Spectrophotometric determination of microquantities of silver(I) using dithizone in the presence of cetyl trimethylammonium bromide

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The spectrophotometric determination of silver(I) as its dithizonate has been carried out in the micellar medium, cetyl trimethylammonium bromide (CTAB). Both ligand and the complex were soluble in water in the presence of the surfactant. The molar absorptivity of the complex at $\lambda_{\text{max}}$ 565 nm was found to be $5.5 \times 10^4$ I mol$^{-1}$ cm$^{-1}$, with stoichiometry of 1:1. Beer's law is obeyed up to 1.0 ppm. The method has been used for the estimation of silver in pharmaceutical ointment and in the waste water of photographic film developing laboratory.

Most of the sensitive spectrophotometric methods for the estimation of microquantities of silver are extractive$^{1-4}$. Dithizone is a specific reagent for silver and is used for titrimetric$^5$ and photometric$^6$ analysis. It forms a yellow water insoluble complex in acidic medium, which can be extracted in chloroform. Although a sensitive reagent, insolubility of the ligand and the complex in water necessitates the use of toxic organic solvents for extraction. The extractive procedures are cumbersome and have inherent sources of errors due to partial miscibility of solvents and adherence of the solvents to the glasswares. Hence, micellar solubilization of ligand and silver-dithizonate forms an attractive process for estimation of silver.

Spectrophotometric determination of silver using dithizone in the presence of nonionic surfactant Triton X-100 has been reported earlier$^7$. Stoichiometry and molar absorptivity of the complex was reported to be 1:1 and $3.34 \times 10^4$ I mol$^{-1}$ cm$^{-1}$ at 500 nm respectively. Yeaw$^8$ has reported estimation of silver as its dithizone at 545 nm using anticoagulant versa -TL.

We are reporting here a more sensitive method for the determination of silver as its dithizone in the presence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB). The proposed method has been successfully used for the estimation of microgram quantities of silver in waste water from photographic film developing laboratories and in the analysis of pharmaceutical ointments.

Experimental

All the chemicals and reagents used were of AR grade. Doubly distilled, deionised water was used throughout. A stock solution of silver(I) ($1.95 \times 10^{-3} M$) was prepared by dissolving 0.1575 g of silver nitrate in water and making the volume up to 100 cm$^3$. The standardization of the solution was carried out by the literature method$^9$. The working solutions were prepared by appropriate dilutions.

As dithizone is sparingly soluble in the CTAB solution, 0.1 g of dithizone was mixed with 50.0 cm$^3$ of 2.74 $\times$ 10$^{-2}$ M CTAB solution. The mixture was shaken for 12 h and then filtered and washed with CTAB solution. The filtrate was made to 100 cm$^3$ with CTAB solution. The concentration of dithizone in this stock solution was determined gravimetrically. Further dilutions were done whenever necessary with CTAB solution. The stock solution was stored in brown bottles covered with black carbon paper to avoid photo-oxidation of dithizone.

Absorption spectra of silver-dithizonate complexes were recorded on a Shimadzu UV-vis 240 spectrophotometer.

Procedure

Extractive method: To silver(I) solution (1.0 cm$^3$ of $1.95 \times 10^{-4} M$), 0.5 cm$^3$ of 0.5 N H$_2$SO$_4$ was added to make the system acidic. The volume of the aqueous phase was made up to 25.0 cm$^3$ with deionised water. To this, 2.0 cm$^3$ of 0.01% ascorbic acid solution to avoid aerial oxidation of dithizone was added and silver-dithizonate complex was extracted twice with 10.0 cm$^3$ aliquots of chloroform. The combined extracts were shaken vigorously with three (10.0 cm$^3$) portions of ammonia water (1.0 cm$^3$ of 25% ammonia solution in 1L water) and then with 10.0 cm$^3$ of 15% acetic acid. The chloroform extract was diluted to 25.0 cm$^3$ with chloroform. The absorption spectrum of the extracted complex was recorded against reagent blank.

Aqueous method: To 2.0 cm$^3$ of $1.95 \times 10^{-4} M$ dithizone solution prepared in 1.0% CTAB solution (2.74 $\times$ 10$^{-2} M$), was added 1.0 cm$^3$ of 0.1% ascorbic acid solution to avoid aerial oxidation of dithizone.
To this, 1.5 cm$^3$ of 0.1 M NaOH (pH 12.5-13.0) was added to provide the alkaline medium required for the complex formation. This was followed by the addition of 1.0 cm$^3$ of 1.95 x 10$^{-4}$ M silver (I) solution. The volume was made up to 25.0 cm$^3$ with water. The absorption spectrum of the silver-dithizonate complex was measured against reagent blank. Various conditions such as pH of the medium and concentration of surfactant, reagent and metal ion were optimised for the proposed method.

Results and discussion

The absorption spectrum of silver (I) - dithizonate complex extracted in chloroform exhibits absorption maxima at 475 nm (Fig. 1) with 3.0 x 10$^4$ I mol$^{-1}$ cm$^{-1}$ molar absorptivity. The absorption spectrum of silver-dithizonate complex in aqueous micellar medium is also shown in Fig. 1 and shows bathochromic shift in the absorption maxima to 565 nm with 5.5 x 10$^4$ I mol$^{-1}$ cm$^{-1}$ molar absorptivity. From the absorption spectra obtained for (i) metal, (ii) metal + surfactant, (iii) reagent in ethanol, (iv) reagent in surfactant, and, (v) reagent in surfactant + metal, it was observed that there is no interaction between metal and surfactant or reagent and surfactant. The enhancement in the sensitivity as well as a bathochromic shift are the results of the interaction between surfactant and silver-dithizonate resulting in improved solubilizations. This was further confirmed by determining the $pK_a$ values spectrophotometrically. The $pK_a$ values for the reagent in Triton X-100 and CTAB medium were observed to be 5.0 and 4.8 respectively and do not differ much from that of the reagent $pK_a = 4.7$. However, the reagent also exhibits another $pK_a$ value above pH 12 which contributes to the increased sensitivity of the complex. The reagent in Triton X-100, however does not exhibit $pK_a$ in alkaline medium and hence there is a difference in the sensitivity of the two complexes.

Dithizone in aqueous medium is oxidised due to dissolved oxygen. It is also easily oxidised when exposed to air. Hence it is necessary to use a reducing agent for stabilization of the reagent. Use of ascorbic acid during complex formation shows no interaction other than its reducing tendency resulting in stabilization of the reagent. Similar observation was reported by Bhajan Singh et al.$^{10}$ in the determination of mercury using dithizone in Triton X-100. No spectral shift was observed for the silver-dithizonate in the presence of ascorbic acid. Slight improvement in the absorbance is the result of improved stabilization of the reagent.

A study of the effect of pH on the extent of complex formation shows that no silver-dithizonate is formed in acidic medium. A pH of 12 and above is required for aqueous complex formation. Varying volumes of 0.1 M NaOH (0.5 to 6.0 cm$^3$) were used in the procedure discussed earlier for the development of the complex in aqueous medium. It was observed that 1.5 cm$^3$ of 0.1 M NaOH gives maximum complexation and hence was used in further studies.

The effect of surfactant on the development of silver-dithizonate was studied by using cationic (cetyl trimethyl ammonium bromide), anionic (sodium dodecyl sulphate), and nonionic (Triton X-100) surfactants during complex formation as per the procedure described earlier. Silver-dithizonate complex has been developed by using non-ionic surfactants earlier. However, in our studies, we observed that a cationic surfactant, cetyl trimethyl ammonium bromide, gives better results than anionic and non-ionic surfactants in alkaline medium. Below the critical micellar concentration of CTAB (0.92 x 10$^{-3}$ M), solubility of the reagent is very low. It was observed that as the concentration of surfactant increases, absorbance of the complex first increases and then remains constant. A 1.0% (2.74 x 10$^{-3}$ M) surfactant solution was found to be optimum for the development of the complex.

Effect of reagent concentration on the development of the silver-dithizonate was studied by developing the complex using 1.95 x 10$^{-4}$ M metal solution and varying concentrations of reagent solution in the procedure described earlier. It was observed that 1.0 cm$^3$ of 1.95 x 10$^{-4}$ M dithizone solution in 1.0% CTAB is sufficient for the complex formation. However, 2.0 cm$^3$ of the reagent was used to ensure complete complex formation.

Beer's law was valid up to 0.10 µg cm$^{-3}$ Ag (I) at 565 nm. The molar absorptivity was found to be 5.5 x 10$^4$ I mol$^{-1}$ cm$^{-1}$ at 565 nm. The correlation
coefficient and Sandell's sensitivity were found to be 0.997 and 0.0039 \mu g/cm\text{mm} respectively. Ringbom plot showed that the observed relative error for 20 to 60% T was less than 2.7% per 1% photometric error.

Stoichiometry of the silver-dithizone was determined by Job's, mole ratio and slope ratio methods. The complex under study shows 1:1 stoichiometry and hence can be represented as:

\[
\text{Ag}^+ + \text{H}_2\text{D}_2 \rightleftharpoons \text{Ag(HD)}_2 + \text{H}^+
\]

Interfering ions

Interference due to various ions was studied by using different ratios of silver (I): interfering ions. An ion was considered to be interfering if the absorbance obtained differed by more than ± 1% from that for silver alone. The following cations added as nitrate, sulphate or acetate caused no interference: Al $\geq$ 300; Th $\geq$ 60; Bi $\geq$ 20; Mn $\geq$ 20 and alkali metals $\geq$ 1000 ppm. However, Hg(II), Cd(II) and Pb(II) interfere seriously even at 1:1 ratio. Amongst the anions, phosphate $\geq$ 400; acetate $\geq$ 300; tartarate $\geq$ 200; carbonate $\geq$ 10; sulphate $\geq$ 100; thiourea $\geq$ 20; oxalate $\geq$ 400; iodide $\geq$ 2 ppm do not show interference. But chloride, bromide, fluoride, cyanide, thiocyanate, thiosulphate, citrate, EDTA interfere seriously.

Determination of silver (I) in waste water and pharmaceutical ointment

The proposed method was successfully applied for the determination of silver in the waste water from the photographic film developing laboratories and in pharmaceutical ointment.

Silver in waste water from the photographic film developing laboratory was determined following the procedure reported by Hung et al.\textsuperscript{11} 5 ml of waste water was treated with 5 drops of 30% \text{H}_2\text{O}_2, 1.0 \text{cm}^3 of 1:1 nitric acid and 1.0 \text{cm}^3 of 1:1 sulphuric acid for decomposition of organic matter. The solution was evaporated to dryness and 1.0 \text{cm}^3 of 1\text{HNO}_3 was added to it. The sides of the container were carefully rinsed with water. The solution was warmed to dissolve the residue, if any, and then diluted to the 500 \text{cm}^3 with conductivity water. Silver was determined in 1.0 \text{cm}^3 of diluted solution as per the procedure described earlier. Standard addition method was also followed for the estimation of silver. The results obtained are given in Table 1. It was observed that the waste water contains 2.56 g/l silver. The standard deviation obtained for the results was ± 0.187 for 5 replicate determinations, whereas RSD was 0.73%. The 99% confidence limit calculated for the mean value of silver (25.6 \mu g/cm\text{mm}) from the standard addition method was observed to be 25.6 ± 0.337. All the values obtained are within this limit indicating the reliability of the method.

Silver in pharmaceutical ointment was determined by heating 0.5 g of silver sulphadiazine (1.0% silver w/w) with a few drops of 1:1 \text{HNO}_3 and 1:1 \text{H}_2\text{SO}_4 to dryness for the decomposition of organic matter. The procedure was repeated once again. Then the container was rinsed with minimum quantity of conc. \text{HNO}_3 and water. The solution was filtered and diluted to 100 \text{cm}^3 with conductivity water. 1.0 \text{cm}^3 of this solution was used for the determination of silver by the proposed method. The results obtained are given in Table 1. The ointment contains 1.0% silver sulphadiazine. Hence, silver concentration in the ointment is 0.314%. By the proposed method, five repeated determinations showed the silver concentration in the ointment to be 0.3024%. The standard deviation for the results was observed to be ± 0.277 and RSD was 0.913%. The 99% confidence limit calculated for the mean value of silver (30.33 \mu g) from the standard addition method was observed to be 30.3 ± 0.5005. All the values obtained are within this range. This further confirmed that the proposed method is reliable for the microlevel analysis of silver.

\begin{table}
\centering
\caption{Estimation of silver (I) in photographic film developing laboratory waste water and pharmaceutical ointment}
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Amount of} & \textbf{Amount of} & \textbf{Amount of} & \textbf{Amount of} & \\
\textbf{Ag(I) added, \mu g} & \textbf{Ag(I) recovered, \mu g} & \textbf{Ag(I) added, \mu g} & \textbf{Ag(I) recovered, \mu g} \\
\hline
21.0 & 25.6 ± 0.189 & 21.0 & 30.3 ± 0.277 \\
10.0 & 25.7 ± 0.187 & 10.0 & 30.4 ± 0.264 \\
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References