MONO-THIOCYANATO MERCURY (II) CHLORIDE: A NOVEL REAGENT FOR SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE IN BEERS

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ABSTRACT
The mono-thiocyanato mercuric (II) chloride \([\text{Hg(SCN)}\text{Cl}]\) reagent was prepared synthetically and implemented for spectrophotometric determination of chloride in beers. In determining chloride, a known aliquot of beer sample was added into Hg(SCN)Cl reagent. The displaced thiocyanate ions were subsequently used to form the red-colored ferric-thiocyanate complex. The absorbance of which was measured at 455-nm was found directly proportional to the concentration of chloride in the beer sample. The experiment was performed by the standard addition method using beer sample and reagent at a time, and further various amount of known chloride was added during the measurement of absorbance. The analysis results show an average standard deviation of 0.02513. The output of this study provides evidence that, the Hg(SCN)2 reagent does not obey Beer’s law, whereas an excellent linearity of absorbance versus concentration of chloride was observed with the ratio of the concentration of Hg(SCN)Cl to chloride is less than 6.66.

Keywords: Mono-thiocyanato-mercury(II) Chloride, Mercuric Thiocyanate, Beers, Spectrophotometric Assay, Beer’s Law Linearity

INTRODUCTION
Wines and beers are important components of the food. The determination of chloride in Beer is the common parameter used for the detection of the quality of the Beer. Wines and beers play a protective role against cardiovascular, cancer, and neurodegenerative diseases,1-4 because they contain components having high antioxidant activity.5,6 Beer is a complex beverage containing many compounds with added flavor and aroma.7 The presence of organic acids, mineral acids and mineral elements gives the salty test to Beer in which chloride is the major component. Beer undergoes the chemical change on storage7, so chemical analysis is required to maintain beer quality.

Literature survey shows following some methods for the analysis of beers. The gas chromatography with a mass spectrometer is used to examine the chemical change occurring during the storage of beers8. The gluten protein in Beer is analyzed by its fragmentation.9 The glyphosate herbicides in Beer were determined by capillary electrophoresis using a mass spectrometry detecting system,10 whereas its elemental analysis by AAS11. The ultraviolet-visible spectral data is also useful for rapid detection of the quality of beer12. The chloride content in beers can be determined by conductometric titration13, radio-activation analysis14 and spectrophotometry15 with solvent extraction. But there is no spectrophotometric method for the determination of chloride in Beer by using mono-thiocyanato mercury(II) chloride reagent. So in this study, this reagent is implemented for accurate determination of chloride in beers by using photometric Beer’s law.

EXPERIMENTAL

Material and Methods
A solution of 0.05N potassium chloride (KCl) and 0.05N potassium thiocyanate (KSCN) were prepared in distilled water. Similarly, a solution of 0.05M mercuric nitrate \([\text{Hg(NO}_3\text{)}_2]\) and 0.1M ferric nitrate
[Fe(NO$_3$)$_3$] were prepared in 1.0M nitric acid (HNO$_3$). The molarity of Hg(NO$_3$)$_2$ was confirmed equal to 0.05M by its titration against 0.05N KSCN using Fe(NO$_3$)$_3$ indicator.

**Preparation of Reagent Solution**

For the preparation of 1.0mN of Hg(SCN)Cl reagent initially, a 10.0-ml of 0.05M Hg(NO$_3$)$_2$ was titrated with 0.05M KSCN using 40.0 ml of 0.1M Fe(NO$_3$)$_3$ up to faint red color endpoint. Then, exactly 10.0-ml of 0.05M Hg(NO$_3$)$_2$ was added in order to form mono-thiocyanato mercury (II) nitrate, [Hg(SCN)NO$_3$]. This mixture obtained in titration flask was further titrated against 0.05N KCl solution to the faint red color endpoint, finally, it becomes 100-ml of 1.0mN of Hg(SCN)Cl reagent. Similarly, 1000-ml of stock solution of 1.0mN of Hg(SCN)Cl reagent was prepared.

**Preparation of Hg(SCN)Cl Reagent**

The 1.0mN of Hg(SCN)Cl reagent was prepared by titrating 10.0-ml of 0.05M Hg(NO$_3$)$_2$ against standard 0.05N KSCN using 40.0-ml of 0.1M Fe(NO$_3$)$_3$ indicator. A 20.0-ml 0.05N KSCN was required for obtaining the endpoint. Later, 10.0-ml of 0.05M Hg(NO$_3$)$_2$ was added to this solution to form Hg(SCN)NO$_3$ reagent. This solution was further titrated against standard 0.05N KCl solution for obtaining the Hg(SCN)Cl reagent. It required 20.0-ml of 0.05N KCl to obtain faint red color as an endpoint. In this manner 1000-ml of 1.0 mN of Hg(SCN)Cl reagent was prepared as a stock solution.

**Instrument**

A Shimadzu UV-1800 Spectrophotometer with software UVProbe 2.33 and 10-mm match quartz cuvettes were used for recording all absorption spectra and absorbance.

**Spectrophotometric Determination of Chloride in Beers**

A 2.0-ml to 5.0-ml aliquot of beer sample was added to 100-ml distilled water and the absorbance of this solution was recorded against distilled water at 455.0nm, for sample background correction. Then 1.0-mM Hg(SCN)Cl reagent solution was placed in the sample as well as reference compartments of the spectrophotometer and the absorbance was made zero at 455.0-nm. Later, the identical sample of the Beer (viz. 2.0 to 5.0-ml) was transferred into the 100-ml of 1.0-mM of Hg(SCN)Cl reagent, after gentle stirring (for about a minute), the absorbance of this reaction mixture was recorded at 455.0nm against 1.0-mM reagent solution as a blank. The absorbance measurement was further continued with the increment of 0.8875-mg of chloride (viz. by adding 1.0 ml of 0.025M KCl solution every time). The background correction in absorbance values was made by subtracting the sample solution's absorbance (recorded in distilled water). Furthermore, the absorbance values were corrected for dilution volume by using the following eqn.-1. The graph of volume corrected absorbance (Cor. Abs.) versus concentration of the chloride added was obtained from the straight line considering the linearity between absorbance and concentration of chloride. The extrapolation of this straight line back to the abscissa/concentration axis gives the chloride concentration (present in that volume of Beer) a negative value. The concentration (Cu in mg/ml) of chloride in the beer sample was calculated by using the following eqn.-2.

**Calculations**

**Correction in Absorbance Due to Dilution**

The volume corrected absorbance (Cor. Abs.) was calculated$^{16}$ by using eqn.-1:

$$A_{Corrected} = \frac{\left( V_{RX} \times V_{S} \right)}{V_{RX}} A_{Observed}$$  

Where, $A_{Observed}$ represents the absorbance with sample background correction, $V_{RX}$ is the initial volume of reagent including the sample and $V_{S}$ is the volume 0.025M KCl added up to any point.

**Calculation of Chloride in Beer**

The chloride concentration in Beer, Cu (in milligram) was calculated by using the formula of standard addition method$^{17,18}$ as shown by eqn.-2:
\[ C_u = \left( \frac{A_X}{(A_{X+S} - A_X)} \right) Cs \]  

(2)

Where, \( A_X \) represents absorbance for the reagent containing known volume, \( V_X \) of the Beer, and \( A_{X+S} \) absorbance for the reagent containing the same volume \( V_X \) of the Beer spiked with a known amount of chloride having concentration \( Cs \) (in mg).

RESULTS AND DISCUSSION

Chemistry of the Reagent

The sufficient difference between two formations constants\(^{19-20}\) log-\( K_2 \) and log-\( K_4 \) of the mercury(II)-thiocyanate complexes make it possible to titrate mercury(II) nitrate against the potassium thiocyanate up to \([Hg(SCN)_2]^{+}\) rather than \([Hg(SCN)_4]^{2-}\), with ferric nitrate indicator.

\[
Hg(NO_3)_2 + 2KSCN \rightarrow Hg(SCN)_2 + 2KNO_3
\]

This difference information constant was also found to be suitable for the formation of the mono-thiocyanato mercury(II) nitrate with the addition of an equivalent amount of mercury nitrate.

\[
Hg(SCN)_2 + Hg(NO_3)_2 \rightarrow 2[Hg(SCN)(NO_3)]
\]

Similarly, the four formation constants\(^{19-20}\) of the mercuric-chloride complex indicate the formation of \([Hg(Cl)]^{+1}\) to \([Hg(Cl)]^{2-}\). The enough difference between the formation constant of \([Hg(Cl)]^{+1}\) and \([Hg(Cl)]^{2-}\) complex designates \([Hg(Cl)]^{2-}\) will formed after the formation of \([Hg(Cl)]^{+1}\). This theme allows mono-thiocyanate mercury(II) chloride formation by using mono-thiocyanate mercury(II) nitrate, with the following reaction.

\[
[Hg(SCN)(NO_3)] + KCl \rightarrow [Hg(SCN)(Cl)] + KNO_3
\]

In a solution containing mono-thiocyanate mercury(II) chloride and excess ferric nitrate, when chloride ions (for example, KCl) are added, it displaces the thiocyanate ions. These displaced thiocyanate ions on reaction with ferric ions form a red-colored mono-thiocyanato-ferric(III) nitrate, as shown below:

\[
[Hg(SCN)(Cl)] + KCl + Fe(NO_3)_3 \rightarrow [Hg(Cl)]_2^{2-} + KNO_3 + [Fe(SCN)(NO_3)]_2
\]

Beer’s Law Linearity

Initially, an acidic solution of the synthetic mercuric thiocyanate \([Hg(SCN)_2]\) was used for the determination of 0.8875-mg of chloride during which the linearity between absorbance and concentration of chloride was studied. The \(Hg(SCN)_2\) is the well-known reagent for spectrophotometric determination of trace amount chloride in different samples.\(^{21-24}\) But the main drawback of the \(Hg(SCN)_2\) reagent is that it does not shows linearity with the photometric Beer’s law when applied for determination of chloride, and it is also confirmed in this study.

For this experiment, the absorption spectra of \(Hg(SCN)_2\) were recorded (against the reagent itself as a reference) with the increment of 0.8875-mg of the chloride (viz. by adding 1.0-ml of 0.025M KCl every time). The first addition of 0.8875-mg of chloride was considered here as a concentration of the sample. The results (are shown in Fig.-1 and Fig.-2), show the average value of chloride concentration in the sample is 1.1386-mg instead of 0.8875-mg (true value). The larger relative error (28.29%) indicates \(Hg(SCN)_2\) reagent is thus not suitable for spectrophotometric determination of chloride.

Furthermore, the results (Fig.-1 and Fig.-2) give a clear picture that the absorbance does not change linearity with the concentration of chloride. So, \(Hg(SCN)_2\) does not obey the photometric Beer’s law for the determination of chloride. It could be probably due to the displacement of the thiocyanate ions from the reagent, which is in fact not the linear function of the concentration of the chloride ions added, and the reaction is not occurring in the 1:2 stoichiometric ratio, as mentioned in many colorimetric methods of determination of chloride concentration.\(^{21-24}\)
Hg(SCN)$_2$ + 2Cl$^-$→HgCl$_2$+ 2SCN$^-$

Practically, depending upon the thiocyanate concentration available, the Fe$^{3+}$ forms a series of red-colored complexes which may be formulated$^{25-27}$ as [Fe(SCN)]$^{2+}$, [Fe(SCN)$_2$]$^{3+}$, [Fe(SCN)$_3$], [Fe(SCN)$_4$]$^{2-}$, [Fe(SCN)$_5$]$^{2-}$ and [Fe(SCN)$_6$]$^{3-}$.

Fig.-1: The absorption spectra of Hg(SCN)$_2$ obtained in the determination of 0.8875-mg of chloride. The curve ‘R’ represents the absorbance of the reagent against distilled water which was made equal to zero (baseline ‘BL’) by using the reagent itself as a reference. The other absorption curves were obtained with a sequential increment of 0.8875-mg of chloride.

Fig.-2: The graph of absorbance of Hg(SCN)$_2$ as a function of the concentration of chloride added, obtained in the determination of 0.8875-mg of chloride by the standard addition method. The line ‘R’ and line ‘C’ represent the calculated (1.1386-mg) and the true (0.8875-mg) concentration of the chloride.

The initial additions of chloride give more absorbance and the negative deviation in graph or absorbance occurs at a higher concentration of chloride (Fig.-2). This is because at the beginning the maximum number of the Hg(SCN)$_2$ molecules can release more amount of thiocyanate ions on reaction with a few numbers of chloride ions. The earlier study illustrates that chloride ions may be linked to Hg(SCN)$_2$ reagent.$^{28}$ Therefore, the initial reaction may take place in the following manner with releasing more thiocyanate ions.

$$2\text{Hg(SCN)}_2 + \text{Cl}^- \rightarrow (\text{SCN})\text{Hg-Cl-Hg(SCN)} + 2\text{SCN}^-$$
The released thiocyanate ions may form only $[\text{Fe(SCN)}]^2+$ with the more amount of ferric ions available when all $\text{Hg(SCN)}_2$ molecules undergo above such reaction through forming a bridged molecule of mercuric ion. The next reactions may occur as shown below.

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

$$\text{Hg(SCN)}\text{Cl} + \text{Cl}^- \rightarrow \text{HgCl}_2 + \text{SCN}^-$$

The deviation in linearity from Beer’s law is due to the following non-stoichiometric reactions that may occur at a higher concentration of chloride with releasing a smaller number of thiocyanate ions.

$$2\text{Hg(SCN)}\text{Cl} + 2\text{Cl}^- \rightarrow [\text{Hg(SCN)}\text{Cl} - \text{HgCl}_3]^- + \text{SCN}^-$$

$$2\text{Hg(SCN)}\text{Cl} + 3\text{Cl}^- \rightarrow [\text{Hg(SCN)}\text{Cl} - \text{HgCl}_4]^2^- + \text{SCN}^-$$

$$2\text{Hg(SCN)}\text{Cl} + 4\text{Cl}^- \rightarrow [\text{HgCl}_2 - \text{HgCl}_4]^2^- + 2\text{SCN}^-$$

Fig.-3: The absorption spectra of 1.0-mN $\text{Hg(SCN)}\text{Cl}$ obtained in the determination of 0.8875-mg of chloride. The curve ‘R’ represents the absorbance of the reagent against distilled water which was made equal to zero (baseline ‘BL’) by using reagent itself reference. The other absorption curves were obtained with a sequential increment of 0.8875-mg of chloride.

Fig.-4: The graph of absorbance of the 1.0-mN $\text{Hg(SCN)}\text{Cl}$ as a function of the concentration of chloride added, obtained in the determination of 0.8875-mg of chloride by the standard addition method. The line ‘Cu’ represents the calculated (0.8902-mg) and the true (0.8875-mg) concentration of the chloride.
Practically at a higher concentration of chloride, the reaction may occur without displacement of the thiocyanate ions.

\[
[Hg(SCN)Cl-HgCl_2] + Cl^- \rightarrow [Hg(SCN)Cl-HgCl_3]
\]

The course of the above-mentioned non-stoichiometric reactions could be clarified on the basis of the formation constant of the mercuric-chloride complexes\(^{19-20}\), which indicates the formation of HgCl\(_3\) and HgCl\(_4\) complexes at a higher concentration of chloride.

Moreover, at a limited number of ferric ions, when all Fe\(^{3+}\) ions get converted into [Fe(SCN)]\(^{1+}\), the further released thiocyanate ions may give [Fe(SCN)]\(^{3+}\) or another ferric thiocyanate complexes\(^{25}\) rather than [Fe(SCN)]\(^{1+}\), which could be another cause for the deviation in Beer’s law linearity.

In this study, the more pronounced results were obtained in Beer’s law linearity with the use of Hg(SCN)Cl reagent. Initially, 1.0-mN Hg(SCN)Cl was in the determination of 0.8875-mg of chloride. These results in the form of absorption spectra (Fig.-3) and the calibration graph of the corrected absorbance versus the milligram concentration of chloride (Fig.-4) show that the absorbance is increasing linearly up to the addition of 6.2125-mg (including 0.8875-mg sample) of chloride. The average value of chloride in the sample was found to be 0.8902-mg instead of 0.8875-mg (true value) with only 3.0% relative error. So, in conclusion, Hg(SCN)Cl was found a better reagent for spectrophotometric determination of chloride.

| Sr. No. | The concentration of the reagent (Milli-normal) | Chloride conc. obeying Beer’s law (including analyte) (mg) | Milli-normal conc. of chloride obeying Beer’s law (mg) | Hg(SCN)Cl: Chloride Conc. ratio found for obeying Beer’s law |
|---------|---------------------------------|-------------------------------------------------|-------------------------------------------------|--------------------------------------------------------|
| 1       | 1.0 (in 100-ml)                 | 6.2125 (0.8875-mg x 7.0-ml)                     | 0.175-mN (0.025N x 7.0-ml)                      | 1: 0.175 = 5.72                                        |
| 2       | 2.0 (in 200-ml)                 | 11.5375 (0.8875-mg x 13.0-ml)                   | 0.325-mN (0.025N x 13.0-ml)                     | 2: 0.325 = 6.16                                       |
| 3       | 4.0 (in 400-ml)                 | 21.3000 (1.775-mg x 12.0-ml)                    | 0.600-mN (0.050N x 12.0-ml)                     | 4: 0.600 = 6.67                                       |

Accordingly, it is seen that (Table-1) the capacity of the reagent for the determination of chloride increases with the concentration of the reagent. The more distinct effect in Beer’s law linearity was observed (Table-1) when the ratio of the concentration of reagent to chloride is less than 6.6667.

Fig.-5: The UV-absorption Spectra of the Hg(SCN)Cl obtained against distilled water with the sequential addition of the chloride.

The excellent linearity between the absorbance and concentration of the chloride is due to the following 1:1 stoichiometric reaction occurring in the presence of a higher concentration of ferric ions.
Hg(SCN)Cl + Cl⁻ → HgCl₂ + SCN⁻  
Fe(NO₃)₃ + SCN⁻ → Fe(SCN)(NO₃)₂ + NO₃⁻

At the higher concentration of chloride, the Hg(SCN)Cl reagent shows the analogous behavior with Hg(SCN)₂ regarding the deviation from the Beer’s law linearity. This may be due to the above-mentioned non-stoichiometric reactions that displace less number of thiocyanate ions. The cause of deviation (or the course of the above-mentioned reactions) may be clarified on the basis of UV absorption spectra. The UV absorption spectra of the Hg(SCN)Cl reagent without adding the Fe(NO₃)₃ indicator were recorded as a function of the sequential addition of chloride. The result of this study, shown in Fig.-5, illustrates that the shift in absorption maxima from 264 nm to 274 nm is due to the formation of the various products as described above reactions. For the formation of an identical reaction product, the shifting in absorption maxima is not possible only a change in absorbance is feasible.

**Study of Reaction Time**
The reaction between chloride ion and the Hg(SCN)Cl is the ionic reaction taking place at a faster rate. Initially, the reaction time was measured for the displacement of thiocyanate ions from the reagent by the KCl, beers, and wines. These results clarify that (Fig.-6), the reaction of KCl and Beer with the Hg(SCN)Cl was occurring faster mode since the rapidly increasing absorbance immediately becomes constant. This means the reaction between Hg(SCN)Cl and chloride in KCl and chloride in Beer are occurring in the identical way (Fig.-6). Also, the organic and inorganic materials present in beers do not play any role in displacing the thiocyanate ions from the reagent. But the contrast results were shown by the red and white wine samples when reacted with the Hg(SCN)Cl. The wine samples slowly increase the absorbance of the reaction mixture and it takes a long time to reach a constant value (Fig.-6). This observation reflects that chloride in wine and the other component(s) present in the wines may be involved in the displacement reaction of the thiocyanate ions. These components other than chloride may be slowly reacting with mercuric ions through the displacement of the thiocyanate. Consequently, Hg(SCN)Cl reagent is not found suitable for the determination of chloride in wines.

When the Hg(SCN)Cl reagent was applied for the determination of chloride in Beer, it was observed that, the sample beer, as well as the reagent both, showed sufficient absorbance (against distilled water) at the wavelength of analysis (455 nm). The contribution of absorbance of sample beer and reagent in the...
absorbance of the reaction mixture becomes the source of the potential error in the determination of Beer chloride using this reagent. So, to eliminate this error, initially, the beer sample (volume equal to taken for the analysis) was diluted in distilled water (volume equal to the reagent) and the absorbance of this solution was recorded. The interference due to the absorbance of the Beer is eliminated by subtracting its absorbance from all the absorbance values and the sample background correction was made.

Fig.-7: The absorption spectra obtained in the determination of chloride in 5.0-ml of Beer using 200-ml of the reagent.

In the figure, curves ‘S’ and ‘R’ represent the absorbance of the Beer and reagent against distilled water. The absorbance of the reagent was made zero (baseline-BL). The curves ‘R+S’ represent the absorbance of the reagent containing 5.0-ml of Beer obtained against the reagent as a reference. The other absorption curves were obtained with the sequential increment of 0.8875-mg of chloride.

Fig.-8: The graph of absorbance of the 2.0-mM Hg(SCN)Cl as a function of the concentration of chloride added, obtained in the determination of chloride in 5.0-ml of Beer by the standard addition method. The line ‘Cu’ represents the calculated (2.1149-mg) concentration of the beer chloride.

The interference due to the absorbance of the reagent was eliminated by recording all absorption values/spectra against the reagent itself. It was done by obtaining the baseline of zero absorbance using reagent itself as a reference/blank (Fig.-7).

The 100-ml and 200-ml of 1.0-mN Hg(SCN)Cl reagent was first applied for the determination of chloride concentration in a 3.5-ml and 5.0-ml a sample of Beer, respectively. The results (Table-2) obtained in the
determination of chloride concentration in a 5.0-ml of Beer are shown in the form of absorption spectra (Fig.-7) and the calibration graph (Fig.-8).

Table-2: The results obtained in the determination of chloride concentration in beers by standard addition method

| Amount of Chloride added (mg) | 5.0 ml Beer Sample | 3.5 ml Beer Sample |
|------------------------------|--------------------|--------------------|
|                             | 200.ml of 1.0 mM of Hg(SCN)Cl | 100.ml of 1.0 mM of Hg(SCN)Cl |
| Corrected Absorbance (Cor. Abs.) | Chloride Conc. by Eq. (2)(mg) | Conc. by up to linearity (mg) | Corrected Absorbance (Cor. Abs.) | Chloride Conc. by Eq. (2)(mg) | Conc. by up to linearity (mg) |
| 0.0000                      | 0.0744              | 2.1087             | 2.1087 | 0.1068              | 1.4663               | 1.4663 |
| 0.8875                      | 0.1057              | 2.1054             | 2.1054 | 0.1714              | 1.4757               | 1.4757 |
| 1.7750                      | 0.1371              | 2.1021             | 2.1021 | 0.2353              | 1.5018               | 1.5018 |
| 2.6625                      | 0.1686              | 2.1075             | 2.1075 | 0.2961              | 1.5024               | 1.5024 |
| 3.5500                      | 0.1997              | 2.1027             | 2.1027 | 0.3592              | 1.5053               | 1.5053 |
| 4.4375                      | 0.2314              | 2.1124             | 2.1124 | 0.4216              | 1.5538               | 1.5538 |
| 5.3250                      | 0.2619              | 2.1167             | 2.1167 | 0.4728              | 1.5735               | 1.5735 |
| 6.2125                      | 0.2928              | 2.1246             | 2.1246 | 0.5285              | 1.5901               | 1.5901 |
| 7.1000                      | 0.3230              | 2.1295             | 2.1295 | 0.5837              | 1.6058               | 1.6058 |
| 7.9875                      | 0.3535              | 2.1396             | 2.1396 | 0.6380              | 1.6198               | 1.6198 |
| 8.8750                      | 0.3830              | 2.1644             | --     | --                   | --                   | --     |
| 9.7625                      | 0.4100              | 2.1727             | --     | --                   | --                   | --     |
| 10.6500                     | 0.4391              | 3.3586             | --     | --                   | --                   | --     |
| 11.5375                     | 0.4689              | 4.7235             | --     | --                   | --                   | --     |
| 12.4250                     | 0.4978              | Average=           | 2.1149 | Average=             | 1.4903               |        |

Table 3: Precision of the spectrophotometric determination of Beer chloride obtained in terms of average standard deviation

| ***Beer Sample No. | Sample Volume (ml) | *Total Chloride (mg/ml) | *Average Chloride Found (mg) | **Mean/Average Deviation | **Standard Deviation | **Average Standard Deviation |
|--------------------|--------------------|-------------------------|-----------------------------|--------------------------|---------------------|--------------------------|
| 1                  | 3.0                | 0.4065                  | 1.2196                      | 0.0081                   | 0.00953             | 0.02463                  |
|                    | 4.0                | 0.4070                  | 1.6281                      | 0.0061                   | 0.00757             |                         |
|                    | 5.0                | 0.4042                  | 2.0211                      | 0.0060                   | 0.00753             | 0.02463                  |
| 2                  | 3.0                | 0.4156                  | 1.2469                      | 0.0083                   | 0.00975             |                         |
|                    | 4.0                | 0.4161                  | 1.6643                      | 0.0062                   | 0.00774             |                         |
|                    | 5.0                | 0.4173                  | 2.0864                      | 0.0062                   | 0.00777             | 0.02526                  |
| 3                  | 3.0                | 0.4242                  | 1.2726                      | 0.0084                   | 0.00994             |                         |
|                    | 4.0                | 0.4238                  | 1.6953                      | 0.0063                   | 0.00788             |                         |
|                    | 5.0                | 0.4128                  | 2.0642                      | 0.0062                   | 0.00769             | 0.02551                  |
| 4                  | 3.0                | 0.4313                  | 1.2939                      | 0.0078                   | 0.00912             |                         |
|                    | 4.0                | 0.4299                  | 1.7195                      | 0.0064                   | 0.00799             |                         |
|                    | 5.0                | 0.4299                  | 2.1497                      | 0.0064                   | 0.00800             | 0.02511                  |

Average: 0.02513

*Average value of six replicate measurements, ** Determined with six replicate measurements ** ***Samples were used differently for titrimetric and spectrophotometric analysis of beer chloride.

The average value of chloride concentration (considering the Beer’s law linearity) in the 3.5 ml beer of beer sample was found 1.4903-mg or 0.4258-mg/ml using 100-ml of 1.0-mN Hg(SCN)Cl reagent. Similarly, by using 200-ml of 1.0-mN Hg(SCN)Cl reagent, the 5.0-ml sample of the same Beer gives a chloride concentration of 0.4230-mg/ml. The results of these two determinations are (0.4258-mg/ml and 0.4230-mg/ml) differs by a factor of 0.0028-mg (or 2.8$\mu$g), indicating the procedure has good precision (Table-3).

**CONCLUSION**

The main achievement of this study is the discovery of the mono-thiocyanato mercury (II)chloride reagent for spectrophotometric determination of chloride in beers. The synthesis of this reagent is quite simple and does not require costly chemicals and solvents. The acidic nature of the reagent maintains the homogenous nature of the reaction medium during the displacement of the thiocyanate ions, which is the
essential requirement of spectrophotometric determination. The reagent works selectively with a smaller sample volume for the determination of chloride in beers as proved by comparing the reaction time with potassium chloride solution. The role of \( \text{Hg(SCN)Cl} \) as a spectrophotometric reagent for the determination of chloride is found to be more pronounced over \( \text{Hg(SCN)}_2 \) reagent as verified through understanding the linearity required for the photometric Beer’s law.

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