentiometric titrations of this redox reaction. The volume of standard thiosulphate consumed (V_2 mL) and the potential at the end point (E_{EP}) are recorded. The potentiometric titration of different molar concentrations of ceric ammonium sulphate is shown in the Fig. 2 and potentials E_M and E_{EP} (mV) are given in Tables 2 and 3.

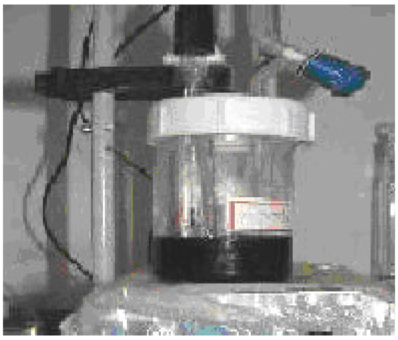

Fig. 1. A two in one cell set up for iodo-potentiometric titrations

TABLE-2
MOLAR CONCENTRATION OF CERIC AMMONIUM SULPHATE (CAS) AND THE MEASURED POTENTIALS, E_M AND AT THE END POINT (E_{EP}) AT pH 1

Molar conc. of CAS (M) taken	Potentials (mV) E_M	Potentials (mV) E_{EP}	Volume of 0.233 M sodium thiosulphate (V_2 mL)	Estimated molar concentrations (M)	Percentage of cerium in ceric amm. sulphate
0.103800	425	145	10.6	0.09879	95.00
0.083000	391	132	8.4	0.07828	94.30
0.060970	357	120	6.2	0.05778	94.76
0.040500	323	108	4.1	0.03821	94.34
0.020400	289	95	2.1	0.01957	94.87
0.009876	272	90	1.0	0.00932	94.34

TABLE-3
CERIMETRIC TITRATIONS: TITRATION OF CERIC AMMONIUM SULPHATE AGAINST STANDARD (0.1008 M) FERROUS AMMONIUM SULPHATE SOLUTION

Weight of ceric ammonium sulphate taken (g)/250 mL	Volume of 0.1008 M FAS consumed (mL)	Molar concentration of ceric ammonium sulphate (M)	Estimated weight of ceric ammonim sulphate (g)/250 mL	Percentage of cerium in cerium in ceric ammonium sulphate
16.4224	24.2	0.09757	15.1754	94.0
13.1258	19.3	0.07780	12.6249	93.8
9.6424	14.2	0.05523	9.0542	95.1
6.4056	9.5	0.03830	6.0573	94.6
3.2625	4.8	0.01935	2.9330	93.8
1.5618	2.3	0.00927	1.4028	93.8

Cerimetric titration: 25 mL of ceric ammonium sulphate is pipette out into a conical flask. 15 mL 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 colour of the solution changed to brownish red colour. Volume of standard ferrous ammonium sulphate consumed, (V_3 mL), are noted for different molar concentration ceric salt solutions and are given in Table-4.

TABLE-4
IODO-POTENTIOMETRIC DATA OF UNKNOWN CERIC AMMONIUM SULPHATE SOLUTIONS

Potentials (mV) recorded E_M	Volume of 0.233 M sodium thiosulphate obtained from Fig. 4, (mL)	Estimated molar concentrations of unknown ceric ammonium sulphate (M)	Estimated weight of cerium in ceric ammonium sulphate (g)/250 mL
376	7.20	0.06710	10.6112
348	5.00	0.04660	7.3693
326	4.10	0.03821	6.0425
296	2.80	0.02610	4.1274
264	0.40 - 0.50	0.00419	0.6626

RESULTS AND DISCUSSION

The redox reaction between Ce^{4+} and I^- ions is feasible since Ce^{4+} is a strong and powerful oxidizing agent due to its high value of reduction potential (E^0Ce^{4+}/Ce^{3+} = 1.44 V)[8] at 1 N H_2SO_4 solution. Literature survey[1] indicated that ceric salts at high acidic solutions are being used as volumetric oxidizing agents. Investigations of Atanasu[2,3], Willard and Young[4], Berry[5] and Wallace and Furman[6] revealed that ceric salts have wonderful applications in analytical chemistry. They also observed that ceric sulphate cannot be used in weak acid or neutral solutions because slightly soluble basic ceric salts are formed. Someya[7,8] carried out potentiometric studies of cerium by conventional method. After a break of few decades of initial research investigations of cerium as oxidizing agent and their applications, Anandamurthy and Palanna[10,11] have reported a novel technique for quantitative estimation of copper in copper salt and brass by iodo-potentiometric method. The redox reactions involved in such cases are rapid and quantitative in acidic solution (pH 1) and hence, can be exploited to carry out investigation to estimate cerium in salts through iodo-potentiometric method.

The redox reactions occurring when KI is added to cerium salt solution at pH 1 is represented as

$$2Ce^{4+} + 2I^- \rightarrow 2Ce^{3+} + I_2 \qquad (E_M)$$

The over all potential (E_M) is attributed due to these individual reactions as given

$$Ce^{4+} + e \rightarrow Ce^{3+} \qquad E^0_{Ce^{4+}/Ce^{3+}} = 1.44\ V \qquad (i)$$

$$2I^- \rightarrow I_2 + 2e \qquad E^0_{I^-/I_2} = -0.535\ V \qquad (ii)$$

The Ce^{4+} ions gets reduced to Ce^{3+} ions (i), whereas iodide (I^-) ions [$E^0_{I^-/I_2}$ = -0.535 V] gets oxidized (ii) quantitatively to free I_2.

The liberated free I_2 can be estimated volumetrically using standard sodium thiosulphate solution and freshly prepared starch as indicator (Table-1).

The iodine-thiosulphate redox reaction can be depicted as

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad (E_{EP})$$

The overall redox potential (E_{EP}) obtained at the end point of reaction is due to the contribution of the following redox reactions.

$$I_2 + 2e \rightarrow 2I^- \qquad E^0_{I^-/I_2} = +\ 0.535\ V \qquad (iii)$$

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e \qquad E^0_{S_2O_3^{2-}/S_2O_4^{2-}} = 0.09\ V \qquad (iv)$$

The I_2 gets reduced to I^- ions in the process and the thiosulphate changes to tetra-thionate ions. The potentiometric data obtained for all ceric salt concentrations are tabulated in Table-2.

The basic principle of iodometry is used for potentiometric titrations of ceric ammonium sulphate against standard sodium thiosulphate using starch as an indicator at pH 1. The iodo-potentiometric data (Table-2) of titrations for different molar concentrations (column 1) of cerium salt are shown in the Fig. 2. The potentials (E_M) are recorded in (column 2), which is due to redox reaction (eqn. 1).

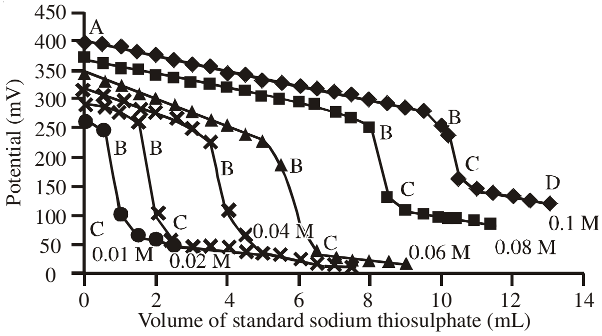

Fig. 2. Potentiometric titrations of ceric ammonium sulphate of different molar concentrations with standard sodium thiosulphate solution

The stoichiometric relationship of reactants and products of the redox reaction is

$$2 \text{ mol } Ce^{4+} = 1 \text{ mol of } I_2 = 2 \text{ mol } S_2O_3^{2-}$$

The potential established at the condition (E_M) may be described as:

$$E_M = E^o - \frac{0.0591}{2}\log_{10}\frac{[Ce^{3+}]^2[I_2]}{[Ce^{4+}]^2[I^-]^2} \tag{3}$$

At the point marked 'A' in the potentiometric titration curves, ceric ammonium sulphate solution develops a potential (E_M) as given by the conditions of eqn. 3, when $[Ce^{4+}]$ = a particular molar concentration (M) and $[I_2]$ = half the initial molar concentration of $[Ce^{4+}]$.

At the end point (E_P) of titration (eqn. 4), the over all potential (E_{EP}) refers to (midpoint of BC) when $[I_2] = 0$, that is, the over all potential is obtained, after all the liberated iodine is consumed completely by standard sodium thiosulphate solution.

$$E_{EP} = E^o - \frac{0.059}{2}\log_{10}\frac{[I^-]^2[S_4O_6^{2-}]}{[I_2][S_2O_3^{2-}]^2} \tag{4}$$

The variation of potential from A to B in the potentiometric curve (ABCD) indicates that the iodine (I_2) concentration decreases with the continuous addition of standard sodium thiosulphate (eqn. 2). Simultaneously, the concentration of $S_4O_6^{2-}$ increases due to the oxidation of $S_2O_3^{2-}$ by iodine into $S_4O_6^{2-}$ during the titration. The eqn. 5 accounts for the over all potential variation from A to B for the above redox reaction (eqn. 2).

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

After the end point (E_P), the change of potential as depicted in curve C to D, is due to the presence of excess titrant, $S_2O_3^{2-}$ along with Ce^{3+} and $S_4O_6^{2-}$ ions in solution. The behaviour is similar for other potentiometric titrations, but the end points are different depending on the molar concentration of ceric ammonium salt solutions.

The differential ($\partial^2E)/\partial^2V$) plots of potentiometric titrations of different molar concentrations of cerium salt solutions are shown in Fig. 3. The end points of potentiometric titrations (E_P) are also noted from differential plots. The potentials E_M (eqn. 1) and the end points of potentiometric titrations (V_2 mL) are tabulated in Table-2.

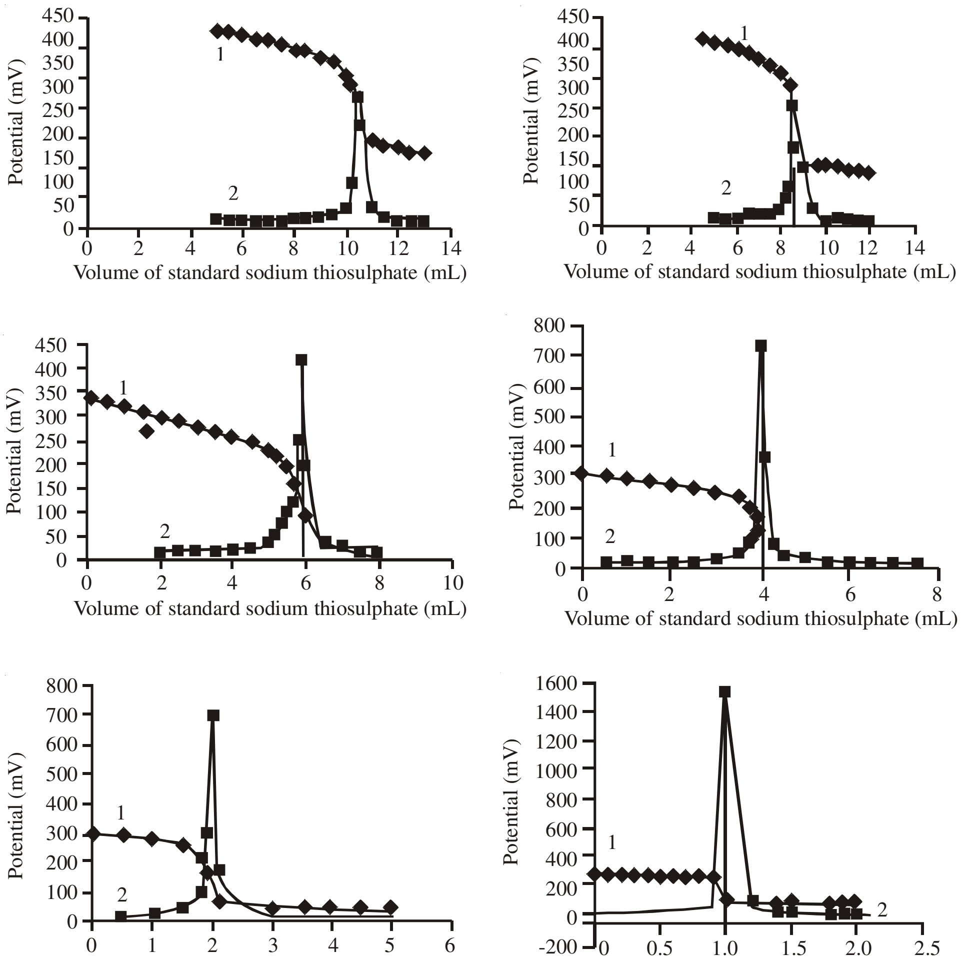

Fig. 3. Iodo-potentiometric titration curves for different concentrations: (1) variation of potential with the addition of standard $Na_2S_2O_3$ and (2) the differential ($\partial^2E)/\partial^2V$) plots of potentiometric titration

The column 2 of Table-2 indicates over all potential (E_M) measured at the conditions referred to (eqn. 1) and is found to vary linearly with different molar concentrations of ceric ammonium sulphate. Fig. 4 shows that a linear plot is observed, when the potentials, E_M, are plotted against the volumes (V_1 mL) of standard sodium thiosulphate consumed (Table-2, column 4) at the end point of titrations (both iodometric and potentiometric methods). A very useful link of information is observed to determine cerium in CAS potentiometrically. The results of investigation of potentiometric, iodometric and cerimetric analysis (Tables 1-4) are in conformity with each other indicating the success of this novel iodo-potentiometric method of determination of cerium using the redox chemistry.

Finally, it can be summarized that the following procedures have to be used to determine the amount of cerium (Ce^{4+}) in ceric ammonium sulphate solution by iodo-potentiometric method.

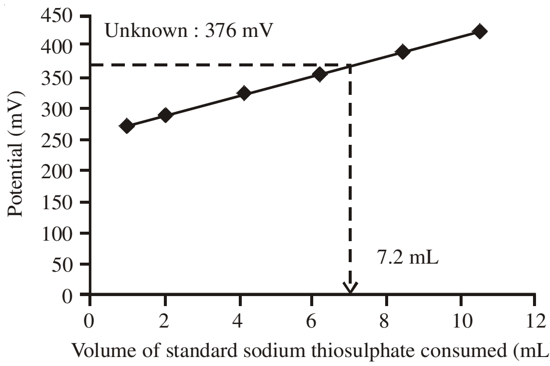

Fig. 4. Plot of potential (E_M) *versus* volume of standard $Na_2S_2O_3$

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