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Titrimetric Analysis of Chloride Concentration in Beers using Synthetic Mercury(II) Compound

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The monothiocyanato-mercuric(II) nitrate [$Hg(SCN)NO_3$] reagent has been prepared synthetically in an aqueous medium and subjected for studies of titrimetric analysis of chloride concentration in beers. In this studies, a measured volume of beer sample was added into known and an excess amount of $Hg(SCN)NO_3$ reagent and the surplus $Hg(SCN)NO_3$ was determined by back titration against standard potassium thiocyanate (KSCN) solution using ferric nitrate [$Fe(NO_3)_3$] indicator. The chloride ion and $Hg(SCN)NO_3$ were found to be reacting in the 1:1 stoichiometric ratio. The amount of chloride in beer was determined with the amount of $Hg(SCN)NO_3$ utilized in the titration reaction. The presence of organic and inorganic materials had no effect on the titrimetric assay of chloride concentration in beers as proved by the chloride recovery experiment. The statistical analysis of results showed average standard deviation of 0.01034 and average relative error 1.12%, which indicates the accuracy of the procedure.

Keywords: Monothiocyanato-mercury(II) nitrate, Titrimetric assay, Beers, Mercurimetric determination, Ferric nitrate indicator.

INTRODUCTION

Determination of chloride concentration in various samples is the common parameter measured in all clinical and chemical laboratories. The assay of chloride concentration in beers is a rather common parameter in quality control studies. Wines and beers are beverages resulting from fermentation and are one of the most important constituents of the food. Beer is the third most popular beverage when compared with water and tea. It is a complex beverage containing more than 3000 compounds, adding flavour, aroma and influences the appearance of beer [1]. These mineral elements, mineral acids, some organic acids may have a key role on a salty taste of beer, with chlorides being a major contributor to saltiness. Beer becomes more complex in storage, as it undergoes chemical changes [1]. Therefore, for maintaining the quality of beer its chemical analysis is required.

Literature survey revealed the following few methods for the analysis of various components in beers. The GC-MS technique is used to monitor the chemical changes occurring during the aging of beer [2], the elemental analysis of beers was done by flame atomic absorption spectroscopy [3], the quality of the beer can be assayed rapidly by using VU-visible spectral data [4], whereas the total carbon dioxide in beer was estimated by acid-base titration [5]. In addition to this, beer was also analyzed for its chloride content by conductometric titration using silver nitrate reagent [6] and radio-activation method [7].

But there is no specific titrimetric method found in the literature for the determination of chloride concentration in beers using monothiocyanato-mercury(II) nitrate reagent. Since, titrimetry is the most common, convenient and favoured analytical method in all analytical laboratories due to its inherent reproducibility, accuracy and low costing absolute method of analysis. So, in this study, an attempt is made to develop this reagent for accurate determination of chloride concentration in beer *via* studying its behaviour regarding obeying the titrimetric reaction stoichiometry.

EXPERIMENTAL

Analytical reagent-grade chemicals and double distilled water were used throughout the experiment. The standard solutions of 0.05 N KCl and 0.05 N KSCN were also prepared in double distilled water. The 0.05 M $Hg(NO_3)_2$ and 0.1 M $Fe(NO_3)_3$ solutions were prepared in 1.0 M nitric acid. The molarity of $Hg(NO_3)_2$ was confirmed exactly equal to 0.05 M by its standardization against standard 0.05 N KSCN using $Fe(NO_3)_3$ indicator. The samples of beer were purchased from the local stores and subjected for analysis after bringing to the normal temperature.

Preparation of $Hg(SCN)NO_3$ reagent: A fresh $Hg(SCN)NO_3$ reagent was prepared *in situ* just before the titration. For its preparation, a 5 mL of standard 0.05 M $Hg(NO_3)_2$ was transferred into a 250 mL titration flask containing 20 mL of 0.1 M $Fe(NO_3)_3$ and 30 mL of distilled water. This solution was titrated against standard 0.05 N KSCN solution till faint red colour obtained. The reaction product was found to be soluble due to acidic pH. Then exactly, 5.0 mL of 0.05 M $Hg(NO_3)_2$ was added to this solution (red colour disappeared). By ignoring the concentration of all other reagents, this becomes 0.5 mN or 10.0 mL of 0.05 N $Hg(SCN)NO_3$ reagent. Furthermore, the strength in the normal term of $Hg(SCN)NO_3$ reagent was confirmed by its titration against standard 0.05 N KSCN and 0.05 N KCl solutions. It consumes exactly 10 mL of 0.05 N KSCN or 0.05 N KCl solution for generation faint red colour endpoint.

Procedure for titrimetric determination of chloride in beer

Back titration: A 5.0 mL to 10 mL sample of beer was transferred into 0.5 mN (or 10.0 mL of 0.05 N) $Hg(SCN)NO_3$ reagent. After vigorous shaking of the mixture, the surplus reagent was determined by titrating against standard 0.05 N KCN solution till red colour was obtained to the solution. This burette reading was considered a back titration reading (B_K mL).

Blank titration: A 0.5 mN (10.0 mL of 0.05 N $Hg(SCN)NO_3$) reagent was prepared and titrated against standard 0.05 N KCN solution till faint red colour was obtained to the solution. This burette reading was considered as a blank titration reading (B_L mL). The amount of chloride in mg/mL of beer sample was calculated by using eqn. 1:

$$C_{Cl\ beer} = \frac{N_{KSCN} \times (B_L - B_K) \times 35.5}{V_{beer}} \quad (1)$$

Titrimetric determination of spiked chloride in beer: Similarly, the known amount of chloride was added (spiked) in the sample of beer and the chloride recovery experiment was carried out with above mentioned back and blank titrations. The amount of spiked/added chloride in the beer sample was calculated by using eqn. 2:

$$C_{Cl\ spiked} = (M_{KSCN} \times (B_L - B_{K2}) \times 35.5)] - [(M_{KSCN} \times (B_L - B_{K1}) \times 35.5)] \quad (2)$$

(**N.B.:** The identical colour intensity at the endpoint of the back and blank titrations was judged by viewing simultaneously both the solutions.)

Titrimetric determination of chloride in beer: The 0.5 mN or 10 mL of 0.05 N $Hg(SCN)NO_3$ reagent was used for both blank as well as back titrations, so the volume difference (B_L-B_K in mL) of standard 0.05 N KSCN was found to be proportional to the amount of $Hg(SCN)NO_3$ utilized for the reaction with chloride. Therefore, using the atomic weight of chlorine (35.5) the concentration ($C_{Cl\ beer}$) of chloride in mg/mL of beer sample was calculated by using eqn. 3:

$$C_{Cl\ beer} = \frac{N_{KSCN} \times (B_L - B_K) \times 35.5}{V_{beer}} \quad (3)$$

In eqn. 1, N_{KSCN} represents the normality of KSCN solution and V_{beer} is the volume of beer sample taken for the titration. The amount of chloride spiked in beer ($C_{Cl\ spiked}$) was calculated using eqn. 4:

$$C_{Cl\ spiked} = [\text{Total chloride found}] - [\text{Beer chloride}]$$
$$C_{Cl\ spiked} = (M_{KSCN} \times (B_L - B_{K2}) \times 35.5)] - [(M_{KSCN} \times (B_L - B_{K1}) \times 35.5)] \quad (4)$$

RESULTS AND DISCUSSION

The argentometric and mercurimetric titrations are suitable methods for the quantitative determination of chloride in the different samples. The argentometric methods of determination of chloride are based on the precipitation of chloride with silver salt and associated with error due to co-precipitation [8-10]. The mercurimetric determination of chloride is defined example of complexometric reaction [9]. But the titration reaction of chloride with $Hg(NO_3)_2$ shows indistinguishable reaction stoichiometry because mercuric ion forms various types of chloride complexes [8-10]. The titrations using silver and mercury salts for the determination of chloride in beers has its own setbacks due to unknown reaction stoichiometry and therefore not suitable for the determination of exact concentration of chloride. Conse-quently, for attending the exactly known reaction stoichiometry, a synthetic $Hg(SCN)NO_3$ reagent has been employed here for titrimetric assay of chloride concentration in beers.

The thiocyanate, as well as chloride both the ions, forms sufficiently stable complexes with mercuric [Hg(II)] ion. The cumulative formation constant (CFC) of mercuric-thiocyanate complexes are reported as log K_2 = 17.42 and log K_4 = 21.23, indicating the formation of $[Hg(SCN)_2]$ and $[Hg(SCN)_4]$ complexes, respectively [11,12]. Furthermore, the sufficient difference between log K_2 and log K_4 of the thiocyanate complexes of Hg(II), makes it possible to titrate Hg(II) against KSCN up to the reaction product $Hg(SCN)_2$, using the ferric ions indicator [10,13]. After formation of $[Hg(SCN)_2]$, ferric [Fe(III)] ion forms red-coloured $[Fe(SCN)]^{2+}$ complex. Similarly, the CFC of the mercuric-chloride complexes are reported as log K_1 = 6.74, log K_2 = 13.22, log K_3 = 14.07 and log K_4 = 15.07. These values indicates the formation of $[HgCl]^+$, $[HgCl_2]$, $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ complexes, respectively. The log K_1 and log K_2 values of the $[HgCl]^+$ and $[HgCl_2]$ complexes differs [11,12] by a factor equal to 6.48. This illustrate that $[HgCl_2]$ will be formed after formation of the $[HgCl]^+$. Consequently, it is possible to prepare the $Hg(SCN)(NO_3)$ reagent by the reaction of $Hg(NO_3)_2$ with KSCN and then KCl, respectively. Furthermore,

log K_2, log K_3 and log K_4 values of the $[HgCl_2]$, $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ complexes does not differs widely, signifies the simultaneous formation of these complexes, when an excess amount of chloride reacted with Hg(II) solution. For this reason, the correct reaction stoichiometry becomes indistinguishable after the formation of $[HgCl]^+$ in the direct titration of chloride against Hg(II). In addition, the reaction of Hg(II) with chloride cannot be controlled up to $[HgCl]^+$ without adding any other competitive reacting ion like thiocyanate.

For the preparation of $Hg(SCN)(NO_3)$ reagent, initially, the reaction of $Hg(NO_3)_2$ against KSCN was carried out in the 1:2 stoichiometric ratio using $Fe(NO_3)_3$ indicator [10,13]. After the formation of mercuric thiocyanate, $[Hg(SCN)_2]$, $Fe(NO_3)_3$ immediately gives the red coloured monothiocyanato-iron(III) nitrate $[Fe(SCN)(NO_3)_2]$.

$$Hg(NO_3)_2 + 2KSCN \longrightarrow Hg(SCN)_2 + 2KNO_3$$

When the equivalent amount of $Hg(NO_3)_2$ was added into this reaction mixture it results in the formation of $Hg(SCN)NO_3$ because of the following disproportionation reaction and the red colour of solution disappeared because of the conversion of $Fe(SCN)(NO_3)_2$ into $Hg(SCN)(NO_3)$:

$$Hg(NO_3)_2 + Hg(SCN)_2 \longrightarrow 2[Hg(SCN)(NO_3)]$$

This $Hg(SCN)(NO_3)$ reagent reacts with chloride ion in the 1:1 stoichiometric ratio and found to be suitable for the titrimetric determination of chloride.

Titrimetric determination of chloride concentration in beers: In this procedure, a measured volume of beer sample was added into known and an excess amount of $Hg(SCN)NO_3$ reagent and the surplus $Hg(SCN)NO_3$ was determined by back titration against standard KSCN solution using $Fe(NO_3)_3$ indicator. The chloride in beer (in the form of KCl) and $Hg(SCN)NO_3$ reagent were found to be reacting 1:1 stoichiometric in presence of $Fe(NO_3)_3$ indicator as shown below:

$$[Hg(SCN)(NO_3)] + KCl \longrightarrow [Hg(SCN)(Cl)] + KNO_3$$
(at the equivalence)

when the titration reaction of chloride with $Hg(SCN)(NO_3)$ was completed, the next drop of KSCN solution generates red coloured $[Fe(SCN)(NO_3)_2]$ at the endpoint.

$$KSCN + Fe(NO_3)_3 \longrightarrow [Fe(SCN)(NO_3)_2] + KNO_3$$
(at the end point)

During the titration, when the sample of beer was added to the reagent, the solution becomes yellowish in colour. So as to eliminate the titration error (may occur due to judgment of endpoint), the red colour intensity [or the amount of $Fe(SCN)(NO_3)_2$ generated] at the endpoints of the back as well as blank titrations, was obtained identical *via* comparing both solutions near the endpoint or with another faint red-coloured solution of the same composition. It was observed that the amount of $Fe(SCN)(NO_3)_2$ generated at the endpoint does not affect the chloride measurement, since the amount $Hg(SCN)(NO_3)$ required was determined by the volume difference of KSCN obtained by using blank and back titrations.

Four different beer samples were analyzed. Using a specific volume of beer with six-replicate determinations of chloride

TABLE-1
PRECISION IN TERMS OF AVERAGE STANDARD DEVIATION OBTAINED IN THE TITRIMETRIC DETERMINATION OF CHLORIDE CONCENTRATION IN BEERS

Beer sample No.	Sample volume tested (mL)	*Total chloride found (mg)	*Average chloride found (mg/mL)	**Mean/average deviation	**Standard deviation	**Average standard deviation
1	5.0	2.2188	0.4438	0.0107	0.0133	0.01048
	6.0	2.6803	0.4467	0.0089	0.0111	
	7.0	3.1063	0.4438	0.0076	0.0095	
	8.0	3.5678	0.4460	0.0067	0.0083	
	9.0	3.9938	0.4438	0.0059	0.0074	
	10.0	4.4375	0.4438	0.0107	0.0133	
2	5.0	2.2412	0.4482	0.0108	0.0134	0.01058
	6.0	2.7073	0.4512	0.0090	0.0112	
	7.0	3.1376	0.4482	0.0077	0.0096	
	8.0	3.6038	0.4505	0.0067	0.0084	
	9.0	4.0341	0.4482	0.0060	0.0075	
	10.0	4.4823	0.4482	0.0108	0.0134	
3	5.0	2.1752	0.4350	0.0104	0.0130	0.01025
	6.0	2.6277	0.4379	0.0087	0.0109	
	7.0	3.0453	0.4350	0.0075	0.0093	
	8.0	3.4978	0.4372	0.0065	0.0081	
	9.0	3.9154	0.4350	0.0058	0.0072	
	10.0	4.3505	0.4350	0.0104	0.0130	
4	5.0	2.1334	0.4267	0.0102	0.0128	0.01007
	6.0	2.5772	0.4295	0.0085	0.0106	
	7.0	2.9868	0.4267	0.0073	0.0091	
	8.0	3.4305	0.4288	0.0064	0.0080	
	9.0	3.8401	0.4267	0.0057	0.0071	
	10.0	4.2668	0.4267	0.0102	0.0128	
					Average:	0.01034

*Average value for **six** replicate measurements; ** Determined for **six** replicate measurements

TABLE-2
ACCURACY IN TERMS OF ABSOLUTE ERRORS AND RELATIVE ERRORS OBTAINED IN THE TITRIMETRIC DETERMINATION OF CHLORIDE CONCENTRATION IN BEER

Beer sample No.	Volume tested (mL)	**Total chloride in beer volume (mg)	Chloride found after spiking (mg)	Amount of spiked chloride (mg)	Spiked chloride found (mg)	Absolute error (mg)	Relative error (%)	*Average relative error (%)
1	7.0	3.1122	10.2477	7.100	7.1355	0.0355	0.50	0.16
	8.0	3.5568	8.9105	5.325	5.3605	0.0355	0.66	
	9.0	4.0014	7.5159	3.550	3.5145	-0.0355	-1.00	
2	7.0	3.1467	10.3177	7.100	7.1710	0.0710	1.00	2.12
	8.0	3.5928	8.9533	5.325	5.3605	0.0355	0.66	
	9.0	4.0419	7.6097	3.550	3.5678	0.0178	0.51	
3	7.0	3.0513	10.1158	7.100	7.0645	-0.0355	-0.50	0.83
	8.0	3.4872	8.8832	5.325	5.3960	0.0710	1.33	
	9.0	3.9231	7.5086	3.550	3.5500	0.0000	0.00	
4	7.0	2.9925	10.1635	7.100	7.1710	0.0710	1.00	1.34
	8.0	3.4200	8.7095	5.325	5.2895	-0.0355	-0.66	
	9.0	3.8475	7.4298	3.550	3.5855	0.0355	1.00	
							Average	1.12

**Average value of analysis taken from Table-1, *Average value for four measurements.

was carried out to study the precision of the titration procedure. The results presented in Table-1, the very small value of the average standard deviation indicates the proposed titration procedure is precise and accurate.

Study of interfering role of sample matrix: The interfering role of sample matrix (organic and inorganic materials other than chloride) present in the beer was studied by chloride recovery experiment, in which the known amount of chloride was added (spiked) in the beer sample and the amount of added chloride was determined. The results presented (Table-2) in the form of relative error indicate the good chloride recovery and no interfering role played any organic or inorganic materials present in the beer. Also, the reaction of $Hg(SCN)(NO_3)$ reagent with chloride is in a selective manner and occurring in the 1:1 stoichiometric ratio.

Conclusion

The synthetic prepared $Hg(SCN)NO_3$ is considered as one of the best reagents for titrimetric determination of chloride concentration in beers. The $Hg(SCN)NO_3$ reagent gives well-defined reaction stoichio-metry with the stable and distinctly visible end-point in the titrimetric determination of chloride concentration in beer. This reagent maintains the homogenous nature of reaction mixture due to acidic pH, hence eliminates the titration errors which are commonly encountered due to co-precipitation. The reagent is highly selective for the determination of chloride concentration as proved by the chloride recovery experiment performed during the interference study. The spiking/standard addition of chloride (amplification method) increases the sensitivity of the titration method for the determination of beer chloride at a trace level with minimum sample volume. The analysis of the statistical data obtained during the experiment indicates the procedure is precise and accurate.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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