Spectrophotometric Determination of Trace Silver with Sodium 2-(8-Hydroxyquinolin-5-ylazo)benzoate

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Synopsis. The reaction between silver and sodium 2-(8-hydroxyquinolin-5-ylazo)benzoate in aqueous media in presence of Na–K tartrate at pH 5.2—6.1 results in an intense purple color which is stable for at least 24 h. The molar absorptivity and Sandell's sensitivity at 525 nm are 3.65×10^4 dm^3 mol^{-1} cm^{-1} and 0.0029 μg cm^{-2}, respectively. The method was applied to the determination of silver in geological samples.

The methods for the determination of silver employing formation of binary complexes suffer from drawbacks(1) like lack of reproducibility, low sensitivity etc. Dithizone complex of silver is photosensitive and the method employing the formation of the complex needs careful standardization while other reagents like pyrogallol red,(2,3) 2-amino-6-methylthio-4-pyrimidinecarboxylic acid(4) etc., suffer from many interferences. The most common reagent, *p*-dimethylaminobenzylidenerhodanine used for the determination of silver, is very sensitive to change of acidity.(5) We report here in a sensitive spectrophotometric method for the determination of silver in sub microgram level using 2-(8-hydroxyquinolin-5-ylazo)benzoic acid (**R**). 5-Arylazo-8-quinolinols form colored complexes with several metal ions but the studies do not give any quantitative analytical application using these compounds.(6) Recently, 5-arylazo-8-quinolinols have attracted the attention of several workers as a promising ligand for forming a wide variety of metal and organometallic complexes.(7–10) In a previous work,(11) we reported a highly sensitive spectrophotometric method for the determination of nickel using **R**. In continuation of our investigative work with **R** a highly sensitive and practical spectrophotometric method has been developed and applied to analysis of geological samples.

Experimental

Apparatus. A Varian 634-S double beam scanning UV-vis spectrophotometer was used for recording spectra and for individual absorbance measurements with 1.0 cm path length quartz cells.

Reagents. All reagents used were of analytical grade. 2-(8-Hydroxyquinolin-5-ylazo)benzoic acid (**R**) was synthesized as described in literature.(12) The reagent (0.293 g) was dissolved in distilled water containing NaOH (0.07 g) and the volume was made up to 100 cm^3. This solution was further diluted with water to get 1×10^{-3} mol dm^{-3} **R** solution. The solution is stable for 1 week. A standard solution of Ag(I) was prepared by dissolving 0.1698 g of silver nitrate in 1 dm^3 of distilled water. Further dilutions were made accordingly.

Procedure. pH of an aliquot of sample or standard solution containing 2.0—32.4 μg of silver was adjusted to 5.2—6.1 with dilute ammonia and nitric acid. To this 1% w/v sodium potassium tartrate solution (1 cm^3) was added and mixed. Then 1 cm^3 of **R** solution was added and the volume was made up to 50 cm^3. Absorbance of the solution was measured after half an hour at 525 nm against the reagent blank.

Dissolution and Pretreatment of Geological Samples. 5.0 g of samples (1 g in case of sulfide minerals) was mixed with 15 cm^3 of hydrofluoric acid, 1 cm^3 nitric acid in a platinum dish, and the solution evaporated to dryness. Then 10 cm^3 of perchloric acid was added and heated until no fumes were evolved. Further, the sample was evaporated to dryness 2—3 times with nitric acid and finally digested with nitric acid (0.5 mol dm^{-3}) and filtered. The filtrate was warmed and treated with excess of ammonia solution. The solution was filtered, the precipitate was washed with dilute ammonia solution (0.3 mol dm^{-3}) and the filtrate was collected. The filtrate was acidified with dilute nitric acid. Then 10 cm^3 of 10% w/v EDTA (disodium salt) solution was added and pH was adjusted to 10 with ammonia and nitric acid solutions. A 0.1% w/v, 0.3 cm^3 sodium diethyldithiocarbamate solution (Na–DDC) was added and silver complex was extracted with two 10 cm^3 fractions of carbon tetrachloride.

Silver was stripped from organic layer with four 10 cm^3 fractions of 0.8 mol dm^{-3} hydrochloric acid solution. The fractions were combined, evaporated to dryness and treated with 5 cm^3 of 1 : 1 sulfuric acid and heated to white copious fumes. The solution was cooled and diluted with (ca. 20 cm^3) distilled water. Silver was estimated as described in general procedure.

Results and Discussion

Absorption Spectra and Effect of pH. Figure 1 shows the absorption spectra of the complex and the reagent blank. The formation of the complex does not shift absorption maximum (495 nm) for the reagent, appreciably. The absorption of the complex against reagent blank is maximum at 525 nm. Formation of the com-

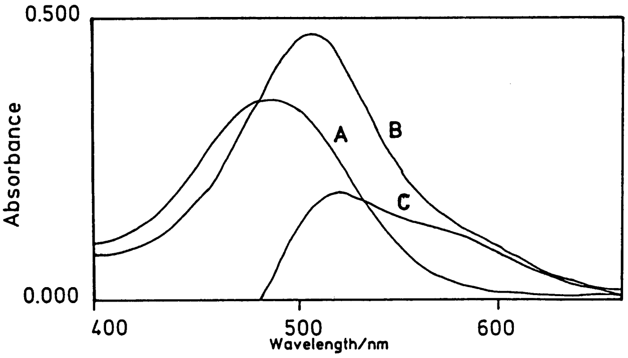

Fig. 1. Absorption spectra of 2-(8-hydroxyquinolin-5-ylazo) benzoic acid and its silver complex in aqueous solution at pH 5.2—6.1. Reagent. 2×10^{-5} mol dm^{-3}; silver 6×10^{-6} mol dm^{-3}; A. Reagent against water; B. Complex against water; C. Complex against reagent blank.

plex is found to start at pH 5, becomes maximal at pH between 5.2 and 6.1, and then decreases at higher pH.

Beer's Law, Sensitivity and Reproducibility. Beer's law is obeyed at 525 nm between 0.05—0.65 μg cm^{-3} of silver in the final solution. The molar absorptivity and Sandell's sensitivity at 525 nm are 3.65×10^4 dm^3 mol^{-1} cm^{-1} and 0.0029 μg cm^{-2} of silver, respectively. The precision is shown in Table 1.

Rate of Complex Formation and Stability of the Complex. The rate of complexation of **R** with silver was slow as shown in Fig. 2 which reveals that more than 2 h is required to attain constant and maximum absorbance. In the presence of 10 mg of Na–K tartrate, the complexation reaction was found to be completed within 10—15 min. The higher concentration of Na–K tartrate does not affect the complexation reaction.

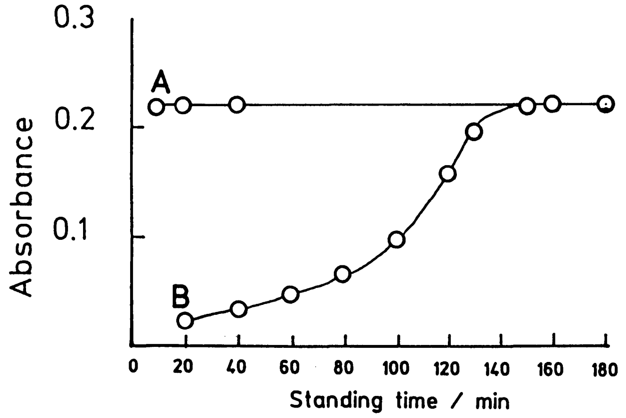

Fig. 2. Influence of standing time on the complexation of 2-(8-hydroxyquinolin-5-ylazo)benzoic acid with silver. 2-(8-Hydroxyquinolin-5-ylazo)benzoic acid 2×10^{-5} mol dm^{-3}; silver 6×10^{-6} mol dm^{-3}; pH 5.2—6.1; reference, reagent blank; wavelength/nm 525; A. silver complex of the reagent in presence of Na–K-tartrate of 0.02% w/v; B. in the absence of Na–K-tartrate.

Table 1. Precision of the Spectrophotometric Determination of Silver by Proposed Method (10 Replicates)

Silver added	Silver found	Standard deviation	r.s.d.
μg	μg	μg	%
5.0	4.91	0.21	4.2
10.0	9.90	0.13	1.3
30.0	30.12	0.11	0.4

Table 2. Tolerances for Other Ions in Determination of 6.0×10^{-6} mol dm^{-3} Silver

Ion	Molar tolerance ratio (ligand/silver)
Na(I), K(I), Ba(II)	1000[b]
Ca(II), Mg(II)	2000[b]
EDTA, Tartrate, Citrate	1000[b]
BrO_3^-	200
F^-, CO_3^{2-}	5
Oxalate[a]	<1

a) Positive interference. b) Maximum ratio tested.

The **R**–Ag complex was found to be stable for more than 24 h.

Effect of R Concentration and Composition of the Complex. The effect of **R** concentration was examined which suggests the formation of 1 : 3 (M : L) complex (Fig. 3). The optimum absorbance of the complex

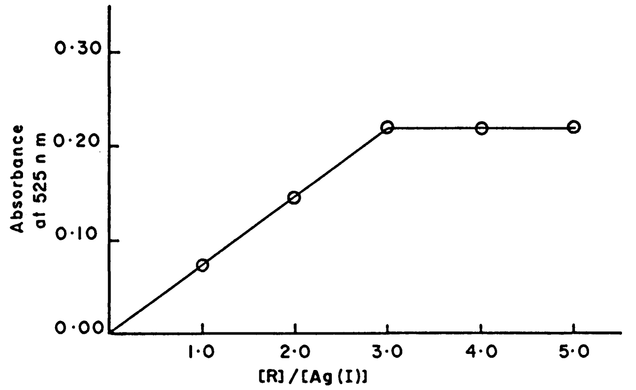

Fig. 3. Influence of 2-(8-hydroxyquinolin-5-ylazo)-benzoic acid (**R**) concentration. Ag(I), 6×10^{-6} mol dm^{-3}; pH 5.2—6.1; reference, reagent blank.

Table 3. Determination of Silver in International Geo-Standard Samples

Ag(I) added	BAS-375 A[a] Ag(I) found, μg/g		BAS-376 A[b] Ag(I) found, μg/g	
μg/g	Atomic absorption spectrometry	Proposed[c] method	Atomic absorption spectrometry	Proposed[c] method
0.50	0.48	0.51	0.48	0.52
1.00	0.98	1.02	0.96	0.98
2.00	1.98	2.01	1.95	1.98
3.00	2.94	3.12	3.08	3.12

a) Composition (%) of BAS-375 A, 67.1 SiO_2, 19.8 Al_2O_3, 0.38 TiO_2, 0.12 Fe_2O_3, 0.89 CaO, 0.05 MgO, 10.4 Na_2O, 0.79 K_2O, 0.39 LOI, and 0.10 Cu, 0.10 Pb, 0.10 Zn, 0.10 Co, 0.10 Ni of metals (%) were added. b) Composition (%) of BAS-376 A, 67.1 SiO_2, 17.7 Al_2O_3, <0.02 TiO_2, 0.10 Fe_2O_3, 0.54 CaO, 0.03 MgO, 2.83 Na_2O, 11.2 K_2O, 0.35 LOI, and 0.20 Cu, 0.20 Pb, 0.20 Zn, 0.20 Co, 0.20 Ni of metals (%) were added. c) Average of eight replicates.

Table 4. Determination of Silver in Sulfide Mineral Samples

Sample	Silver content/ppm	
	Proposed method[a]	Atomic absorption spectrometry
A	11±0.31	9
B	21±0.15	22
C	14±0.26	12
D	4±0.42	4
ASK-3[b]	18±0.22	17

a) Mean±standard deviation. b) Recommended value: 18 ppm; "Geo-standards News Letters," Vol. 8, No. 1—2, p. 05 of Appendix 1 (1984).

Table 5. Comparison of Spectrophotometric Methods for the Determination of Silver

Reagents	Wavelength nm	Molar absorptivity $dm^3 mol^{-1} cm^{-1}$	System	Reference
Pyrogallol red	390	1.00×10^4 [a]	Aqueous	2
5-(2-Methyl-3-hydroxy-5-hydroxymethyl -4-pyridylmethylene) rhodanine	530	1.50×10^4	Aqueous	18
Thiacrown compound, 1,4,8,11-tetrathiacyclotetradecane	378	1.80×10^4	Non-aqueous	19
5-(*p*-Diethylaminobenzylidene) rhodanine	495	2.12×10^4 [a]	Aqueous	17
6,7,10,11,17,18-hexahydro-5*H*, 9*H*-dibenzo (*e*,*n*)(1,4,10,7,13) trithiadiazacyclopentadecin and dipicrylamine	380	2.50×10^4	Non-aqueous	20
1,10-Phenanthroline and bromopyrogallol red	590	3.20×10^4	Non-aqueous	21
Sodium 2-(8-hydroxyquinolin-5-ylazo) benzoate	525	3.65×10^4	Aqueous	This work

a) Calculated on the basis of Sandell's sensitivity.

coupled with minimum blank absorbance was found with 1 cm^3 (3 mol per mol of silver) of **R** solution. The molar ratio[13] and continuous variation[14] method also supported the stoichiometry of the complex.

Effect of Temperature. The reaction of silver with **R** to form the colored compound was found to be independent of temperature in the range, 20 to 40 °C.

Effect of Diverse Ions and the Removal of Interferents. The effect of various diverse ions was studied individually (Table 2). The criterion for the studies was a ±2% change in the absorbance for 32.4 µg of silver.

Mo(VI), W(VI), Zr(IV), and Ni(II) complexes do not cause spectral interference but the reagent is consumed while Hg(II), Zn(II), Co(II), Ce(III), La(III), Al(III), Th(IV), V(V), and U(VI) interfere either by forming complexes or by consuming the reagent.

Silver is separated alongwith Co, Ni, Cu etc. as amino complex from elements forming insoluble hydroxides such as Fe, Al, Ti, Cr, V, Nb, Ta, Mo, W, Zr etc. by precipitating them with aqueous ammonia. Silver is separated from other amino complexes by selective extraction with Na–DDC in presence of EDTA (disodium salt) at pH 10 in carbon tetrachloride. Calculated quantity of Na–DDC was used such that it formed complex preferably with silver as silver forms less dissociated complex with Na–DDC.[15] Mercury was found to be removed during sample preparation. Silver is then stripped into HCl (0.8 mol dm^{-3}). Silver chloride in colloidal form is brought into active ionic state by fuming with sulfuric acid.

Practical Application. The validity of the method is tested to sulfide mineral, rock and international geostandard samples (BAS-375 A and BAS-376 A containing 0.5, 1, 2, 3 µg/g of added silver). The results agreed very closely (Tables 3 and 4) with the values obtained by atomic absorption spectrometry after co-precipitating[16] silver with tellurium.

Conclusion. The proposed method for the determination of silver is simple, quick in operation and compares favorably in sensitivity with published methods[2,17–21] (Table 5).

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