



Trade Science Inc.

ISSN : 0974-7419

Volume 10 Issue 12

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 10(12), 2011 [803-808]

Determination of chloride by direct titration with 1:1mercuric-thiocynate reagent

Shivaji R.Labhade^{*1}, Vishwas B.Gaikwad²

¹Department of Analytical Chemistry, K.T.H.M. College, Nashik (INDIA)

²University of Pune, Pune; Maharashtra State, (INDIA)

E-mail : srlabhade3571@rediffmail.com

Received: 13th July, 2011 ; Accepted: 13th August, 2011

ABSTRACT

A simple, sensitive, precise and rapid analytical method has been proposed for titrimetric determination of chloride using 1:1 mercuric-thiocynate reagent. The reaction of chloride ion with $[\text{Hg-SCN}]^+$ reagent and stoichiometric relationship required for determination of chloride are investigated. The results obtained in chloride determination by the proposed method are confirmed by Mohr's method. The effects of concentration of mercuric and thiocynate ions (in the reagent) on the analytical performance of the method are studied. Feasibility of the method furthermore tested for quantitative determination of hydrochloric acid, hydroxylamine hydrochloride, aniline hydrochloride and determination of level of chloride in synthetic mixture of anions and cations. The average accuracy is found good, which is evaluated by comparison of the results obtained with those claimed by other methods. Ions like H^+ , NH_4^+ , Li^+ , Na^+ , K^+ , Ca^{+2} , Mg^{+2} , Sr^{+2} , Ba^{+2} , Mn^{+2} , Zn^{+2} , Pb^{+2} , Cd^{+2} , Al^{+3} , BO_3^{-3} , NO_3^{-} , SO_4^{-2} , CO_3^{-2} , F^- , CH_3COO^- , HPO_4^{-2} do not show interference while ions such as Bi^{+3} , Ag^+ , Hg^{+2} , SCN^- , $\text{C}_2\text{O}_4^{-2}$, Br^- , I^- , $\text{S}_2\text{O}_4^{-2}$ and S^{-2} showed interference in determination of chloride by proposed method.

© 2011 Trade Science Inc. - INDIA

KEYWORDS

Chloride determination;
1:1 Mercuric-thiocynate reagent;
Hydrochloric acid;
Hydroxylamine hydrochloride;
Aniline hydrochloride.

INTRODUCTION

Chloride determination is the most common parameter measured in clinical and chemical laboratories. Level of chloride in blood is an important diagnostic index of various health problems related to hyper- or hypochloremia. Amount of chloride is an important aspects tested for judgment of extent of water pollution. So, many methods have been developed for determination of trace concentration of chloride. The most common are the spectrophotometric methods^[1-7], based on the measurement of absorbance of the red colored Fe(III)-thio-

cyanate complex, which is formed by the reaction of thiocynate ions (replaced by chloride analyte) with Fe(III). Accuracy of these methods is totally governed by the quantitative replacement of thiocynate ions by chloride ions. The electro-analytical methods^[8-10] are also found suitable for determination trace concentration of chloride using chloride ion sensitive/selective electrode; but preparation and maintenance of ion sensitive electrodes is a tedious job. Turbidimetric method is based on the reaction of chloride with silver ions and measurement of the turbidity caused by silver chloride precipitation^[11-13], but these methods are highly sensi-

Full Paper

tive to particle dimensions and applicable to colorless, opaque suspensions that do not show selective absorption^[14]. Traditionally, the commonly used titrimetric methods^[15] for determination of chloride are Mohr's method and Volhard's method. In Mohr's method, chloride solution is directly titrated against standard silver nitrate solution using potassium chromate indicator. Volhard's method of chloride determination involves the precipitation of chloride with an excess of silver nitrate in presence of nitric acid and titration of this excess of silver nitrate with a standard solution of ammonium thiocyanate. Both of these titrimetric methods are simple, rapid, and accurate, and need not required so costly sophisticated instrument for analysis but Mohr's method of determination of chloride is suitable only to neutral chloride solution. The spectrophotometric method^[16] proposed for determination of trace concentration of chloride through measurement of permittance^[17] of 1:1 mercuric-thiocyanate absorbing system was not found suitable for determination of chloride in a samples those shows the absorbance at 263nm. Consequently in this manuscript, we employed the same reagent *viz.* [Hg-SCN]⁺, for determination of chloride by direct titration.

EXPERIMENTAL

Reagents and solutions

All chemicals used were of analytical reagent grade and used without further purification. Double distilled water was used throughout the experimental work.

- 1.0L of 0.05M Hg(NO₃)₂ solution was prepared by dissolving 17.131 g of Hg(NO₃)₂.H₂O in 32.0ml of fuming HNO₃, followed by dilution with distilled water to make the final solution in 0.05M HNO₃. For exact molarity, Hg(NO₃)₂ solution was standardized against standard 0.05M EDTA using solid hexamine (buffer) and xylenol orange indicator.
- 1.0L of 0.05N KSCN solution was prepared by dissolving 4.859g of KSCN in distilled water. This solution was standardized against above 0.05M Hg(NO₃)₂ using ferric nitrate indicator.
- 1.0L of 0.1N chloride (3.55mg.ml⁻¹) solution was prepared by dissolving 5.85g of NaCl in distilled water. This solution was standardized against standard 0.05N AgNO₃ using potassium chromate indicator and 0.05N and 0.025N chloride solutions were also prepared.
- 1.0L of 0.05N AgNO₃ solution was prepared by

dissolving 8.494g of AgNO₃ in distilled water.

- 1.0L of 0.01M K₂CrO₄ solution was prepared by in distilled water.
- 1.0L of 0.5M Fe(NO₃)₃ solution was prepared 1.0M HNO₃.

Method for determination of chloride

The proposed method was first tested for determination of chloride in standard 0.1N NaCl solution, which was filled into a titration burette whose least count was 0.05ml. In a 100ml titration flask, 10.0ml of 0.025N [Hg-SCN]⁺ reagent was prepared by mixing 5.0ml of 0.05N KSCN solution into 5.0ml of 0.05M Hg(NO₃)₂ solution. In this prepared reagent, 5.0ml of 0.5M of ferric nitrate solution (in 1.0M HNO₃) was added as indicator and titrated against 0.1N NaCl solution till a slight reddish coloration was obtained to the titration mixture. Same titration was repeated three to four times. Normality and strength of chloride in the sample solution were determined and average value of chloride is determined. The same procedure was used for determination of chloride in 0.05N and 0.025N NaCl solution. Accuracy of the proposed method was confirmed through comparison of the results obtained with those claimed by Mohr's method. Efficacy of the method was then practiced for determination of chloride in different samples.

RESULTS AND DISCUSSION

Mercuric complexes

Both thiocyanate and chloride ions forms sufficiently stable complexes with mercuric ion. The cumulative formation constant (CFC) of mercuric-thiocyanate^[14, 18] complexes are log K₂=17.47 and log K₄=21.23, elucidates the formation of [Hg(SCN)₂] and [Hg(SCN)₄]⁻² complexes. Similarly, the CFC of mercuric-chloride^[14, 18] complexes are log K₁=6.74, log K₂=13.22, log K₃=14.07 and log K₄=15.07; which indicates respectively the formation of [Hg(Cl)]⁺, [Hg(Cl)₂], [Hg(Cl)₃]⁻ and [Hg(Cl)₄]⁻² complexes. Comparison of log K₂ and log K₄ values of both the complexes indicates that, thiocyanate complexes are more stable than chloride complexes. Although CFC values of thiocyanate complexes are greater but the reactivity of chloride towards the mercuric ion is quite more since chloride ions displaces the thiocyanate ion from mercuric-thiocyanate reagent^[1-7]. Furthermore the stability (of the complexes)

and reactivity are not consistent with each other^[19].

Chemical nature of the reagent

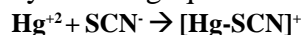
The method proposed for determination of chloride is based on the utilization of $[\text{Hg}(\text{SCN})]^+$ reagent, which is formed by mixing equivalent amount of thiocyanate ions and mercuric ions. The CFC of mercuric-thiocyanate does not provides the value of $\log K_1$ which indicate no possibility of formation of $[\text{Hg}(\text{SCN})]^+$ complex. When concentration of mercuric and thiocyanate ions is controlled in a 1:1 stoichiometric ratio, probably the species in the reagent is $[\text{Hg}(\text{SCN})]^+$.

Analyte quantification capacity

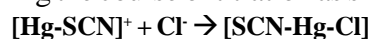
When 5.0ml of 0.05N SCN^- solution is mixed with 5.0ml of 0.05M Hg^{+2} solution, then 10ml of 0.025N $[\text{Hg-SCN}]^+$ reagent is obtained; which was when titrated against 0.05N chloride (analyte) solution using ferric nitrate indicator the end point of the titration was observed at 5.0ml chloride solution. According, 10ml of 0.025N $[\text{Hg-SCN}]^+$ reagent has capacity of determination of chloride exactly up to 8.875mg (*viz.* 5.0ml of 0.05N Cl^-). Likewise it was observed that, chloride quantification capacity of the reagent was observed to increase with increase in its volume. When 12.0ml and 14.0ml volumes of 0.025N reagent titrated against 0.05N chloride solution then end points of the titration were observed at 6.0ml and 7.0ml respectively. Thus, $[\text{Hg}(\text{SCN})]^+$ reagent showed the stoichiometric reactivity with the chloride ion represented by following chemical reaction.

Stoichiometry of titration reaction

Course of the reaction is also previously studied in detail with the help of absorption spectra^[16]. When equivalent amount of thiocyanate and mercuric ions are mixed together, the formation of reagent is represented by following equation.

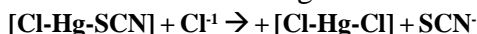


In $[\text{Hg-SCN}]^+$ reagent, one valency of mercuric ion is already satisfied by thiocyanate (when reagent is prepared) and second valency is fulfilled by chloride during the course of titration as shown below.



After fulfillment of both the valency of mercuric by two ions, a drop of addition of chloride solution displaces the thiocyanate ions from $[\text{Cl-Hg-SCN}]$ complex, which generates red coloration of ferric iron at the

end point of titration. End point and equivalence point of the titration are coincides with each other as reagent itself involved in showing the color change.



Second reaction completed at equivalence point of the titration indicates that, $[\text{Hg-SCN}]^+$ reagent and chloride ion reacts with each other in a 1:1 ratio, so the stoichiometric relationship required for determination of chloride is shown as under:

One gram equivalent of $[\text{Hg-SCN}]^+$ reagent = one gram equivalent of chloride

That is, 1000ml 1.0N $[\text{Hg-SCN}]^+$ reagent = 35.5 g of chloride

Therefore, 10ml 0.025N $[\text{Hg-SCN}]^+$ reagent = 0.008875 g = 8.875 mg of chloride

In this experiment 10ml 0.025N $[\text{Hg-SCN}]^+$ reagent solution is allowed to react with chloride analyte (always added from the burette) and burette reading is recorded. Suppose, this much amount (10ml 0.025N) of reagent when reacts with 0.1N chloride solution the end point is obtained at 2.50ml, then milligram level of chloride per milliliter of chloride sample is:

$$\begin{aligned} \text{The amount of chloride} &= \frac{8.875 \text{ mg}}{\text{Burette reading}} = \frac{8.875 \text{ mg}}{2.50 \text{ ml}} \\ &= 3.55 \text{ mg ml}^{-1} \end{aligned}$$

Alternatively, normality (of chloride solution) is determined and is multiplied by 35.5 (equivalent weight) that gives the strength of chloride in grams per liter. For quantitative determination of sample containing ionisable chloride, the normality is multiplied by the equivalent weight of the sample gives the strength in grams per liter.

Course of the titration

In this experiment, a fixed volume of the reagent (standard solution) taken in a titration flask is titrated in presence of ferric iron (indicator) against the chloride analyte (added from the burette), till red coloration to the titration mixture developed because of the reaction of displaced thiocyanate ion with $\text{Fe}(\text{III})$. In contrast, when chloride solution taken in a titration flask (along with the ferric iron) is titrated against the reagent, addition of a drop of reagent generates red color to the titration mixture. Because the addition of reagent into a solution containing excess of chloride ions, that results in formation of $[\text{Hg}(\text{Cl})_2]$, $[\text{Hg}(\text{Cl})_3]$ or $[\text{Hg}(\text{Cl})_4]^{-2}$ com-

Full Paper

plexes and which involved in rapid displacement of thiocyanate ions from the reagent as soon as it added. It was also tested that, chloride ion solution initially treated with excess of mercuric ion solution and for unused valency of mercuric ions when titrated against standard solution of thiocyanate using ferric iron indicator; then non-stoichiometry in burette readings was observed. Same is the reason for this non stoichiometry that is, the formation of $[\text{Hg}(\text{Cl})_2]$, $[\text{Hg}(\text{Cl})_3]^-$ or $[\text{Hg}(\text{Cl})_4]^{2-}$ complexes along with $[\text{SCN-Hg-Cl}]$ complex. Consequently 1:1 mercuric-thiocyanate reagent was found good for determination of chloride.

Effect of excess thiocyanate and mercuric ions

The surplus concentration of mercuric ions or thiocyanate ions (in the reagent) affects the chloride quantification capacity of the reagent consequently end point of the titration was observed to be changed. This study was carried out by testing 10.0ml of the reagent in two compositions. The first composition formed by mixing 6.0ml of 0.05N SCN^- in 4.0ml of 0.05M Hg^{+2} solutions; this reagent when titrated against 0.05N NaCl solution the end point was observed at 1.95ml. This is because most of the reaction sites on mercuric ions are blocked due to the formation of $\text{Hg}(\text{SCN})_2$ along with $[\text{Hg-SCN}]^+$. The second composition tested which was having composition of 4.0ml of 0.05M SCN^- in 6.0ml of 0.05M Hg^{+2} , by this reagent chloride determination capacity was increased and end point was observed at 8.10 ml (for 0.05N Cl⁻); since more reaction sites becomes available on free mercuric ions. This study elucidates that extra concentration of mercuric and thiocyanate ions in the reagent also generate non-stoichiometry in burette readings; theoretically, these burette readings must be at 2.0ml and 8.0ml respectively. In this experiment, it is necessary to prepare the reagent in which the concentration of mercuric and thiocyanate ions should in a 1to1 ratio. When the concentration of both mercuric and thiocyanate solutions are accurately known by standardization, it is easy to prepare reagent in a 1:1 ratio, and is this composition is also essential for calculation of chloride ion concentration in the sample using reaction stoichiometry. The preparation of reagent should be just before the course of titration otherwise the formation of precipitate in previously prepared reagent changes the composition of the reagent and that affect the measurement.

Testing of other compositions of the reagent

The other compositions of the reagent in which concentration of mercuric to thiocyanate ions was controlled in a 2:1 and 3:1 stoichiometric ratio, are also tested for determination of chloride. For testing of 2:1 composition 5.0ml of 0.05N SCN^- solution was added in 10.0ml of 0.05M Hg^{+2} solution and total 15.0ml of this reagent when titrated against 0.05N NaCl solution then end point of the titration was observed at 15.40ml (true value 15.0ml). Similarly, 3:1 composition tested in which 5.0ml of 0.05N SCN^- solution was added in 15.0ml of 0.05M Hg^{+2} solution and total 20.0ml of this reagent when titrated against 0.05N NaCl solution then end point was observed at 25.80ml (true value 25.0ml). Thus, destroyed stoichiometry in burette readings was observed by the application of 2:1 and 3:1 composition of the reagent, consequently the reagent in which mercuric and thiocyanate ions are in a 1:1 stoichiometric composition was observed best for determination of chloride.

Analytical performance of the method

Analytical performance of the proposed method was tested with quantitative determination of chloride in 0.10N, 0.05N and 0.025N solutions of NaCl by using 10.0ml of 0.025N $[\text{Hg-SCN}]^+$ reagent. The normality of these chloride solutions was determined by proposed method and it was also confirmed by Mohr's method using 0.05N AgNO_3 titrant. The results of these assay is summarized in TABLE 1.

TABLE 1 : Results obtained in quantitation of chloride by proposed method and Mohr's method.

Strength of chloride (N)	Amount of chloride (g/L)	Average chloride found (n=4) (g/L)	
		Proposed method	Mohr's method
0.1000	3.5500	3.5498	3.5498
0.0500	1.7750	1.7795	1.7740
0.0250	0.8875	0.8863	0.8863
0.0125	0.4438	0.4413	0.4427

Effect of nitric acid

Fuming nitric acid was used for preparation 0.05M $\text{Hg}(\text{NO}_3)_2$ and 0.5M $\text{Fe}(\text{NO}_3)_3$ solutions. Excess amount of nitric acid does not affect the analytical performance of the method. It was tested by adding extra 5.0ml and 10.0ml aliquots of 1.0M HNO_3 solution in the reagent as well as in chloride solution during the titration. Unaffected stoichiometric burette readings in-

dicates non interfering role of nitric acid.

Interference study

One to one stoichiometric reaction of chloride ion with the 1:1 mercuric-thiocyanate reagent is the best judgment of detection of the interfering role of foreign ions, the disturbance in stoichiometry executes the interference. The interference study of H^+ , NH_4^+ , Li^+ , Na^+ , K^+ , Mg^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mn^{+2} , Zn^{+2} was carried out through quantitative determination of chloride in their 0.05N chloride solutions. For interference study of SO_4^{2-} , NO_3^- , CO_3^{2-} , F^- , CH_3COO^- and HPO_4^{2-} ions 0.1N solutions of their sodium salt and for BO_3^{3-} 0.01N H_3BO_3 solution was used. For confirmation of interfering role of Pb^{+2} , Cd^{+2} and Al^{+3} 0.1N solutions of their nitrate salt were used. The detection of interfering role of these anions and cations, 10.0ml of 0.1N solution of foreign ion was added to 10.0ml of 0.1N NaCl solution and this mixture (filled in a burette) was titrated against reagent for determination of exact normality (theoretically 0.05N) by proposed method. The normality of mixtures was also confirmed by Mohr's method. The normality determined experimentally when matched to theoretical value was the conclusion employed for detection of non interference role of the added ion. All above anions and cations do not interfere in the determination of chloride by proposed method. But the cations like Ba^{2+} , Pb^{2+} , Cd^{2+} and Al^{3+} shown the interference in chloride determination by Mohr's method (the solution of Pb^{2+} , Cd^{2+} and Al^{3+} are acidic). Oxalate interfere in chloride determination by proposed method (not by Mohr's method) because it reacts with indicator and produces yellow colored ferric oxalate, consequently the detection of end point becomes difficult and takes more amount of chloride for generation of red color to the titration mixture. The anions like I^- , $S_2O_4^{2-}$ and S^{2-} generates precipitate with the reagent hence are the serious interfering ions. In addition, the cations such as Bi^{3+} and Ag^+ are the interfering ions, which generate the precipitate with the chloride which remains stable in presence of the reagent. Determination of chloride is based on the stoichiometric relationship of concentration of reagent and concentration of analyte consequently presence of Hg^{+2} and SCN^- in the reagent or analyte interfere

Applications of the method

The feasibility of the proposed method has been then tested for quantitative determination samples con-

taining ionisable chloride ions through the reaction of chloride with $[Hg-SCN]^+$ reagent. Standard solutions of hydrochloric acid (HCl), hydroxylamine hydrochloride (HAHCl), aniline hydrochloride (AHCl) were analyzed for exact normality and strength is determined by multiplying normality with equivalent weight. The results of this assay are shown in TABLE 2. Mohr's method do not gives the results for assay of these samples since it is applicable to neutral solution of chloride, so strength is alternatively confirmed by the direct titration against standard NaOH solution using phenolphthalein indicator.

The level of chloride in synthetic mixture of anions (SMA) (having composition: 50.0ml of 0.1N NaCl + 10.0ml of 0.1N Na_2CO_3 + 10.0ml of 0.1N Na_2SO_4 + 10.0ml of 0.1N Na_2HPO_4 + 10.0ml of 0.1N CH_3COONa + 10.0ml of 0.1N H_3BO_3) and synthetic mixture of cations (SMC) (having composition: 50.0ml of 0.1N NaCl + 10.0ml of 0.1N $Ni(NO_3)_2$ + 10.0ml of 0.1N $Ca(NO_3)_2$ + 10.0ml of 0.1N $MgSO_4$ + 10.0ml of 0.1N $ZnSO_4$ + 10.0ml of 0.1N $MnSO_4$) were analyzed by using 10.0ml of 0.025N reagent. The results of this assay are also confirmed by Mohr's method and shown in TABLE 2.

TABLE 2 : Results obtained in quantitative determination of samples containing ionisable chloride

Sample tested	Strength (N)	Strength (g/L)	Strength found (g/L) (n=4)
HCl	0.10	3.650	3.650
	0.05	1.825	1.821
AHCl	0.10	12.95	12.95
	0.05	6.475	6.443
HAHCl	0.10	6.943	6.943
	0.05	3.472	3.472

CONCLUSIONS

This manuscript gives the method of employment of $[Hg-SCN]^+$ absorbing reagent for titrimetric determination of chloride. The reaction of chloride ion with $[Hg-SCN]^+$ reagent is fast, irreversible, quantitative and occurred according to reaction stoichiometry, so the method showed enormous selectivity which can also be judged from the interference study. Determination of sensitivity is not the aim of this study however; method was work effectively for determination

Full Paper

TABLE 3 : Results obtained in determination of level of chloride in synthetic mixture of anions and cations

Mixture with chloride strength	Amount of chloride (mg/ml)	Chloride found (mg/ml) (avg. n=4)	
		Proposed method	Mohr's method
0.050N SMA	1.7750	1.7661	1.7662
0.025N SMA	0.8875	0.8876	0.8920
0.050N SMC	1.7750	1.7751	1.7745
0.025N SMC	0.8875	0.8831	0.8869

of chloride in 0.1N to 0.025N NaCl solution. Detection of the exact end point at lower concentration of chloride can be done by increasing the volume of indicator solution. In this experiment, 10.0ml of ferric nitrate indicator was used for titration of 0.025N NaCl solution. The results reported in TABLE 1, 2 and 3 shows the method has good accuracy and precision. The results obtained in determination of chloride in synthetic mixture of cations and anions also execute the applications of the method for analysis of different samples including water. The proposed method does not involve the formation of precipitate during the course of titration consequently it is free from co-precipitation of chloride ions. As reagent it self involved in generation of color near end point consequently does not associated with titration error. The method works well for analysis of chloride in neutral as well as acidic sample solutions. Method is quite simple, free from interference and need not require so much costly chemicals, organic solvents and sophisticated instrument. The method does not produce accurate results with 0.0125N NaCl solution. For samples containing lower concentration the chloride the spectrophotometric method based on permittance measurement was observed good.

ACKNOWLEDGEMENTS

Authors thank the Sarchitanis and the Managing Committee of Maratha Vidya Prasarak (MVP) Samaj, Nashik for providing the necessary infrastructure and Board of College and University Development (BCUD), University of Pune, Pune for providing the funds. This article is dedicated to our colleagues *late Prof. K. S. Khachane* and *late Prof. U. G. Patil* who were actively involved in improving the teaching, learning and evaluation processes in MVP Samaj.

REFERENCES

- [1] Tetsutaro Yoshinaga, Koki Ohta; Analytical Sciences. **6**, 57-60 (1990).
- [2] J.F.van Staden, S.I.Tlowana; Fresenius J.Anal.Chem., **371**, 396-399 (2001).
- [3] O.W.Lau, C.S.Mok; Journal of the Science of Food and Agriculture, **31**, 1275-1278 (1980).
- [4] F.Maya, J.M.Estela, V.Cerdà, Talanta., **74**, 1534-1538 (2008).
- [5] V.J.Koshy, V.N.Garg; Talanta., **34**, 905-908 (1987).
- [6] L.N.Moreira, L.A.Ramos, C.R.T.Tarley, P.O.Luccas; J.Flow Injection Anal., **24**, 13-16 (2007).
- [7] P.Venkatesan, P.V.R.S.Subrahmanyam, D.R.Pratap; International Journal of Chem. Tech. Research, **2**, 54-56 (2010).
- [8] R.K.Mahajan, I.Kaur, R.Kaur, S.Uchida, A.Onimaru, S.Shinoda, H.Tsukube; Chem.Comm., 2238-2239 (2003).
- [9] R.K.Mahajan, R.Kaur, S.Tabassum F.Arjmand, S.Mathur; Electrochimica Acta., **52**, 408-414 (2006).
- [10] R.K.Mahajan, I.Kaur, R.Kaur, A.Onimaru, S.Shinoda, H.Tsukube; Anal.Chem., **76**, 7354-7359 (2004).
- [11] Snell and Snell, Colorimetric Methods of Analysis, 3d Edtion, Van Nostrand, Princeton, NJ, (a) Vol. I, (1949) and (b) Vol. II, (1959).
- [12] E.B.Sandell; Colorimetric Determination of Traces of Metals, 3d Edtion, Interscience, New York, (1959).
- [13] Challis and Jones; Analyst., **81**, 703 (1956).
- [14] P.Patnaik, 'Dean's Analytical Chemistry', McGraw-Hill, New York, 2nd Edtion pp. 6.42, 2.9, (2004).
- [15] G.H.Jeffery, J.Bassett, J.Mendham, R.C.Denny; 'Vogel's Textbook of Quantitative Analysis', 5th Edition, Longman Group UK Ltd., England pp. 349, 353-356 (1989).
- [16] S.R.Labhade, V.B.Gaikwad; Anal.Chem.An Indian Journal, Vol. 10, Article in Press.
- [17] S.R.Labhade, V.B.Gaikwad; Asian J.of Chem., **21**, 5285-5294 (2009).
- [18] J.G.Speight; 'Lange's Handbook of Chemistry', McGraw-Hill, New York, 16th Edition pp. 1.358-1.362 (2005).
- [19] H.Taube; Chem.Rev., **50**, 69-125 (1952).