ISSN : 0974-7419 Volume 10 Issue 10

Trade Science Inc.

Analytical CHEMISTRY
An Indian Journal

Full Paper

ACAIJ, 10(10) 2011 [657-664]

Utilization of the ideal composition of mercuric-thiocynate absorbing system for spectrophotometric determination of chloride ion through measurement of permittance

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Received: 22nd June, 2011 ; Accepted: 22nd July, 2011

ABSTRACT

A simple, sensitive, precise and rapid analytical method has been proposed for indirect spectrophotometric determination of chloride. The extent of absorbance quenching capacity of chloride towards different compositions of mercuric-thiocynate reagent and the linearity of permittance against concentration are the parameters tested in search of the best composition of reagent. The reactions of chloride ion with 1:1 $[Hg\text{-}SCN]^+$ absorbing reagent are investigated and method is examined for determination of chloride at 263nm. Average values of permittance coefficient, relative error and RSD for quantitation of chloride in the range of 2.0×10^{-4}g to 1.8×10^{-3}g are found 4.3917 lit.$g^{-1}cm^{-1}$, 0.198% and 0.4725% respectively. The effects of concentration of mercuric and thiocynate ions on the analytical performance of the method are studied. The limit of determination of chloride with the variable volumes of reagent is determined. Feasibility of the method furthermore tested for estimation of chloride in standard solutions of hydrochloric acid, hydroxylamine hydrochloride, 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 standards. Ions like H^+, NH_4^+, Li^+, Na^+, K^+, Ca^{+2}, Mg^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Zn^{+2}, SO_4^{-2}, CO_3^{-2}, F^-, CH_3COO^-, HPO_4^{-2} do not show interference while ions such as Bi^{+3}, Ag^+, $C_2O_4^{-2}$, NO_2^-, Br^-, I^-, $S_2O_4^{-2}$, and S^{-2} showed interference in determination of chloride by this method.

KEYWORDS

Chloride determination;
Mercuric-thiocynate reagent;
Permittance;
Permittance coefficient;
Hydrochloric acid;
Hydroxylamine hydrochloride.

INTRODUCTION

Determination of trace quantity of chloride ion in various types of sample is a challenging problem in current chemical analysis. Chloride ion determination is most common parameter measured in clinical laboratories and its amount in blood is an important diagnostic index of various health problems related to hyper- or hypochloremia. Chloride determination is also one of the important aspects tested for the judgment of level of water pollution. Consequently, numerous analytical methods have been developed for determination of trace concentration of chloride. Out of these the most common are the spectrophotometric methods[1-5], based on the measurement of absorbance of the red colored Fe(III)-thiocyanate complex, which is formed by the reaction of thiocynate ions (replaced by chloride analyte) with Fe(III). Medical preparations available in the form of chloride salt are also analyzed on the basis of their chloride ion concentration with the same approach[6,7]. Accuracy of these methods of determination of the chloride at a trace level, is totally governed by the quantitative replacement of thiocynate ions (from mercuric thiocynate reagent) equivalent to chloride ions; since the $[Hg\text{-}(SCN)_2]$ reagent is quite stable. In addition, rather than the replacement of the thiocynate, chloride ions may directly unite with $[Hg\text{-}(SCN)_2]$ reagent and it may form the thiocynate-chloride complex of mercuric ion with coordination number greater than two. In present manuscript, with the help of absorption spectra we have investigated reactions of chloride ion with 1:1 mercuric-thiocyanate reagent, since it was observed the ideal composition for determination of chloride. Likewise to the earlier study[8-12], the absorbance quenching capability of analyte (chloride ion) towards the absorbing system viz. $[Hg\text{-}SCN]^+$ is the theme employed for determination of permittance[8].

EXPERIMENTAL

Chemicals and solutions

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

a) 1.0L of 0.01M Hg^{+2} solution was prepared by dissolving 3.427g of $Hg(NO_3)_2.H_2O$ in 12.6ml of fuming HNO_3, followed by dilution with distilled water to make the final solution in 0.2M HNO_3. For exact molarity, this $Hg(NO_3)_2$ solution was standardized against standard 0.01M EDTA using solid hexamine (buffer) and xylenol orange indicator.

b) 1.0L of 0.01N SCN^- solution was prepared by dissolving 0.972g of KSCN in distilled water. This solution was standardized against above 0.01M $Hg(NO_3)_2$ using ferric nitrate indicator.

c) 1.0L of 0.01N chloride ($0.355mg.ml^{-1}$) solution was prepared by dissolving 0.585g of NaCl in distilled water. This solution was standardized against standard 0.01N $AgNO_3$ using potassium chromate indicator and then $0.200mg.ml^{-1}$ chloride solution was also prepared.

Instruments and accessories

a) Shimadzu UV-Vis. Spectrophotometer (model UV-1800) was used for measurement of %T. The software UVProbe version 2.33 was used to obtain the absorption spectra.

b) Equip-tronics pH-meter (model EQ-610) was used to check the pH of test solutions.

Method for determination of chloride

The proposed method was primarily tested for determination of chloride in the range of 0.355mg to 1.775mg by using 1:1 $[Hg\text{-}SCN]^+$ absorbing reagent. Initially, 200.0ml of 0.005M reagent was prepared by adding 100.0ml of 0.01M KSCN solution into 100.0ml 0.01M $Hg(NO_3)_2$ solution. The test solutions (TS) of chloride in this concentration range were prepared by adding 1.0ml, 2.0ml, to 5.0ml aliquots of $0.355mg.ml^{-1}$ chloride (viz. 0.01N NaCl) solution sequentially into 25ml graduated flasks (numbered as 2 to 6) each containing 10.0ml of 0.005M absorbing system/reagent. Flasks were shaken thoroughly for quantitative complexation of chloride with $[Hg\text{-}SCN]^+$ reagent and further diluted up to the mark with distilled water. Similarly excluding only chloride solution, the reagent blank (RB) solution[8] was prepared in flask No.1. The true blank (TB) or reference solution[8] used here was distilled water. The %T of RB as well as each TS was measured at 263nm against distilled water as a reference. %T of the RB was used to obtain the clearance[8] value of test solutions. The graph of logarithm of clearance viz. permittance[8] against the concentration of chloride was used for determination of chloride. Efficacy of the method was then practiced for determination of chloride with 2:1, 3:1 and 4:1 stoichiometric composition of mercuric-thiocynate reagent and further applied for quantitative determination of chloride in different samples.

RESULTS AND DISCUSSION

Stability of mercuric-chloride and mercuric-thiocyanate complexes

Mercuric ion forms complexes with many anions including chloride and thiocynate. The cumulative formation constant (CFC) of mercuric-chloride[13,14] complexes are $\log K_1=6.74$, $\log K_2=13.22$, $\log K_3=14.07$

and log K_4=15.07; which indicates respectively the formation of $[Hg(Cl)]^+$, $[Hg(Cl)_2]$, $[Hg(Cl)_3]^-$ and $[Hg(Cl)_4]^{-2}$ complexes. The valves CFC illustrate that, all chloride complexes are sufficiently stable. Similarly, the CFC of mercuric-thiocynate[13,14] complexes are log K_2=17.47 and log K_4=21.23, elucidates the formation of $[Hg(SCN)_2]$ and $[Hg(SCN)_4]^{-2}$ complexes. Comparison of log K_2 and log K_4 values of both the complexes indicates that, thiocynate complexes are more stable than chloride complexes. Although CFC values of thiocynate complexes are greater but the reactivity of chloride towards the mercuric ion is quite more; since the stability and reactivity are not consistent with each other[15].

Selection of the wavelength for measurement

The method proposed here for determination of chloride is based on absorbance quenching ability of chloride ion towards $[Hg\text{-}SCN]^+$ reagent. The absorption spectra of mercuric-thiocynate and mercuric- chloride complexes were obtained against distilled water as a reference. The solutions for absorbance measurement are prepared by controlling their concentration in such a way that, it will appear nearly same in the test solutions. Figure 1 illustrates that, the spectral region 260 to 265nm (centered at 263nm) at which chloro-complexes exhibits minimum absorbance and absorbing reagent in a 1:1 stoichiometric ratio (viz. $[Hg\text{-}SCN]^+$ system) exhibits sufficient absorbance. The quench in absorbance was observed on addition of chloride ion represented by spectrum of the [Cl-Hg-SCN] complex. In addition, dilute HNO_3 showed minimum absorbance at 263nm and the solutions of free thiocynate (KSCN) and free chloride (NaCl) ions were observed nearly transparent at 263nm.

Absorption spectra of mercuric-chloride complexes

Controlling chloride ion concentration with the fixed concentration of mercuric nitrate, the solutions of chloro-complexes such as, $[Hg(Cl)]^+$, $[Hg(Cl)_2]$, $[Hg(Cl)_3]^-$ and $[Hg(Cl)_4]^{-2}$ were prepared and their absorption spectra were obtained against distilled water. This absorption spectra interprets that, all mercuric-chloride complexes show negligible absorbance at 263nm (figure 1), but complex with coordination number (CN) two viz. $[Hg(Cl)_2]$, reveals the lowest absorption. On addition of chloride solution, same truth is responsible for decrease in absorbance of the $[Hg(SCN)]^+$ system since that results in formation of [SCN-Hg-Cl] complex with CN two.

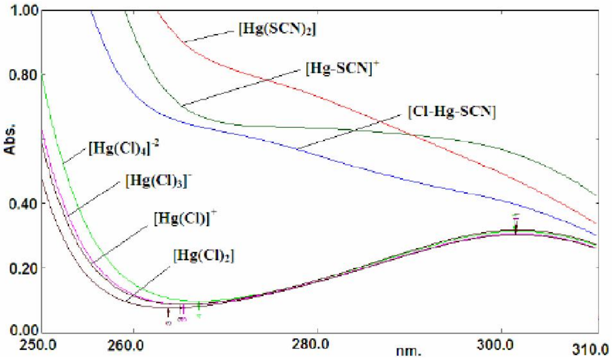

Figure 1 : Absorption spectra of mercuric-chloride complexes and mercuric-thiocynate complexes obtained against distilled water.

Absorbance quenching mechanism

The absorbance quenching action of chloride analyte on 1:1 $[Hg\text{-}SCN]^+$ absorbing system was studied by preparing the test solutions of chloride in the range of 0.355 to 5.325mg. These solutions were prepared at 25ml dilution with 10.0ml of 0.005M absorbing reagent by adding sequentially 1.0ml, 2.0ml, to 15.0ml aliquots of 0.355mg ml^{-1} of chloride (0.01M NaCl) solution. The measurement at 263nm was observed inconsistency in the %T reading (TABLE 1) which reveals the possibility of formation of different reaction products with the absorbing reagent. Therefore, the absorption spectra (figure 2) of these test solutions were also taken to study the course of complexation reactions.

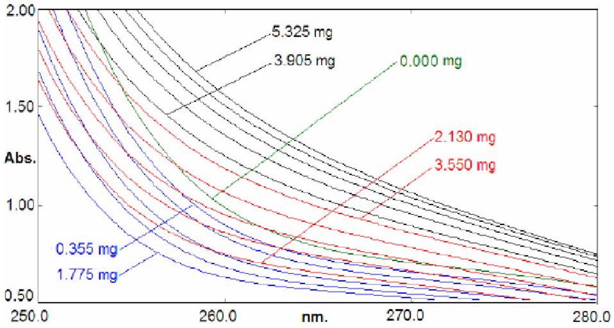

Figure 2 : Absorption spectra of test solutions containing different concentration of chloride (figures in mg) obtained against distilled water

Absorption spectra (figure 2) demonstrate that, the RB solution containing no chloride ions exhibits enough absorbance. As the concentration of chloride in the test solutions increased successively from 0.355mg, 0.710mg, up to 1.775mg; the absorbance of test solutions was observed to decrease linearly because of the conversion of $[Hg\text{-}SCN]^+$ into [SCN-Hg-Cl] viz. complex with CN two (figure 1 and 2). When the concentration of chloride ion in the test solutions was increased more than 1.775mg, viz. 2.130mg, 2.485mg and so on, the absorbance of the solutions was also observed to increase successively because of the formation of complexes having CN three and four, which exhibits more absorbance (figure 2).

Chemical composition of absorbing reagent

The CFC of mercuric-thiocyanate does not provides the value of log K_1 which indicate no possibility of formation of $[Hg(SCN)]^+$ complex and it was also confirmed through absorption spectra of $[Hg(SCN)]^+$ and $[Hg(SCN)_2]$ complexes, which appeared to be nearly same but showed different value of absorbance. Accordingly, when concentration of mercuric and thiocyanate ions is controlled in a 1:1 stoichiometric ratio, probably the species in the absorbing reagent are $[Hg(SCN)_2]$ and Hg^{2+}. When chloride ions are added to the absorbing reagent definitely that get unite with free Hg^{2+} ions and produces chloro complex such as $[Hg(Cl)]^+$, $[Hg(Cl)_2]$, $[Hg(Cl)_3]^-$ or $[Hg(Cl)_4]^{-2}$. If the reaction of the added chloride occurred with free Hg^{2+}, then at the selected spectral region (figure 1), the absorbance of Hg^{+2} and all chloro complexes is almost same consequently, no quench in system's absorbance. However, significant quench in absorbance is because of the reaction of chloride ions with other species present in the absorbing reagent. Chemically, at equal concentration of mercuric and thiocyanate ions, the species that exist in the absorbing reagent is $[Hg(SCN)]^+$ or Hg^{+2} associated with SCN^- ions. Furthermore, it was tested that, $[Hg(SCN)_2]$ species do not showed the absorbance quenching mechanism with the chloride ions. Similarly no decrease or increase in %T reading was observed when an experiment was run for determination of chloride using only mercuric ions solution.

Course of the complexation reactions

Addition of chloride ion solution into 1:1 mercuric-thiocyanate reagent, the reactions which likely occurred in the test solutions and are responsible for decrease or increase in absorbance of the solutions, are suggested below.

(1) $Hg^{+2} + SCN^- \rightarrow [Hg\text{-}SCN]^+$

This reaction is the formation of absorbing reagent with equal concentration of mercuric and thiocyanate ions. Therefore, reagent blank (RB) solution, showing sufficient absorbance (figure 1 and 2) contain only $[Hg\text{-}SCN]^+$ species.

(2) $[Hg\text{-}SCN]^+ + Cl^- \rightarrow [SCN\text{-}Hg\text{-}Cl] + [Hg\text{-}SCN]^+$

The second reaction occurred in test solutions those contained insufficient chloride analyte; as a result part of the absorbing system is converted into product having CN two, which reflects the quench in the absorbance.

(3) $[Hg\text{-}SCN]^+ + Cl^- \rightarrow [SCN\text{-}Hg\text{-}Cl]$

The third reaction possibly takes place into those test solution in which the concentration of $[Hg\text{-}SCN]^+$ reagent and chloride ion is exactly in a 1:1 stoichiometric ratio. This is the limit of determination of the chloride by this method. It is judged by maximum quench in absorbance and associated with the formation of [SCN-Hg-Cl] product. Test solutions in which reactions 2 and 3 occurred, those consumes all the added chloride ions and do not replaces the thiocyanate ions for generation of red color with ferric ions (TABLE 1).

TABLE 1 : Test solutions of chloride in the range of 0.355mg to 5.325mg were prepared with 10.0ml of 0.005M absorbing reagent and measurement was carried out at 25ml dilution

0.01M NaCl (ml)	Cl^- (mg)	%T at 263 nm.	%T*at 460 nm.
0.0	0.000	10.47	99.13
1.0	0.355	12.09	99.18
2.0	0.710	13.96	99.13
3.0	1.065	16.11	99.15
4.0	1.420	18.57	99.19
5.0	1.775	21.33	99.11
6.0	2.130	16.94	97.64
7.0	2.485	13.62	84.35
8.0	2.840	10.81	71.86
9.0	3.195	8.61	60.89
10.0	3.550	6.76	52.46
11.0	3.905	5.41	45.14
12.0	4.260	4.31	38.76
13.0	4.615	3.45	33.17
14.0	4.970	2.74	28.27
15.0	5.325	2.27	24.55

***Solutions spiked with 1.0ml of saturated $Fe(NO_3)_3$ and %T was measured at 460nm.**

At greater concentration of chloride, the possibility of formation of $[Hg(Cl)_2]$, $[Hg(Cl)_3]^-$ or $[Hg(Cl)_4]^{-2}$ complexes increases along with the other complexes such as, $[SCN\text{-}Hg(Cl)_2]^{-1}$, $[SCN\text{-}Hg(Cl)_3]^{-2}$ etc. (reactions 4 and 5). The formation of such a larger sized chloro thiocynato complex anions increases the optical density of test solutions (figure 2). The reactions 4 and 5 also showed the mechanism of replacement of the thiocynate ions from the absorbing reagent, which generates the red color with ferric ions (TABLE 1). Thiocynate ions and chloro complexes show insignificant absorbance at 263nm, however significant increase in absorbance is only because of the formation of chlorothiocynato complexes having CN greater than 2.

(4) $[Hg\text{-}SCN]^{+1} + Cl^{-1} \rightarrow [SCN\text{-}Hg(Cl)_2]^- + [Cl\text{-}Hg\text{-}Cl] + SCN^-$

(5) $[Hg\text{-}SCN]^{+1} + Cl^{-1} \rightarrow [SCN\text{-}Hg(Cl)_3]^{-2} + [Hg(Cl)_4]^{-2} + [Cl\text{-}Hg(Cl)_2]^- + SCN^{-1}$

Reaction stoichiometry and analyte quantification capacity

According to the course of complexation reactions, the limit of determination of chloride is confined by reaction 3 at which the chloride concentration with absorbing reagent is in a 1:1 stoichiometric ratio. When 5.0ml of 0.01M SCN^- solution is mixed with 5.0ml of 0.01M Hg^{+2} solution, then 10ml of 0.005M $[Hg\text{-}SCN]^+$ absorbing reagent is obtained; which has capacity of determination of chloride exactly equal to 1.775mg (viz. 5.0ml of 0.01N Cl^-). Likewise to earlier[10-12] study, it was observed that analyte quantification capacity of the reagent was observed to increase with increase in its volume. When 8.0ml, 10.0ml, 12.0ml and 14.0ml volumes of 0.005M reagent tested for determination of chloride then system shows linearity respectively up to 1.420mg (4.0ml of 0.01N Cl^-), 1.775mg (5.0ml of 0.01N Cl^-), 2.130mg (6.0ml of 0.01N Cl^-) and 2.485mg (7.0ml of 0.01N Cl^-) of chloride. Thus, absorbing system showed the stoichiometric reactivity with the analyte.

Effect of excess thiocynate and mercuric ions

The surplus concentration of mercuric or thiocynate in absorbing reagent does not affect the analytical performance of the method, but it affect the chloride quantification capacity of the reagent. This study was carried out by testing 10.0ml of absorbing reagent in two compositions. The first composition formed by mixing 120ml of 0.01M SCN^- in 100ml of 0.01M Hg^{+2} solutions; with this the system showed linearity up to 1.065 mg of chloride. This is because most of the reaction sites on mercuric ions are blocked due to the formation of $Hg(SCN)_2$. The second composition tested which was having composition of 100ml of 0.01M SCN^- in 120ml of 0.01M Hg^{+2}; by this system chloride determination capacity was increased up to 2.130mg, since more reaction sites becomes available on excess mercuric ions. Surplus mercuric or thiocynate ions in the absorbing reagent affect the values permittance and hence permittance coefficient, because of the change in composition of absorbing medium. It was observed that, with extra concentration of thiocynate, the value of permittance coefficient was observed to increase and it was get decreased with excess of mercuric ions.

Utilization of other compositions of the reagent

Other compositions of the absorbing reagent in which concentration of mercury to thiocynate was controlled in a 2:1, 3:1 and 4:1 stoichiometric ratio, are also tested for determination of chloride. Chloride determination capacity of the absorbing reagent (at fixed concentration of thiocynate) was observed to increase with increase in concentration of mercuric ions, because maximum quench in absorbance was observed at higher concentration of chloride. As explained earlier, the reaction stoichiometry with 10.0ml volume of 1:1 [Hg-SCN] absorbing reagent was observed at 1.775mg (5.0ml of 0.01N Cl^-) since the concentration more than 1.775mg of chloride absorbing system showed deviation by decreasing the %T reading. Similarly, 10.0ml volume of 2:1, 3:1 and 4:1 system the reaction stoichiometry was observed respectively at 10.0ml, 13.0ml (theoretical value 12.5ml) and 14.0ml volumes of 0.01N NaCl solution.

Though the reaction stoichiometry is maintained at each composition of the absorbing reagent but it was observed that with increase in concentration of mercuric ions the non-linearity in the calibration curve was observed to increase. With 2:1 composition of the reagent, slight non-linear nature of calibration curve was observed. For 3:1 and 4:1 compositions, the absorbance quenching effect was observed insignificant at lower concentration and it was observed significant at higher concentration of chloride. Consequently, only 1:1

mercuric-thiocyanate system was found best for determination of chloride.

Analytical performance of the method

Analytical performance of the proposed method was tested with quantitative determination of chloride in the range of 0.2mg to 2.0mg by using 10.0ml of 0.005M $[Hg\text{-}SCN]^+$ reagent at 25ml and 50ml dilution (TABLE 2). After measurement of %T at 263nm of each TS and RB against distilled water as a reference, clearance (Cr) and permittance (Pr) of each test solution were calculated by following equation 1 and 2 respectively.

$$Cr = \frac{\%T_{TS}}{\%T_{RB}} \qquad (1)$$

$$Pr = \log \frac{\%T_{TS}}{\%T_{RB}} \qquad (2)$$

Where, $\%T_{TS}$ and $\%T_{RB}$ designates %T of test solution and reagent blank solution (containing nil chloride) respectively, both measured against the same reference solution TB. Calculated values of permittance are plotted against the concentration of chloride and the calibration curve was obtained for determination of chloride. TABLE 2 interprets that permittance is directly proportional to the concentration of chloride, since the extent of reaction that occurred between chloride and absorbing reagent (of fixed concentration) is totally subjective to the concentration of chloride only. Here 10.0ml of 0.005M absorbing reagent is sufficient to react with only 1.775mg or nearly equal to 1.800mg of chloride. When concentration of chloride greater than 1.800mg or equal to 2.0mg then absorbing system get deviated from the linearity through decrease in %T reading because of the formation of additive reaction products as explain earlier. The feasibility of the proposed method has been repeated three to four times at 25ml final dilution. The average value of permittance coefficient was observed 4.3917 $lit.g^{-1}cm^{-1}$ for determination of chloride in the range of 0.2mg to 1.8mg with the 10ml of 0.005M absorbing reagent in 0.1M HNO_3. Furthermore, for a sample of weak electrolyte such as hydroxylamine hydrochloride, the quantitative ionization of chloride ion is not possible in such a case the value of permittance coefficient was observed small. But higher or lower value of proportionality constant does not affect the measurement since, spectrophotometric analysis are the comparative methods of analysis.

TABLE 2 : Analytical performance of the method tested through quantitative determination of chloride in the range of 0.2mg to 2.0mg using 10.0ml of 0.005M absorbing reagent.

Conc. Chloride (g)	Measurement at 25ml dilution					Measurement at 50ml dilution				
	%T 263nm	Cr	Pr	Prop. Const.	Pr. Coeff.	%T 263nm	Cr	Pr	Prop. Const.	Pr. Coeff.
0.0000	10.51	1.000	0.0000	--	--	32.38	1.000	0.0000	--	--
0.0002	11.39	1.084	0.0349	174.61	4.3651	33.72	1.041	0.0176	88.05	4.4027
0.0004	12.34	1.174	0.0697	174.28	4.3570	35.14	1.085	0.0355	88.81	4.4406
0.0006	13.46	1.281	0.1074	179.07	4.4768	36.57	1.129	0.0528	88.08	4.4040
0.0008	14.52	1.382	0.1404	175.45	4.3864	38.05	1.175	0.0701	87.60	4.3799
0.0010	15.75	1.499	0.1757	175.68	4.3919	39.67	1.225	0.0882	88.19	4.4093
0.0012	17.17	1.634	0.2132	177.64	4.4410	41.27	1.275	0.1054	87.80	4.3899
0.0014	18.43	1.754	0.2439	174.23	4.3558	42.90	1.325	0.1222	87.27	4.3636
0.0016	20.11	1.913	0.2818	176.13	4.4033	44.79	1.383	0.1409	88.07	4.4033
0.0018	21.54	2.049	0.3116	173.13	4.3284	46.55	1.438	0.1576	87.58	4.3790
0.0020	18.66	1.775	0.2493	124.65	3.1164	43.11	1.331	0.1243	62.15	3.1075
	Avg. values			**175.58***	**4.3895***	**Avg. values**			**87.94***	**4.3969***

***Average value of permittance coefficient (in $lit.g^{-1}cm^{-1}$) are calculated up to which absorbing system shows linearity**

Accuracy and precision of the method

The accuracy and precision of the method was tested by means of determination of chloride in the solutions of known concentration of chloride. Permittance values of these standard test solutions were measured at 263nm at 25ml dilution and the average value of proportionality constant (175.58) given in TABLE 2, was used to determine the amount of chloride. For different measurements, accuracy (TABLE 3) of the method in terms of average relative error is observed as 0.198% and precision (TABLE 4) in terms of relative standard deviation (RSD) is found as 0.4725%.

TABLE 3 : Determination of accuracy of the method (n=2)

Cl^- taken (mg)	Pr (n=2)	Cl^- found (mg)	Abs. error	Rel. Error (%)
0.300	0.0527	0.301	0.001	0.34
	0.0528	0.301	0.001	0.34
0.600	0.1049	0.598	-0.002	-0.34
	0.1060	0.604	0.004	0.67
0.900	0.1592	0.907	0.007	0.78
	0.1580	0.900	0.000	0.00
1.500	0.2619	1.492	-0.008	-0.54
	0.2634	1.501	0.001	0.34
			Avg.	**0.198**

TABLE 4 : Determination of precision of the method (n=3)

Cl^- taken (µg)	Mean result (µg)	Avg. Devi. (n=3)	S.D.	R.S.D. (%)
200	200.7	1.17	1.54	0.77
400	399.7	1.74	2.55	0.64
800	801.3	1.20	1.61	0.20
1600	1602.7	3.10	4.41	0.28
Average values:			**2.5275**	**0.4725**

Effect of nitric acid

The solution of mercuric nitrate was prepared in 0.2M HNO_3 and absorbing reagent in 0.1M HNO_3; with 10ml of absorbing reagent pH of the test solutions was observed in the range 2.4 to 2.5. When more amount of fuming HNO_3 was used for dissolution of the $Hg(NO_3)_2$ that decreases the pH of the solutions but does not affect the analytical performance of the method (since permittance values were observed proportional to concentration of chloride). Nitric acid also shows sufficient absorbance at 263nm; therefore, %T readings of all test solutions including reagent blank solution were to observed decrease as the composition of absorbing species changes with the addition of extra nitric acid that alters the value of permittance coefficient. With the solutions of determination for chloride in the range of 0.2mg to 1.8mg, when initially spiked with 5.0ml of 0.5M HNO_3, the value of permittance coefficient was observed equal to 5.4227 $lit.g^{-1}cm^{-1}$.

Interference study

One to one stoichiometric reaction of chloride ion with the absorbing reagent is the best judgment of detecting the interfering role of foreign ions; disturbance in stoichiometry observes the interference. In this experiment, interference was confirmed by considering the following factors. First, the stability of the absorbing system in presence of added ion; for example, I^-, $S_2O_4^{-2}$ and S^{-2} ions generate precipitate with absorbing reagent hence are the serious interfering ions. Second, interfering ions generate the precipitate with the analyte (chloride) which remains stable on addition of the absorbing reagent. The Bi^{+3} and Ag^+ are the interfering cations of such kind. Third, the ions (for example, $C_2O_4^{-2}$) that exhibit sufficient absorbance at wavelength analysis showed the tendency of disturbing the linearity of permittance against concentration but oxalate does not alter the reaction stoichiometry. The fourth kind of interfering ions are the NO_2^- and Br^- which directly masks the absorbing quenching mechanism. However, the H^+, NH_4^+, Li^+, Na^+, K^+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Zn^{+2}, SO_4^{-2}, NO_3^{-2}, CO_3^{-2}, F^-, CH_3COO^- and HPO_4^{-2} do not show interference in determination of chloride by this method.

Applications of the method

Samples containing ionisable chloride ions and are nearly transparent at 263nm were quantitatively determined through the reaction of chloride with $[Hg\text{-}SCN]^+$ reagent. Standard solutions of 0.01N hydrochloric acid (HCl), 0.01N Hydroxylamine hydrochloride (HAHCl) synthetic mixture of anions (SMA) (having composition: 50.0ml of 0.01N NaCl + 10.0ml of 0.01N Na_2CO_3 + 10.0ml of 0.01N Na_2SO_4 + 10.0ml of 0.01N Na_2HPO_4 + 10.0ml of 0.01N CH_3COONa + 10.0ml of distilled water) and synthetic mixture of cations (SMC) (having composition: 10.0ml of 0.01N NaCl + 10.0ml of 0.01N KCl+ 10.0ml of 0.01N NH_4Cl + 10.0ml of 0.01N $CaCl_2$ + 10.0ml of 0.01N $MgCl_2$ + 10.0ml of 0.01N $ZnSO_4$ + 40.0ml of distilled water) were analyzed by calibration curve method by using 10.0ml of 0.005M absorbing reagent. The proportionality constant value for determination of chloride in HCl and HAHCl were obtained via analysis of standard 0.01N HCl and 0.01N HAHCl solutions. Because of the partial ionization, the proportionality constant value obtained in analysis of 0.01N HAHCl solution was observed small. For analysis of SMA and

SMC proportionality constant value was obtained by analysis standard 0.01N NaCl solution. The result of this assay is shown in TABLE 5.

TABLE 5 : Result obtained in the determination of chloride

Sample tested	Chloride taken (µg)	Mean (n=4) (µg)	Dev.	Avg. Dev	Std. Dev.	Rel. Std. Dev. (%)
HCl	710	710	0	0.00	2.58	0.37
	1065	1065	-2	-0.50	2.71	0.26
	1420	1422	-2	-0.50	2.71	0.26
SMA	710	709	0	0.00	1.42	0.20
	1065	1065	1	0.25	1.73	0.16
	1420	1420	-1	-0.25	3.51	0.25
SMC	710	709	-2	-0.50	2.00	0.28
	1065	1064	0	0.00	2.16	0.21
	1420	1421	0	0.00	2.16	0.21
HAHCl	710	709	0	0.00	3.65	0.51
	1065	1067	-2	-0.50	3.91	0.37
	1420	1425	-1	-0.25	3.32	0.24

CONCLUSIONS

This manuscript gives the method of employment of $[Hg\text{-}SCN]^+$ absorbing reagent for UV-spectrophotometric determination of chloride. The limit of quantitation of chloride is totally related to 1:1 stoichiometric reaction of chloride with absorbing reagent. The reaction of chloride ion with $[Hg\text{-}SCN]^+$ reagent is fast, irreversible and quantitative; 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, the method was work effectively for determination of chloride in the range 200µg to 1800µg. The results reported in TABLE 2, 3, 4 and 5 shows the method has good accuracy and precision. The results obtained for analysis of chloride in synthetic mixture of cations and anions also execute the applications of the method for analysis of different samples including water. The method is quite simple, free from interference and need not require so much costly chemicals and organic solvents. Samples showing the absorbance at the wavelength of analysis can not be analyzed by this method.

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 late Adv. Vitthalrao Hande, the former Sabhapati of MVP Samaj, Nashik; who had played a key role in making MVP Samaj a Qualitative Educational Institute.

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