

# SPECTROPHOTOMETRIC DETERMINATION OF SILVER USING THE REACTION BETWEEN BROMOPHENOL RED AND PEROXIDISULPHATE

K. Vaheesar<sup>1</sup>, CD. Jayaweera<sup>2</sup>, P.M. Jayaweera<sup>3</sup>  
Department of Chemistry, Eastern University<sup>1</sup>,  
University of Sri Jayewardenepura, Gangodawila, Nugegoda<sup>2,3</sup>

## INTRODUCTION:

Silver is a rare but naturally occurring metal, often found deposited as a mineral ore in association with other elements. Emissions from smelting operations, manufacture and disposal of certain photographic and electrical supplies, coal combustion, and cloud seeding are some of the anthropogenic sources of silver in the biosphere.

The most recent measurements of silver in rivers, lakes, and estuaries using clean techniques show levels of about  $0.01 \text{ ug dm}^{-3}$  for pristine, unpolluted areas and  $0.01\text{-}0.1 \text{ ug dm}^{-3}$  in urban and industrialized areas.

A variety of spectrographic, colorimetric, polarographic, and other analytical techniques are used for routine measurement of silver in biological and abiotic samples. Atomic absorption and plasma emission spectroscopy are perhaps the most widely used analytical techniques for the determination of silver levels in air, soil, and water.

Inductively coupled argon plasma with atomic emission spectroscopy has been recommended for determining silver in air and for analyzing dissolved, suspended, or total silver in drinking-water, surface water, and domestic and industrial wastewaters. Inductively coupled plasma-mass spectrometry is used to measure silver in environmental media at a detection limit of  $0.4 \text{ ug dm}^{-3}$ .

Sensitive voltammetric techniques using anodic stripping have been developed to measure free silver ion in solution at concentrations as low as  $0.1 \text{ ug dm}^{-3}$ . However, the anodic stripping voltammetric method does not work well with natural samples containing large amounts of organic matter, such as those found in sewage treatment plants.

But most these instruments are highly expensive, their day-to-day maintenance cost is high and are not free from various types of inherent interferences. Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination even when present in trace amounts.

Experimental A solution of Bromophenol Red ( $4 \times 10^{-3} \text{ mol dm}^{-3}$ ) was prepared by dissolving 0.5129 g of Bromophenol Red (BDH) in 20% ethanol and diluting to 250 ml in a volumetric flask with 20% ethanol. A Silver nitrate stock solution ( $2 \times 10^{-3} \text{ mol dm}^{-3}$ ) was prepared by dissolving 0.0849 g  $\text{AgNO}_3$  (Park) in distilled water and diluting to 50 ml in a volumetric flask and it was covered with a carbon paper. A diluted solution  $1 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{AgNO}_3$  solution was also prepared from the stock solution. A stock solution of  $\text{K}_2\text{S}_2\text{O}_8$  (BDH,  $0.2 \text{ mol dm}^{-3}$ ) was prepared

by dissolving 54.0620 g in water and diluting to 1 dm<sup>3</sup> in a volumetric flask. A phosphoric acid solution 2 mol dm<sup>-3</sup>, was also prepared. A 1,10- phenanthroline (0.01 mol dm<sup>-3</sup>, Aldrich) was prepared by dissolving 0.4521 g in distilled water and diluting to 250 ml in a volumetric flask.

#### APPARATUS

A UV-Visible spectrophotometer (Thermospectronic, HeA-ios) with 1.0 cm glass cells was used for recording the change in absorbance with time.

#### ADAPTABILITY OF BEER'S LAW

A series of Bromophenol Red solutions of varying concentration ranging from 2 x 10<sup>-4</sup> mol dm<sup>-3</sup> to 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> was prepared from the stock solution and the absorbance of these solutions at 425 nm was measured using a UV -Visible spectrophotometer.

#### RECOMMENDED PROCEDURE

Table 1 shows the method of preparation of the test solutions to select a suitable concentration of peroxydisulphate solution.

Table 1: Preparative method of solutions to select suitable concentration of p peroxydi sulphate

Volume of 4 x 10 <sup>-3</sup> mol dm <sup>-3</sup> Bromophenol Red (ml)	Volume of 2 mol dm <sup>-3</sup> H <sub>3</sub> PO <sub>4</sub> (ml)	Volume of 1 x 10 <sup>-4</sup> mol dm <sup>-3</sup> Ag+(ml)	Volume of distille water (ml)	Volume of 0.2 mol dm <sup>-3</sup> S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (ML)
4.00	2.00	5.00	7.00	2.00
4.00	2.00	5.00	6.00	3.00
4.00	2.00	5.00	5.00	4.00
4.00	2.00	5.00	4.00	5.00
4.00	2.00	5.00	3.00	6.00
4.00	2.00	5.00	1.00	8.00

Table 2 shows the method of preparation of the test solutions to select a suitable concentration of H<sub>3</sub>PO<sub>4</sub> solution.

In a typical experiment to obtain a calibration curve to determine Ag+ using slope method, 4.0 ml of Bromophenol Red (4.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>), 2.00 ml of H<sub>3</sub>PO<sub>4</sub> solution (2.0 mol dm<sup>-3</sup>), calculated quantities of distilled water and silver solution ( 1.0x10<sup>-4</sup> mol dm<sup>-3</sup>) to make the total volume to be 20.0 ml and 4.0 ml of Szot (2.0x10<sup>-1</sup> mol dm<sup>-3</sup>) were taken into a boiling tube (Table3).After shaking the solution was transferred into the 1.0 cm cell of the spectrophotometer. The variation in absorbance of BPR (max = 425 nm) with time was measured for 5 minutes after the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> solution.

Table 2: Preparative method of solution to select suitable concentration of H<sub>3</sub>PO<sub>4</sub>

Volume of 4 x 10 <sup>-3</sup> mol dm <sup>-3</sup> Bromophenol Red (ml)	Volume of 2 mol dm <sup>-3</sup> H <sub>3</sub> PO <sub>4</sub> (ml)	Volume of 1 x 10 <sup>-4</sup> mol dm <sup>-3</sup> Ag+(ml)	Volume of distille water (ml)	Volume of 0.2 mol dm <sup>-3</sup> S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> (ML)
4.00	5.00	5.00	2.00	4.00
4.00	4.00	5.00	3.00	4.00
4.00	3.00	5.00	4.00	4.00
4.00	2.00	5.00	5.00	4.00
4.00	1.00	5.00	6.00	4.00

**Table:3** Preparative method to plot a calibration curve in the absence of 1,10-Phenanthroline

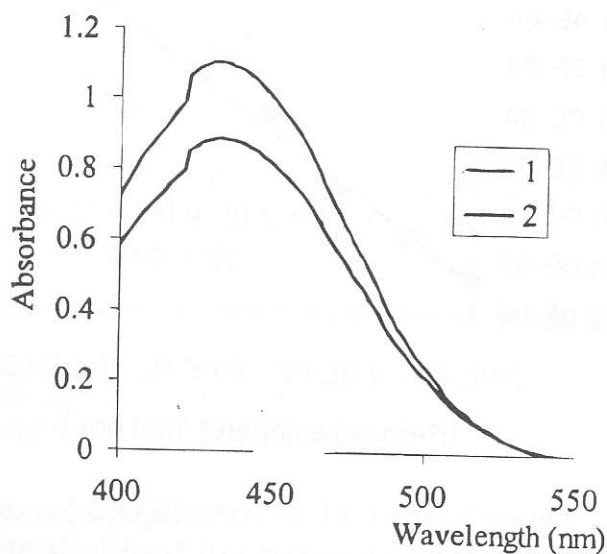
Volume of $4 \times 10^{-3} \text{ mol dm}^{-3}$ Bromophenol Red (ml)	Volume of $2 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ (ml)	Volume of $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$ (ml)	Volume of distille water (ml)	Volume of $0.2 \text{ mol dm}^{-3} \text{ S}_2\text{O}_8^{2-}$ (ML)
4.00	2.00	10.00	0.00	4.00
4.00	2.00	8.00	2.00	4.00
4.00	2.00	6.00	4.00	4.00
4.00	2.00	4.00	6.00	4.00
4.00	2.00	2.00	8.00	4.00
4.00	2.00	1.00	9.00	4.00

Table 4 shows the method of preparation of the test solutions to polt calibration curve in the presence of 1,10-phenanthroline.

Volume of $4 \times 10^{-3} \text{ mol dm}^{-3}$ Bromophenol Red (ml)	Volume of $2 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$ (ml)	Volume of $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ Ag}^+$ (ml)	Volume of $0.01 \text{ mol dm}^{-3}$ 1,10-Phenanthraline	Volume of Distilled water (ml)	Volume of $0.2 \text{ mol dm}^{-3} \text{ S}_2\text{O}_8^{2-}$ (ML)
4.00	2.00	8.00	2.00	0.00	4.00
4.00	2.00	6.00	2.00	2.00	4.00
4.00	2.00	4.00	2.00	4.00	4.00
4.00	2.00	2.00	2.00	6.00	4.00
4.00	2.00	1.00	2.00	7.00	4.00
4.00	2.00	0.50	2.00	7.50	4.00

### RESULTS AND DISCUSSION:

figure 1 shows that bromophenol red in acidic medium has a characteristic absorbance at around 425 nm. Therefore the change of absorbance of bromophenol Red at 425 nm was measured at this work.

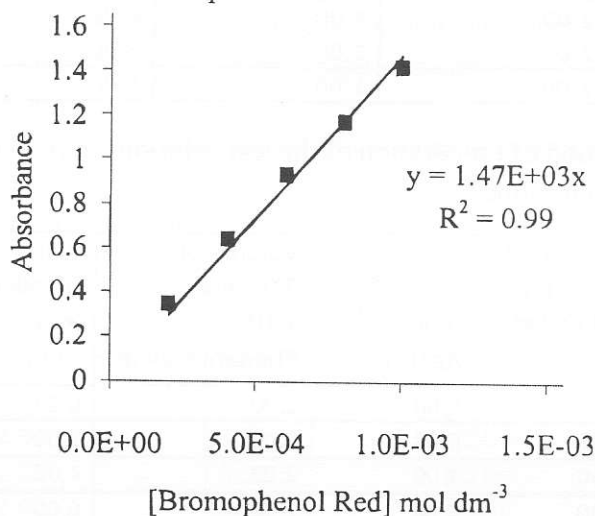


**Figure 1:** A plot of absorbance versus wavelength for Bromophenol Red

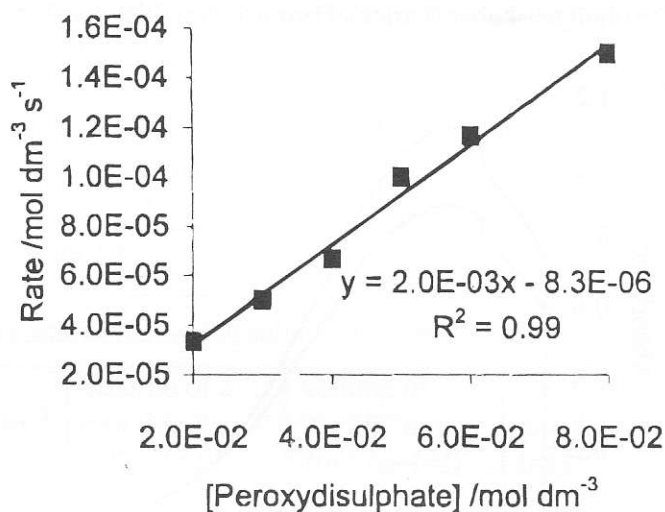
1 - Bromophenol Red in neutral medium,

2 - Bromophenol Red in acidic medium

Figure 2 shows the variation of absorbance at different Bromophenol Red concentrations and it shows that the absorbance varies linearly in the absorbance range of 0.34 to 1.42. From this observation  $8 \times 10^{-4} \text{ mol dm}^{-3}$  was chosen as the initial concentration of bromophenol red since at the time of reading the first absorbance of the reaction mixture, the absorbance value was found to be approximately 1.00, which is an acceptable value.



**Figure 2:** Variance of absorbance with different Bromophenol Red concentrations After selecting a suitable concentration of bromophenol red, the concentration of suitable concentration of peroxydisulphate was selected by varying its concentration. It was observed that the rate increases with increasing  $\text{S}_2\text{O}_8^{2-}$  concentration (Figure 3). Peroxydisulphate concentration of  $0.04 \text{ mol dm}^{-3}$  was judged as the best as it shows a good measurable rate at this concentration.



**Figure 3:** A plot of Rate versus  $[\text{S}_2\text{O}_8^{2-}]$

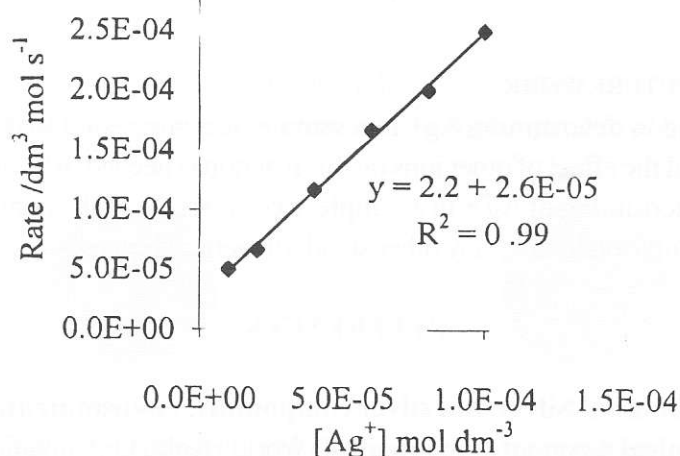
When the acid concentration was changed from  $0.1 \text{ mol dm}^{-3}$  to  $0.5 \text{ mol dm}^{-3}$ , it was observed that rate constants are almost the same (Table 5).

**Table 5:** Rate values for different [H<sup>+</sup>]

[H <sup>+</sup> ]	Rate (x 10 <sup>-5</sup> ) Mol dm <sup>-3</sup> S <sup>-1</sup>
0.5	8.66
0.4	8.33
0.3	8.50
0.2	8.00
0.1	8.33

The reaction between Bromophenol Red and Peroxydisulphate in acidic medium is catalyzed by silver ion. A linear calibration graph (Figure 4, R<sup>2</sup> = 0.99) was obtained and the detection limit of silver was observed to be 0.54 /-Lg mr1 and this graph has an intercept on the rate axis, suggesting that the uncatalyzed reaction is also occurring.

It was observed that 1,10-phenanthroline could act as an activator in the catalyzed reaction. When 1,10-phenanthroline was used the detection limit of Ag<sup>+</sup> was found to be 27 ngr<sup>-1</sup>. It was also noticed that in the presence of 1,10-phenanthroline un-catalyzed reaction was not observed i.e., the graph goes through the origin (Figure 5).

**Figure 4:** Calibration curve in the absence of 1,10-phenanthroline

The rate law for the reaction can be written as

$$\text{Rate} = \{k_1 + k_2 [\text{Ag}^+]\} [\text{BPreD}]^a [\text{S}_2\text{O}_8^{2-}]^b [\text{H}^+]^c$$

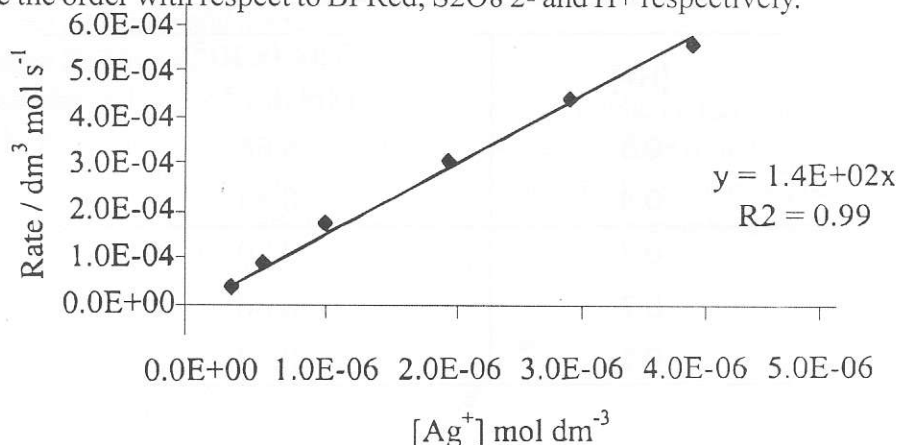
Where;

k<sub>1</sub> is rate constant in the absence of Ag<sup>+</sup>

k<sub>2</sub> is rate constant in the presence of Ag<sup>+</sup>

BPreD - Bromophenol Red

a, b and c are the order with respect to BPRed, S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and H<sup>+</sup> respectively.



**Figure 5:** Calibration curve in the presence of 1, 10-phenanthroline

To evaluate the accuracy of this method, solutions of known strengths of Ag<sup>+</sup> were analyzed. Table 6 shows that the accuracy was found to be satisfactory.

True Value Ag <sup>+</sup>	Rate	Experimental Value of Ag <sup>+</sup>	RSD (n = 5)
1.50x10 <sup>-6</sup>	2.23 x 10 <sup>-4</sup>	1.57 x 10 <sup>-6</sup>	4.09
3.50x10 <sup>-6</sup>	4.87 x 10 <sup>-4</sup>	3.42 x 10 <sup>-6</sup>	1.53

#### SUGGESTIONS FOR FUTURE WORK:

To apply this method in determining Ag<sup>+</sup> in a sample, it is suggested that a detailed study of complete rate law and the effect of other ions on this reaction is needed. Also to check the validity of this method in determining of Ag<sup>+</sup> in a sample, a comparison of the results obtained by this method with the results obtained by any other standard method is necessary.

#### REFERENCES

1. P.D.Howe and S.Dobsonl **Silver and silver compounds: environmental aspects Concise international Chemical Assment Document 44**, World Health Organization, Geneva (2002)
2. Rains T, Watters R, and Epstein M. Application of atomic absorption and plasma- emission spectrometry for environmental analysis. **Environment International**, (1984)10:163-168.
3. ATSDR, **Toxicological profile for silver**. Atlanta, GA, US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (TP-90-24) (1990)
4. Schildkraut D, Dao P, Twist J, Davis AI- Robillard T)i'Determination of silver ions at sub microgram-per-liter levels using anodic square-wave stripping voltammetry. **Environmental Toxicology and Chemistry**, (1998), 17(4):642-649.
5. W.R. Hill., D.M. Plilsbury and Argyria - **The pharmacology of silver**, William and Wilkinson, Baltimore, 1939