The studies of Chromogenic Reagents of Heterocyclic Azo Dyes for Extraction- Photometric Determination of Ag(I).

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ABSTRACT

The interaction of Ag(I) with 1-(2-quinolylazo)-2-acenaphthylenol (QAAc) and 1-(2-lepidylazo)-2 acenaphthylenol (LAAc) to give red coloured (1:1) water-insoluble complexes at moderately alkaline pH's. The complexes are extractable in various water-immiscible organic solvents and exhibit maximum absorbance at 540-45nm. The Sandell's sensitivity of the colour reaction is 0.0052 μg Ag/cm² ($\in= 2.08 \times 10^{4}$) for silver–QAAc complex and 0.0037 μg Ag/cm² ($\in= 2.08 \times 10^{4}$) for silver-LAAc complex. The regents have been found to be fairly selective for the determination of silver(I) in presence of various interfering base metals.

Keywords :

Spectrophotometric, Refluxing, Spectrophotometer, Expandomatic, Calibration, Aliquot, Exhibited, Sensitivity, Deviation, Recommended, Dithizone, Rhodanine, Optimum, Intensity, Interference, Sensitivites.

Introduction :

Some spectrophotometric reagents of Ag^{+} ions. The extractive dithizone method, and the rhodamine method, are of particular importance[1,2]. A little information has been given about a few heterocyclie azo dyes[3]. A method of determination of silver with PAR[4] has been reported. 1-(2-Quinolylazo)-2 acenaphthylenol (QAAc) has already been used for the spectrophotometric determination of various metal ions[5-7]. In the present communication, the use of QAAc and another azo dye, 1-(2-lepidylazo)-2-acenaphthylenol (LAAc) has been explored for the spectrophotometric determination of Ag.

Experimental :

Reagents : A stock solution of silver (I) was prepared by dissolving appropriate amount of silver nitrate (reagent grade) in double distilled water. QAAc was synthesized[8] and its stock solution was prepared by dissolving appropriate amount (0.323 g/1 for 10^{-3} *M*) in pure methanol. LAAc was synthesized by. Coupling 1, 2-acenaphthaquinone with 2-hydrazinolepidine (obtained by refluxing 2-chlorolepidine[9]

with hydrazine hydrate) in methanolic medium. Purity of the reagent was checked by t.l.c. and its stock solution was prepared in pure methanol (0.337 g/1 for $10^{-3}M$). A few drops of pure chloroform can be added, if necessary, to the reagents before dissolving them in methanol, as these are highly soluble in chloroform. In no case reagent solutions older than four days were used.

Dilute solutions of hydrochloric acid, sodium acetate and sodium hydroxide were used for pH adjustments.

Phosphate-sodium hydroxide buffer was used for adjustment of pH around 10.0.

Apparatus : A Unicam SP-600 spectrophotometer with 10 mm matched glass cells was used for absorbance purposes.

A Beckman pH meter model Expandomatic SS-2, with a saturated calomel and glass electrode assembly was used for pH measurements.

Recommended Procedure : To a suitable aliquot containing 11 to 40 μg of silver(I), add sufficient excess of QAAc solution or to a suitable aliquot containing 12 to 37 μg of silver (I), add sufficient excess of LAAc solution, followed by 2.0 ml of phosphate/hydroxide buffer (pH~10.0). Raise the volume to 10ml keeping 50% (v/v) methanol–aqueous medium. Keep for two minutes and extract in 10ml of freshly distilled chloroform. Measure the absorbance at λ_{max} (540-45 nm) against a reagent blank prepared under identical conditions. The amount of silver can be deduced from the calibration curve drawn under similar conditions.

Results and Discussion :
Methanolic solution of the reagent (QAAc of LAAc) is added to a very dilute aqueous solution of silver(I) resulted a water-insoluble red precipitate in moderately alkaline medium, which was soluble when methanolic concentration was kept more than 75% (v/v). The precipitate was extractable in various water-immiscible organic solvents, however, chloroform of carbon tetrachloride was used for extraction purposes, as the absorbance was maximum in these and the complexes were stable at least four hrs.

Characteristics of the complexes :
A number of solutions containing Ag(I) ($2x10^{-5}M$) and the reagent QAAc of LAAc ($2x10^{-4}M$) at different pH were prepared keeping 50% (v/v) methanolic concentration and extracted in 10ml of freshly distilled chloroform. Their spectra were recorded against a reagent blank. At all pH levels. Both the complexes had maximum absorbance at 540-5 nm.

Effect of pH :
The complexes exhibited constant and maximum absorbance in the pH range 8.5–10.7 when QAAc was used and 9.0–10.1 when LAAc was used. A phosphate/hydroxide buffer of appropriate pH(~10.0) was used during further studies.

Effect of Reagent Concentration :
The data recorded absorbed by a series of solutions containing silver(I) ($2\times10^{-5}M$) and varying amounts of reagent (at PH~10.0) showed that 30 molar times of

QAAc or 20 molar times of LAAc are required for full colour development of the complexes.

Other Physico-Chemical Characteristics :

Beer's law validity and optimum range for accurate determination of metal ions at a pH of 9.5$\pm$ 0.5, determined by Ringbom plots, are 0-4.2 ppm and 1.1 – 4.0 ppm respectively for silver-QAAc complex and 0-4.6 ppm and 1.2 – 3.7 ppm respectively for silver-LAAc complex. The Sandell's sensitivity of the colour reactions calculated from Beer's law plots comes out to be 0.0052 μg Ag/cm² ($\in=2.08 \times 10^4$ 1.mole^{-1} cm^{-1}) for silver–QAAC and 0.0037 μg Ag/cm² ($\in=2.88 \times 10^4$ 1. Mole^{-1} cm^{-1}) for silver-LAAc complex at their λ_{max}.

Composition of Complexes :

The using of Job's method of the continuous Composition of the complexes was determined variation. Results obtained showed that the metal ion and reagent interact in 1:1 ratio in both the cases.

Absorbance Deviations :

Measured under the experimental conditions, the mean absorbance of eight solutions containing 1 ml of 2 x 10^{-4} M silver was found to be 0.415, with a standard deviation of 0.005 for silver-QAAc complex and the mean absorbance was 0.576 with a standard deviation of 0.043. for silver-LAAc complex.

Effect of Diverse Ions :

The studied of diverse ions effect, taking 2.16 μg/ml of silver(I), adding different amounts of diverse ions and determining the amounts of silver content following the recommended procedure. It was found that lanthanides (15-fold each), In (III), Mn(II), Fe(II) and (III), Au(III), platinum metals in cold except Pd(II) (5 fold each) did not interfere. However, I-, CNS$^-$, CN$^-$, $S_2O_3^{2-}$ thiourea, Zn(II) interfere seriously. The amounts of other ions (in ppm), which did not cause deviation of more than ±3% in absorbance are- PO_4^{3-}, BO_3^{3-} (1000) ; oxalate, cltrate, tartrate (500) ; F$^-$, Cl$^-$, NO_2^-, SO_4^{2-} (200), Br$^-$, SO_3^{2-} Cd(II), Hg(II), Cu(II), Ni(II), Pd(II).

Conclusion :

Dithizone and dimethylaminobenzylidenerhodanine have been shown to be the most useful reagents for silver[1,2], but neither of them is specific. Silver is determined with dithizone by the monocolour, mixed colour and extractive titration methods. In case of rhodanine method, the absorbance of the complex formed, depends on the acidity of the solution, the concentration of rhodanine and time. The optimum acidity corresponds to 0.05M HNO$_3$ and at the optimum rhodanine concentration (0.001 – 0.002%), maximum absorbance is obtained in five min, the colour fades after this. The temperature is also kept constant since large variations affect the colour intensity. In practical analysis, the separation of silver from the other metals is required before applying either of the method mentioned above. Gold and palladium react with both the reagents and cause interference. Small amounts of mercury(II) can be tolerated in direct rhodanine method but not in the dithizone method. Dagnall and West[10]

recommended pyrogallol red and bromopyrogallol red methods, in which the cationic complex of silver with 1, 10-phenanthroline reacts with the reagents to yield and ion-association complex. Among the heterocyclie azo dyes, only the colour reactions with PAN, p-PAN and 7-(2-pyridylazo)-8-quinolinol have been reported[3], but details are lacking. However, PAR[4] has been shown to be a sensitive reagent for silver. The present methods are direct and rapid. The complexes formed are fairly stable at least for four hrs and the colour intensity is not affected by heat. The reagents have been found to be sensitive as well as selective as many of the interfering cations could be masked with complexing anions like oxalate and citrate. The sensitivities of the colour reactions are compared with some other well known reagents reported for silver in Table 1.

Table : Sensitivities of some Determination of Ag

Reagents	Sensitivity $(\mu g\ Ag/cm^2\ for\ \log I_o/I = 0.001)$	Reference
Dithizone (mixed colour)	0.01 (yellow filter)	1
p- Dimethylaminobenzylidenerhodanine (direct)	0.005/495 nm	1
Bromopyrogallol red	0.0034/590 nm	10
Thiodibenzoylmethane (C_6H_6)	0.01/420 nm	12
Methyl phenyldimercaptothiopyrone	0.014/510 nm	11
1-(2-Quinolylazo)-2-acenaphthylenol (QAAc) method	0.0052/840 nm	present

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