

COLORIMETRIC DETERMINATION OF SILVER IN GALENA WITH *p*-DIETHYLAMINO BENZYLIDENERHODANINE

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(Received April 25, 1961; revised November 11, 1961)

Silver is always present in galena, but the quantity greatly varies. Some ores contain only traces, while others may have proportions as high as 0.2%. Samples of galena were procured from different localities in West Pakistan and their silver contents determined. The determination of silver in microgram amounts in the presence of large amount of interfering elements is rather difficult and hence the factors influencing the colorimetric method of determination of silver using *p*-diethylaminobenzylidenerhodanine has been studied in detail both by the direct and indirect methods. The silver content in Pakistani galena has been found to range from 0.003% to 0.096%.

Silver forms an insoluble red compound with *p*-diethylaminobenzylidenerhodanine or simply called rhodanine, which is used as a basis for the colorimetric estimation of silver. Fiegl¹ first used it as a qualitative reagent for silver and since then it has been developed in a quantitative optical method by Sandell and Neumayer,² and Gave and Hume.³ These authors studied the reproducibility of the method and determined the effects of acidity, concentration of the reagent, time of standing, presence of foreign ions, etc., in relation to the determination of silver.

The present investigation was undertaken in order to standardize the method for the determination of small amounts of silver in galena and use the same for different samples of galena occurring in Pakistan.

It has been observed that the method requires very careful manipulation of reagents and apparatus and slightest impurities in the distilled water, in the acids, and in other reagents seriously affect the accuracy of the results. Difficulties were also encountered by the authors due to non-availability of Vycor glass, as silver is very easily absorbed by soft glass apparatus which had to be digested for long hours with strong acids to get rid of the contamination.

The determination of silver was made by two methods: (1) direct method and (2) indirect method.

Direct Method

In this method,^{2,3} enough of the alcoholic solution of the reagent rhodanine was added to an acidic solution of silver in nitric acid and diluted to a measured volume (100 ml.). The absorbancy of the coloured suspension measured in the colorimeter gave directly the silver content of the sample.

Apparatus.—1. Lange's colorimeter (double photocell) with cuvettes of 100 ml. capacity, and green filter.

Reagents.—(a) *p*-diethylaminobenzylidenerhodanine, 0.05 g. in 100 ml. of absolute alcohol; and (b) standard silver solution, 0.001% silver as the nitrate in 0.5 N nitric acid.

Behaviour of the Reagent Rhodanine in Solution of Acids and Alkalies.—As the reagent is itself coloured and forms a significant blank, its behaviour, as regards stability and absorbancy against increasing acid concentration, was studied first.

The reagent is readily soluble in alkali but is sparingly soluble in acids. The alcoholic solution of the reagent, however, remains apparently in solution when mixed with acid but the intensity of the colour diminishes with the increase of acid concentration. (Fig. 1)

Optimum Concentration of Acid.—The concentration of acid in the development of stable silver suspension is very critical. Whereas the stability of suspension increased with the increase of acid concentration, the sensitivity of the method (or molar absorbancy) decreased steadily (Table 1). Therefore, a concentration of 0.05N acid was considered optimum.

Mineral Acids Other than Nitric Acid.—Acids other than nitric acid had also been tried to see if it could make the silver suspension more stable. Sulphuric acid in a few instances behaved well, the stability of the blank was quite good, but the readings for silver were not found to be better than nitric acid medium. Perchloric acid gave results as good as nitric acid and it was felt that the acid could very well be substituted for nitric acid. In fact, in the estimation of silver in galena the sample could be fumed out with perchloric acid and the resulting solution used with proper

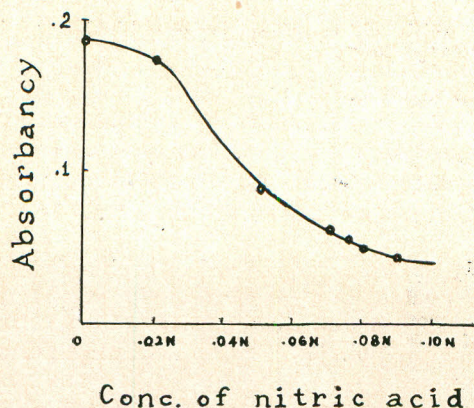


Fig 1—Effect of increasing acid concentration on absorbancy of a 0.001% solution of rhodanine in 4% alcohol.

adjustment of acid without introducing any nitric acid.

Stability of Silver Rhodanate Suspension.—Perfectly stable suspensions could not be obtained in any case. In many cases where the reagents were not purified by crystallization and the glass apparatus and colorimeter cuvetts were not washed perfectly clean with chromic acid treatment, the suspensions precipitated within a few minutes and no reliable readings could be obtained.

With all the precautions regarding cleanliness of glass-ware and using crystallized reagent in solutions of absolute alcohol, readings could be taken with 2 to 5 per cent accuracy when they were taken within 5 to 10 minutes of the addition of reagents.

TABLE I.

No.	Conc. of rhodanine	Amount of silver taken	Concentration of acid	Absorbancy
1.	0.001%	50 microgram	0.025N	0.28
2.	"	"	0.05N	0.28
3.	"	"	0.075N	0.26
4.	"	"	0.09N	0.23
5.	"	"	0.10N	0.21
6.	"	"	0.25N	0.14

Order of Addition of Reagents.—The stability and optimum development of colour depends to a considerable extent on the order and manner of addition of reagents. The best results are obtained when to the alcoholic solution of reagent, the requisite amount of 0.1N acid added with slow but constant shaking. The sample solution containing silver is then added and volume made up. The final concentration of acid is kept at 0.05N.

These experiments show that the direct method is very delicate even with pure silver and it would not suit the determination of silver in galena which invariably contains high ionic concentration. The

TABLE 2.

No.	Reagent conc.	Acid conc.	Silver taken	Absorbancy				
				Immediately	after 5 mins.	after 10 mins.	after 15 mins.	after 20 mins.
1	.001%	.05N	nil	0.085	0.085	0.085	0.090	—
2	"	"	10 microgram	0.105	0.110	0.110	0.118	0.120
3	"	"	20 "	0.135	0.140	0.145	0.147	0.150
4	"	"	30 "	0.180	0.185	0.185	0.189	0.190
5	"	"	40 "	0.230	0.230	0.235	0.276	0.286
6	"	"	50 "	0.270	0.270	0.270	—	—
7	"	"	60 "	0.310	0.310	0.310	—	—
8	"	"	70 "	0.350	0.350	0.350	—	—
9	"	"	80 "	0.360	0.360	0.360	—	—
10	"	"	90 "	0.375	0.375	0.375	—	—
11	"	"	100 "	0.380	0.380	0.375	—	—

indirect method was therefore considered preferable.

Indirect Method

Rhodanine which forms suspension with silver is co-precipitated with silver rhodanate when kept in the dark for a couple of hours. The precipitate is filtered in sintered crucible and digested with alcohol which dissolves the free reagent but not the silver complex, which is washed free from reagent and then dissolved in alkaline potassium cyanide solution. The absorbancy of the liberated reagent is then measured and the silver concentration calculated from a standard curve obtained by taking known amounts of silver.

Discussion.—The solubility of silver rhodanate depends on the pH of the solution. From a measurement of dissociation constants of the reagent (HR) and the solubility of corresponding silver salt (AGR), Sandell and Neumayer arrived at the equation $(Ag^+) = aH 10^{-5.3}$ at an ionic strength of 0.05. In other words, to maintain the silver ion concentration below $10^{-8}M$ (corresponding to ca. 1μ g. of Ag/1), it would be necessary to work at pH above 2.7. At higher ionic strength, the concentration of silver in solution will increase and it is therefore necessary to precipitate the silver in slightly acid or neutral solution.

As many other metals like iron, copper, nickel, cobalt, zinc, aluminium and lead will precipitate in neutral solution either as rhodanates or hydroxides, it is necessary to mask these metals as soluble complexes.

Ethylenediamine tetraacetic acid (EDTA) has been used for this purpose. Fortunately however silver does not form any strong complex with EDTA. The complexity constant measured by Ringbom and Linko⁴ is of the order of $pK = 7$, which shows that the complex is so weak that no appreciable amounts of silver rhodanate will dissolve in a solution of EDTA.

Apparatus.—(1) Eppendorf photometer, Blue filter ($436m\mu$) and 1 cm.^2 cell. (2) Beckman pH meter, model G.

Reagents.—(1) *p*-Diethylaminobenzylidenerhodanine. Dissolve 20 mg. of the reagent, recrystallized from alcohol in 100 ml. of absolute alcohol. (2) Potassium cyanide 0.5% in 0.001N sodium hydroxide. (3) Disodium ethylenediamine tetraacetate, 0.2M aqueous solution.

Procedure.—Finely agated sample (0.5 g.) was

mixed with 10 g. of potassium bisulphate in a fairly large silica crucible and heated slowly over a Bunsen flame. Care was taken so that there was no spattering and heating was continued until a clear melt was obtained. Finally it was kept in the molten state for another 5 minutes to make sure that all reactions were complete.

The crucible was allowed to cool and the melt was extracted in a beaker with about 50 ml. of water. The solution was heated until all soluble matter dissolved. The solution with the undissolved matter (mainly lead sulphate) was transferred to a 100 ml. volumetric flask and after making up the volume, allowed to settle, preferably overnight.

Fifty ml. aliquot was then transferred to a beaker and diluted to 100 ml. Enough EDTA, about 25 ml. was added and the solution was made alkaline with ammonia. Three ml. of alcoholic reagent solution, being only in slight excess, was then added and the solution carefully neutralized with acetic acid to a pH 6-7, using the Beckman pH meter. Alternately to the neutral solution, 10 ml. of a buffer solution of ammonium acetate of pH 6.5 was added at one stroke.

The solution was allowed to stand for 2 hours or longer until the supernatant liquid was clear. It was then filtered through sintered crucible No. G4 and washed with water 2 or 3 times. The crucible was placed in the beaker in which the precipitation was made and 40 ml. of ethyl alcohol added. The beakers were covered with cover glasses and heated on the steam bath for 15 to 20 minutes. The alcohol should boil briskly to extract fully the reagent in solution.

The alcoholic solution was then washed from the silver rhodanate precipitate in the crucible by suction and washed with warm alcohol until washings were clear. The suction flask was then emptied and cleaned.

Fifty ml. of potassium cyanide solution was then poured in the beaker and passed through the sintered crucible to dissolve and wash the reagent solution. The operation was repeated once and then finally washed twice or thrice with water.

The solution was then transferred from the suction flask to a 50-ml. volumetric flask and diluted to the mark. The absorbancy was determined by using a blue filter. The color was stable and the readings were constant (for at least two days).

Standard Curve.—The standard calibration curve (Fig. 2) was prepared by taking 1, 5, 10, 15, 20, 30,

Fig 2—Standard calibration curve.

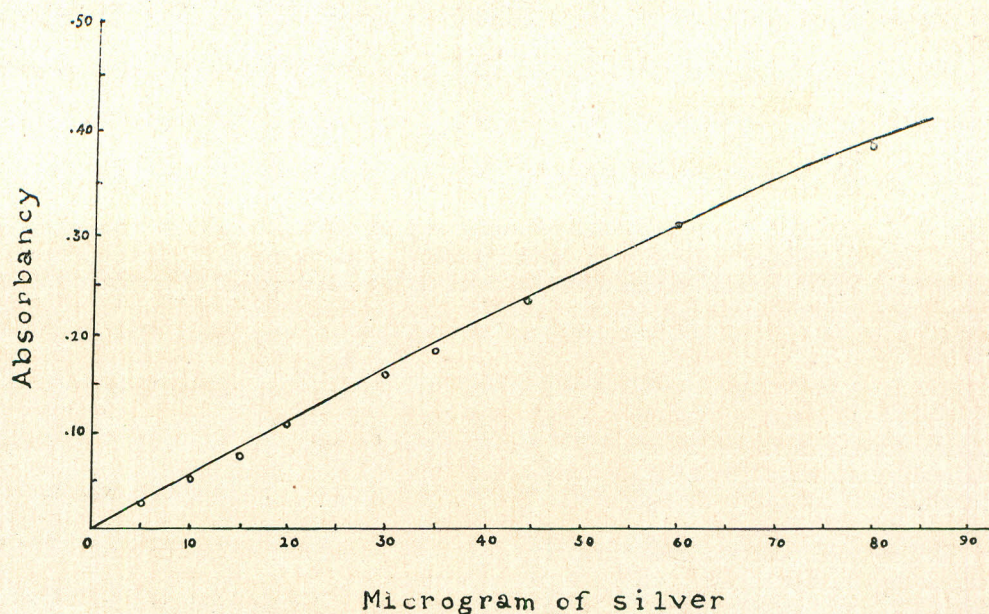


TABLE 3.

Occurrence	Amount taken for analysis	Chemical composition (metallic)	Aliquot	Extinction	Microgram of silver calculated from calibration curve	% of Ag
Khyber	0.5 g.	Lead 72.5% Iron trace.	50/100	0.052	1	0.0044
Chitral (Ozor valley)	0.5 g.	Lead 59.65% Iron 12.0% Copper 2.7%	10/100	0.26	48	0.096
Kalam Ushu	0.5 g.	Lead 36.74% Iron 6.14%	50/100	0.23	43	.017
Ughi	0.5 g.	Lead 72.50% Iron 3.51%	50/100	0.044	8	.0032
Bagra	0.5 g.	Lead 76.38%	50/100	0.042	8	.0032
Piswal No. 1	Lead 17.2% Iron 2.9%	..	0.05	9	.0036
Piswal No. 2	Lead 56.33% Iron 3.95%	..	0.164	30	.012
Imported sample from U. S. A.	Not done	..	0.002	trace	trace
Imported sample from U. S. A.	Not done	..	0.28	53	.021

45, 60, micrograms of silver from a solution of silver nitrate in dilute nitric acid and passing them through all the steps of the procedure, starting from fusion with potassium bisulphate.

Results and Discussion

All determinations of silver have been made in at least triplicates and a few of them repeated several times. The results along with the chemical composition (only metallic) of the samples are given in Table 3.

As will be seen from Table 3, results were not always concordant. As a matter of fact, unless extreme precautions were taken results were unreliable and had to be discarded.

It has been observed that the pH of the precipitating medium, the purity of the reagent solution, and the temperature at which the precipitation was made, all vitally affected the results. For example, when the precipitation is made, it is the silver rhodanate which is precipitated along with the excess of the reagent. Naturally no reagent should precipitate before all the silver is precipitated. The amount of the reagent in the precipitating medium is also critical, because a high excess of it would contaminate the silver rhodanate precipitate which would be difficult to wash free from reagent.

Another source of error is the separation of lead as lead sulphate which tended to absorb some silver. This could be verified by dissolving the lead sulphate in excess of ammonium acetate and precipitating the silver from the solution in the

usual way as silver rhodanate. The amount of silver thus lost varied from a trace to a significant 10% of the metal.

Another interfering factor was the fusion of silver salts in silica crucible with potassium bisulphate. Whereas pure silver salts just mixed with bisulphate and run through all the steps of the analysis persistently gave lower results than the same quantity of silver salts fused with bisulphate in silica crucible, the rest of the procedure being the same in both the cases. Had the interference been due to silica which might have gone in solution from the silica crucible by fusion, added silica in the form of sodium silicate would have produced the same results, but there was practically no interference noted by introducing sodium silicate in the solution. The experiment was also repeated in platinum crucible which showed better results but the tendency of higher results with fusion persisted.

Acknowledgement.—The authors are indebted to Col. M. K. Afridi and Dr. M.O. Ghani, the former directors of these Laboratories, for their keen interest in the work and their constant encouragement.

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