COLORIMETRIC DETERMINATION OF MICRO-AMOUNTS OF SILVER WITH POTASSIUM FERROCYANIDE AND αα′DIPYRIDYL

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A Colorimetric method, for the estimation of micro-gram amounts of silver, based on the reaction between K_4 (Fe(CN)6 and ammoniacal AgCl has been developed. The quantitative determination of silver by this method can be carried out at pH 7.5 at 70°C. The colour developed by this method is stable and obeys Beer-Lambert's law in the silver concentration range 5-80γ. This method is also applicable for the determination of silver in galena.

Introduction

Potassium ferrocyanide has been used for the detection of microquantities of silver by spot test(1) The method is based on the dissociation of ferrocyanide ion in ammoniacal solution in the presence of silver halides which liberate Fe^{++} ion. The latter gives a red colouration with αα′-Dipyridyl.

$$[Fe\ (CN)_6]^{-4} + 3\ [Ag\ (NN_3)_2]^{+} = 3\ [Ag\ (CN_2)] + Fe^{++} + 6NH_3.$$

However, this reaction has not been used for the quantitative determination of silver. The present investigation was undertaken to develop a precise and simple method based on this colour reaction for the estimation of small amounts of silver with its possible application to the galena ores. Nabi Bux and Akram Khattak,[2] of this laboratory, have reported that the rhodanine colorimetric method of determining silver in galena is difficult and requires very stringent experimental conditions to get accurate results.

Experimental

Apparatus.—(1) Glass apparatus used was of hard glass, (2) Hilger's Photoelectric colorimeter with 15 ml. cuvett and green filter (520 mμ), (3) The pH was adjusted with a Cambridge pH meter and (4) 'Ultra Thermostat' was used to maintain constant temperature.

Reagents.—(1) Standard silver solution containing 2γ silver/ml. was prepared by dissolving silver chloride in minimum amounts of ammonia and diluting it to the desired volume, (2) 0.1 percent solution of K_4 [Fe (CN)6] was prepared in distilled water, (3) 0.1 percent ethanol solution of αα′-Dipyridyl and (4) Buffer of 7.5 pH was prepared from 38 ml. of 0.1 M HCl and 42 ml. of 0.05 M borax solutions.

Optimum Temperature and pH.—A stable red colour of the complex $[Fe\ (dipy)_3]^{++}$ is obtained in the pH range of 7.3 to 8.0 at 65-80°C. Above pH 8 red colour of the solution changes to yellow. Heating above 80°C. also changes the red colour very readily to yellow. It takes 15 minutes for the colour development. Heating for longer time decreases the colour intensity which gradually changes to yellow. pH 7.5 and the temperature 70°C. were selected as the optimum parameters for measuring the colour intensity.

Effect of the Concentrations of Reagents.—The colour intensity is independent of the quantity of 0.1 percent dipyridyl solution added. The same colour intensity is obtained with 2,4,6,8, and 10 ml. dipyridyl solutions added to the 10γ silver solution.

Potassium ferrocyanide solutions of concentrations 1.0 percent and above have yellow colour which may interfere in the estimation. Therefore, the strength of the ferrocyanide solution was kept at 0.1 percent as the solution of this concentration is almost colourless.

Calibration Curve

Procedure.—10 ml. of 0.1 percent K_4 [Fe (CN)6] solution and 10 ml. of buffer solution were placed in a 100 ml. beaker. Then 4 ml. of dipyridyl solution and an aliquot of the silver solution were added. pH was adjusted to 7.5, when necessary, by using dilute HCl. The contents were transferred to a 100 ml. measuring flask and the volume was made to 100 ml. with distilled water.

A blank was also prepared and the pH was adjusted to 7.5.

The flasks containing silver solution and blank were placed in a thermostat at 70°C. for 15 minutes. Then they were allowed to cool to room temperature. The transmittance percentage was

determined using a green filter. The colour was stable and readings were constant. The results are shown inTable 1 and Fig. 1.

Table 1.—Amount of Silver and Colour Intensity.

S. No.	Amount of silver (γ/100 ml.)	% Transmittance	Absorbance
1.	5	97.5	0.011
2.	10	94.0	0.027
3.	25	87.5	0.058
4.	40	82.0	0.086
5.	60	76.0	0.119
6.	70	74.0	0.131
7.	80	72.0	0.143
8.	85	70.5	0.152
9.	90	70.0	0.155
10.	95	68.5	0.164
11.	100	68.0	0.165

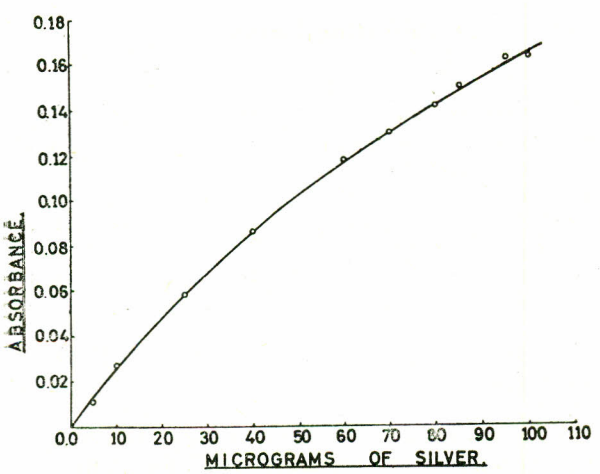

Fig.—Absorbance vs. amount of silver.

Fig. 1 shows that the colour obeys Beer-Lambert's law upto silver concentration of 80γ. At higher concentrations, deviations occur. Hence the amount of silver for colour development in an unknown sample should be adjusted in the range of 5 to 80γ/100 ml.

Determination of Silver

Silver was determined in five solution samples containing different amount of micrograms of silver by this method. The results are shown in Table 2.

Table 2.— Analysis of Silver Solutions.

S. No.	Amount of Ag taken (γ)	Amount of Ag found (γ)	% Error
1.	21.576	21.500	−0.34
2.	10.790	11.000	+0.09
3.	5.394	5.360	−0.63
4.	4.315	4.300	−0.34
5.	2.158	2.150	−0.35

It is evident that microamounts of silver can be determined with one percent accuracy by the method described in this paper.

Interference by other Ions

It was observed that lead and antimony do not interfere upto 200γ for 10γ of Ag. Copper interferes in quantities above 20γ, while Fe^{++}, Fe^{+++} and Hg^{++} interfere even when present in quantities less than 2γ.

Determination of Silver in Galena.—Three different samples of galena were analysed for silver determination. The ore was opened with nitric acid[3] and silver was separated by coprecipitation with Te.[4] Silver nitrate obtained was converted to AgCl by adding dilute HCl in the presence of nitric acid. AgCl formed was dissolved in the minimum amount of ammonia solution and the volume was made to 100 ml. in a volumetric flask.

An aliquot of 10 ml. was analysed by ferrocyanide and dithiazone methods separately. The results are given in Table 3.

TABLE 3.—PERCENT SILVER IN GALENA.

S. No.	Sample (occurrence)	% Ag dithiazone method	% Ag ferrocyanide method
1.	Sherwan	0.023	0.024
2.	Near Mansehra	0.007	0.0072
3.	Piswal II	0.0119	0.012

The ferrocyanide method seems to give accurate results comparable with those obtained by the dithiazone method. Sample No. 3 was also analysed by Nabi Bux and Akram Khattak[3] and result of the present authors is in agreement with the percentage of Ag reported by them.

Discussion

The reaction between K_4 [Fe $(CN)_6$] and AgCl in the presence of ammonia can be used quantitatively for the colorimetric determination of micro-amounts of silver. The colour developed at pH 7.5 and 70°C. is stable and follows Beer-Lambert's law in 5 to 80 γ silver concentration range per 100 ml. Results obtained are accurate with in one percent. No special precautions are required in this method except the use of hard glass appratus against the extreme control of experimental conditions in the rhodanine method.[2] The interfering ions can be removed by the usual procedures.[4] The ferrocyanide method can be successfully used for the determination of small amounts of silver present in galena.

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