

## Spectrophotometric Determination of Silver and Mercury

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**Summary:** The method described is based on the reaction of silver or mercury (II) with potassium tetracyanonickelate (II). The liberated nickel is determined colorimetrically using dimethylglyoxime at 326 nm. As little as 1 $\mu$  mole of silver and mercury (II) can be determined with a relative standard deviation (rsd) of  $\pm$  3%. The effect of various ions on the reaction is also investigated.

### Introduction:

The most spectrophotometric methods used for determination of silver are based on the formation of organic complexes. The common method using *p*-dimethylaminobenzylidinerhodanine<sup>1</sup> is very sensitive to pH changes. The dithiazone<sup>2</sup> method is very sensitive but needs careful standardizing of laboratory technique and the complex is photosensitive. Pyrogallol<sup>3</sup> red has a low sensitivity and suffers from many interferences. Feigl<sup>4</sup> described a spot test for detecting silver halides based on the reaction of silver with potassium tetracyanonickelate (II). The liberated nickel is detected by adding dimethylglyoxime. The same reaction was later used for the colorimetric determination of silver<sup>5</sup>. The absorbance of the complex formed was measured at 400 nm. The method is time consuming because the colour needs 3 hours to become fully developed and suffers from many interferences. Elements forming complexes with the reagent or with pyridine which is used to dissolve the nickel dimethylglyoxime or ammonia interferes seriously. The method described here is also based on Feigl's test with some modifications in order to improve sensitivity and to avoid the effect of interferences. The method is similarly used for the determination of mercury (II).

### Experimental:

A DMR 11, Recording Spectrophotometer, Zeiss was used throughout this work.

### Reagents

Ammonia, chloroform, silver nitrate and dimethyl-

glyoxime are all supplied from BDH (Analar qualities). Potassium tetracyanonickelate(II) was prepared following the method described by Vogel<sup>6</sup>.

1mM of silver nitrate was prepared by dissolving 0.169 gram of silver nitrate in 1 liter of distilled water. Ammoniacal dimethylglyoxime solution (0.1%) was prepared by dissolving 0.5 g in 250 ml of ammonia and diluting to 500 ml with distilled water, 0.1% potassium tetracyanonickelate(II) solution was prepared by dissolving 0.5 g in 500 ml of distilled water.

### General Procedure

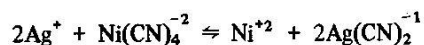
The sample containing 1.2 – 7.2  $\mu$ mole of silver is treated with 2 ml of 0.1% potassium tetracyanonickelate(II) solution and 2 ml of 0.1% dimethylglyoxime ammoniacal solution. The mixture is left for 30 minutes to complete the reaction. The red complex formed is extracted in 20 ml chloroform and the absorbance measured at 326 nm in 1cm silica cuvettes.

### Results and discussion

The method used here is based on Feigl's test as that of Siggia<sup>5</sup> but with some modifications. The nickel dimethylglyoxime formed is extracted in chloroform and determined colorimetrically by measuring the absorbance at 326 nm. This wavelength was found to be different from that obtained by Siggia probably because the measurement was made in chloroform while that of Siggia was made in partially non-aqueous medium. Fig. (1) shows the spectrum obtained for nickel dimethylglyoxime in chloroform. The colour was found to be completely developed after 30 minutes at room tempera-

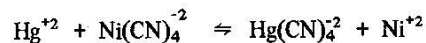
ture as shown in Fig. (2). Calibration graph was prepared for 1.2 – 7.2  $\mu$ mole of silver as illustrated in Fig. (3). The rsd was calculated from the absorbance measurement of 10 replicates of 5  $\mu$ mole of silver. The effect of some interfering ions on the absorbance of 5  $\mu$ mole of silver was investigated. The results obtained are summarized in Table 1. The significant interference is that which cause a change in the absorbance of more than 2 standard deviations i.e. 6%. Upto 10-fold excess of aluminium, barium, bismuth, calcium, magnesium and manganese did not interfere. Iron(II) interfered by forming ferrous dimethylglyoxime and should be oxidized to iron(III) which can be tolerated if only 3-fold excess is present but more than that interfered, probably by forming ferricyanide. Lead forms precipitate and decreases the absorbance probably due to trapping the liberated nickel by adsorption process. Cobalt, copper, mercury(II) and zinc react with tetracyanonickelate(II) as does silver, and liberate nickel which can similarly be used for their colorimetric determination. The reaction was found to be insensitive for copper, cobalt and zinc and reasonably sensitive for mercury(II) which encouraged the application of this method for the colorimetric determination of mercury(II). Linear calibration graph was obtained as shown in Fig. (3).

According to the reaction equation:

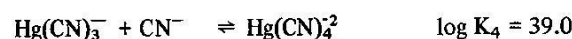
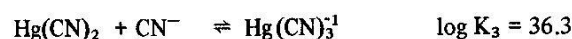
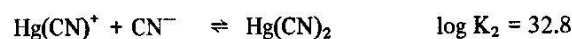
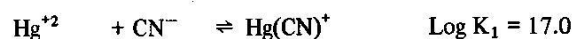


2 Moles of silver liberated 1 mole of nickel that was exactly found from the calibration graph shown in Fig. (3). In the case of mercury(II) the results obtained from

the calibration graph was not as expected from the reaction equation:



where 1 mole of mercury(II) liberates 1 mole of nickel, but the results obtained experimentally showed that 2 moles of mercury(II) are needed to liberate 1 mole of nickel and the calibration graph obtained for mercury(II) coincides with that obtained for silver as shown in Fig. (3). This could be explained from the equations by which mercury cyanides are formed.<sup>7</sup>



From these equations we can see that log  $K_1$  for the formation of  $\text{Hg}(\text{CN})^+$  is very small compared to that of  $\text{Hg}(\text{CN})_2$ . On the other hand, there is no big difference between log  $K_2$  for  $\text{Hg}(\text{CN})_2$  and that of  $\text{Hg}(\text{CN})_3^{-1}$  or that of  $\text{Hg}(\text{CN})_4^{2-}$ , so we can assume that only the step of formation of  $\text{Hg}(\text{CN})_2$  is the dominant which can be advocated from the calibration graph shown in Fig. (3) and can be illustrated from the equation below:

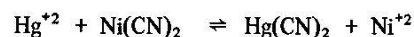
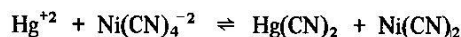


Table 1. Effect of interferences on the absorbance of 5  $\mu$  mole of silver  
Change in absorbance (%)

Amount	Ca <sup>+2</sup>	Mn <sup>+2</sup>	Pb <sup>+2</sup>	Cu <sup>+2</sup>	Co <sup>+2</sup>	Hg <sup>+2</sup>	Zn <sup>+3</sup>	Cr <sup>+3</sup>	Bi <sup>+3</sup>	Fe <sup>+3</sup>	Ba <sup>+2</sup>	Mg <sup>+2</sup>	Al <sup>+3</sup>
1-Fold	0.5	3	- 8	25	58	89	9.6	2	2	2	0.5	3	3
2-Fold	2	1	-23	55	134	191	20	2	2.5	3	0.5	3	2
3-Fold	2	3	-33	86	205	267	38	3	3	2	2	3	4.5
4-Fold	2	1	-49	91	257	364	53	2	2	9.5	4	3	4.5
5-Fold	2	2	-49	93	277	583	94	2.5	3.5	17	5.6	3	4.5

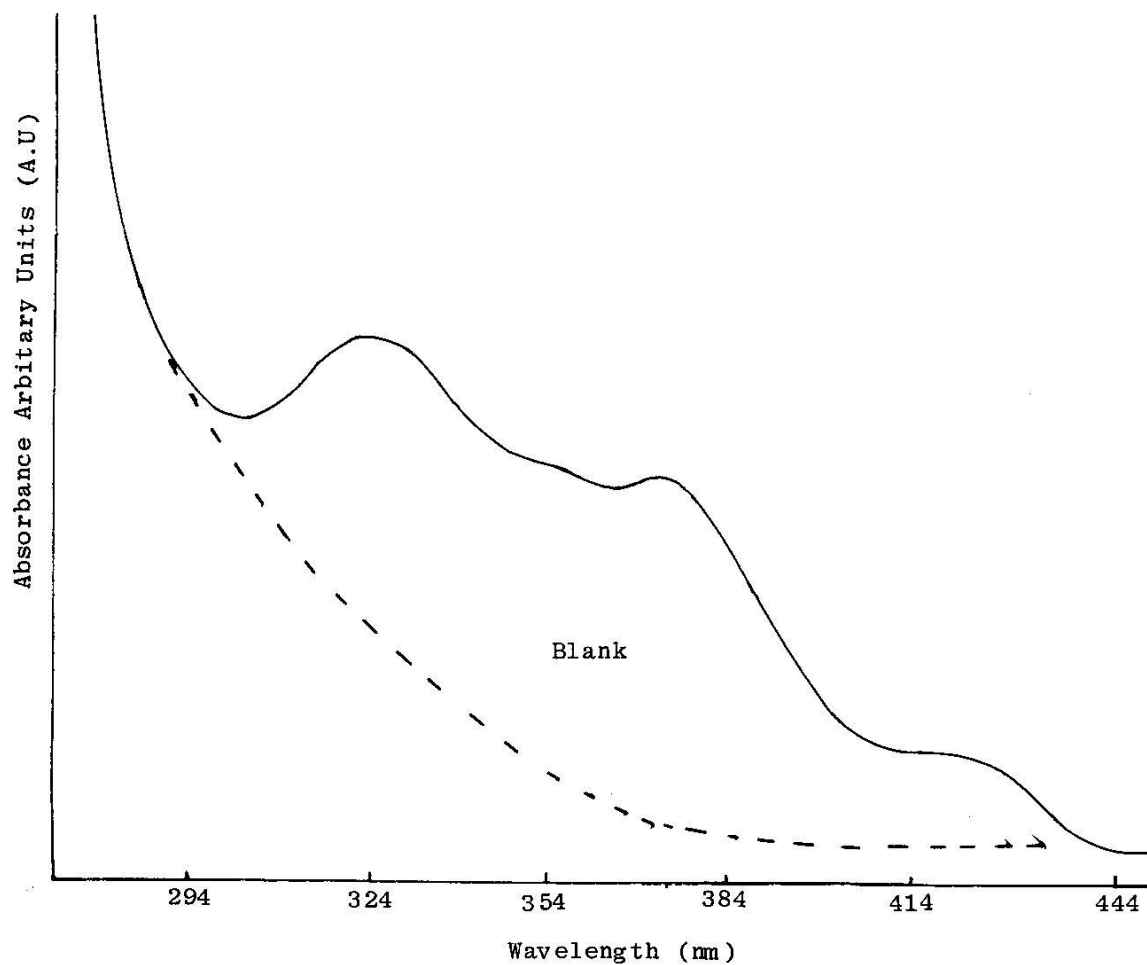


Fig. 1: The spectrum of nickel dimethylglyoxime in chloroform.

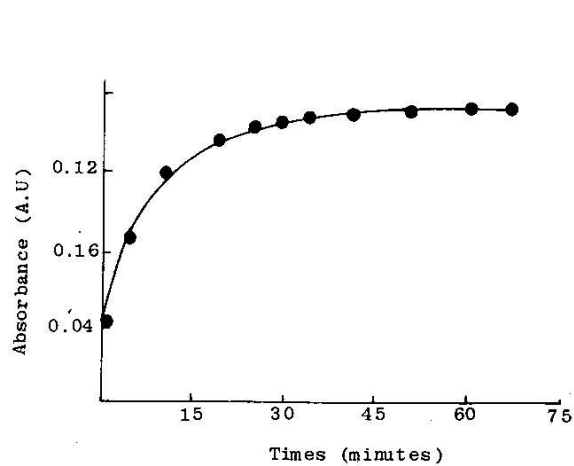


Fig. 2: Effect of time on the reaction of silver with potassium tetracyanonickelate(II).

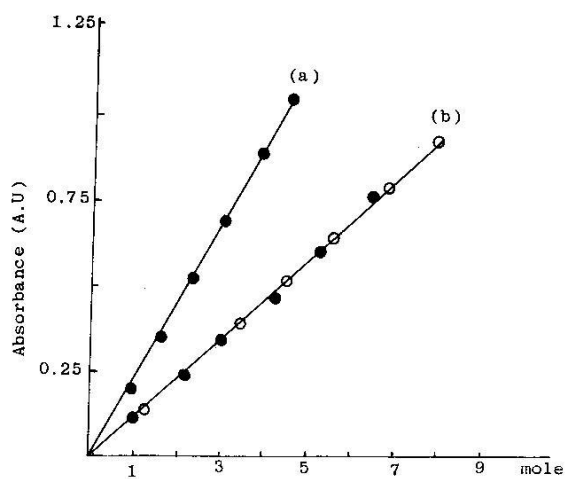
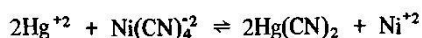


Fig. 3: Calibration graphs for: (a) Nickel, (b) Silver (●) or Mercury (II) (○).

The overall reaction is:



i.e. 2 moles of mercury(II) liberate 1 mole of nickel which was found from the calibration graph.

The method of Siggia has many disadvantages. It needs 3 hours to complete the reaction, probably because of the presence of pyridine used to dissolve the nickel dimethylglyoxime. The method also suffers from many interferences, elements forming coloured complexes with pyridine, ammonia and dimethylglyoxime interfered seriously. The method investigated here is very simple and rapid, only 30 minutes are needed to complete the reaction. The effect of most interferences specially those elements which form coloured complexes with ammonia or pyridine was eliminated by extracting the nickel complex in chloroform.

The method can also be applied to the determination of some anions which form sparingly soluble salts

with silver or mercury(II) particularly those of halides. The salts can be treated in a similar manner to that of silver or mercury(II).

#### References

1. E.B. Sandell and J.J. Neumayer, *Anal. Chem.*, **23**, 1863 (1951).
2. T.B. Pierce, *Analyst*, **85**, 166 (1960).
3. R.M. Dagnall and T.S. West, *Talanta*, **11**, 1533 (1964).
4. F. Feigl "Qualitative Analysis by Spot Tests, p.254, New York, Nordeman Publishing Co. (1939).
5. S. Siggia, *Anal. Chem.*, **19**, 923 (1947).
6. A.I. Vogel, "Text book of Quantitative Inorganic Analysis", 4th Edn., Longman, p.323 (1978).
7. L.G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes", special publication No. 17, The Chemical Society, London (1964).