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A COLORIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF SILVER BY USE OF *p*-DIMETHYLAMINOBENZALRHODANINE

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ABSTRACT

Recent interest in the use of silver as a bactericidal agent led to the study of analytical methods suitable for determining silver in the small concentrations employed for these purposes. A sensitive and accurate colorimetric method, in which *p*-dimethylaminobenzalrhodanine is used, was developed. Soft-glass dishes are not suitable for use in the analytical procedure because of a very pronounced adsorption of silver on such surfaces. Dishes of fused silica or of Pyrex glass were satisfactory. Chlorides, sulfates, and cupr us and mercurous salts interfere with this colorimetric determination.

CONTENTS

I. INTRODUCTION

As one phase of the work of a research associateship on engineering uses of silver, sponsored by a group of American silver producers, an attempt was made to find a rapid and accurate method for the quantitative determination of small concentrations of silver in water. The need for such a method arises from recent interest in the "oligodynamic" properties of silver, and in particular, the use of silver as a sterilizing agent for drinking waters, swimming pools, etc. The concentrations of silver said to be necessary for most sterilizing purposes vary between the limits of 0.030 to 0.300 mg/liter of silver.

A survey of the methods used by Whitby,[1] Hickman,[2] Lamb, Carleton, and Meldrum,[3] Egg and Jung,[4] Wernicke and Modern,[5] Johnston, Cuta, and Garrett,[6] and Jelley[7] for the determination of

[1] 7th Int. Cong. Appl. Chem. Sec. I, 112 (1909).
[2] Phot. J. **62,** 512 (1922).
[3] J. Am. Chem. Soc. **42,** 251 (1920).
[4] Schweiz. med. Wochschr. **59,** 84 (1929).
[5] Compt. rend. Soc. Biol. **99,** 1519 (1928).
[6] J. Am. Chem. Soc. **55,** 2311 (1933).
[7] J. Soc. Chem. Ind. **51,** 191 (1932).

silver indicated that they are not entirely suited to the present problem, as either a complicated apparatus must be employed or large volumes of water must be evaporated to bring the silver content within the limit of sensitivity of the methods.

Feigl [8] reported a method for the qualitative detection of very small amounts of silver based upon the color produced when an acetone solution of *p*-dimethylaminobenzalrhodanine is added to a nitric-acid solution of silver, claiming a sensitivity of 1 part of silver in 5 million parts of water. Later, Kolthoff [9] confirmed the findings of Feigl and extended the use of the rhodanine compound to the qualitative detection of cuprous copper and mercurous mercury. Ettish and Tamehyna [10] used this compound for the detection of silver and claimed that by their procedure the reagent is sensitive to 1 part of silver in 40 million parts of water.

In the present study, a colorimetric procedure for the quantitative determination of silver by use of this reagent has been developed. Silver may be determined directly, without evaporations, in solutions containing as little as 0.06 mg/liter of silver and up to 9 mg/liter, with an accuracy of 3 percent or better. The more serious complications encountered in this method are the adsorption of silver on the walls of glass containers and the interference of certain elements, particularly chlorides. However, by following certain percautions excellent results may be obtained.

II. MATERIALS AND METHODS

Solutions of silver used as standards in this study were prepared by dissolving weighed portions of pure silver (99.993 percent Ag) in nitric acid, using fused-silica volumetric flasks. A 0.02 percent alcoholic solution of *p*-dimethylaminobenzalrhodanine was the color-producing agent.

Blood-sugar tubes of 20-ml capacity were used in the preliminary experiments in making color comparisons. Later, fused-silica test tubes of 30-ml capacity were used for this purpose.

Volumetric flasks, pipettes, and evaporating dishes made of fused silica were used for the most precise and dependable determinations. Pyrex glass was later proved suitable for handling the silver solutions at room temperatures.

The procedure followed varied but little from that outlined by Feigl,[8] and later by Kolthoff,[9] for the qualitative detection of silver. For the preliminary experiments color tubes used as standards for evaluating the silver content of an unknown solution were prepared by placing portions of a silver-nitrate solution containing 0.001607 g of silver/liter in a series of fused-silica tubes.[11] Each successive tube in a series contained 0.1 ml more of this silver-nitrate solution than the preceding tube. To each tube were then added 0.5 ml of approximately $4N$ HNO_3 solution and sufficient water to make the total volume 15 ml. These solutions were thoroughly mixed, using a clean rubber stopper to close the end of the tube. Then 0.5 ml of a 0.02-percent alcoholic solution of *p*-dimethylaminobenzalrhodanine was added and the contents were again mixed to develop the pink or red color characteristics of the silver-rhodanine solution.

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[8] Z. anal. Chem. **74**, 380 (1928).
[9] J. Am. Chem. Soc. **52**, 2222 (1930).
[10] Mikrochemie **10**, 92 (1931).
[11] Pyrex-glass tubes may be substituted for fused silica.

To determine the sensitivity of the color comparisons in ranges of different concentrations of silver, several series of color tubes were prepared representing concentration ranges from 1 to 10 ml of the above-mentioned silver-nitrate solution. The colors developed in these series were observed at 5-minute intervals for a period of 45 minutes. The maximum depth of color developed after 30 minutes, and did not fade on standing for an hour or more. The color varied from a pale pink in the tubes containing the smallest concentration of silver to a deep red in those having the greatest concentration of silver. The differences between any two tubes in a series and also between any single tube and a blank containing no silver were readily recognizable.

In this procedure the concentration of nitric acid, as well as the order in which it is added, is important. The addition of too much acid appreciably decreases the sensitivity of the test, while the addition of the acid following the rhodanine reagent causes the formation of a yellow precipitate, which is not readily soluble and interferes with the color comparisons. In cleaning the tubes after any determination, it was found advisable to rinse them thoroughly with concentrated nitric acid, as there is a tendency for some of the colored silver compound to cling to the walls of the tubes and to impart a slight color.

III. EXPERIMENTAL RESULTS

1. ADSORPTION EFFECTS

Early in this study it was observed that silver was lost when very dilute silver solutions were prepared by repeated dilution in soft-glass volumetric flasks. The losses in some cases amounted to 10 to 20 percent of the silver calculated to be present and varied with the number of determinations made and the nature and previous history of the flasks. Later experiments showed that this loss was due to adsorption of silver on the surface of the flasks.

The adsorption of silver ions from solutions has been reported by a number of investigators. Freundlich and Söllner [12] found a nearly irreversible adsorption of silver from solutions contained in glass and porcelain, but none in fused-silica containers; Horovitz and Zimmermann [13] reported that silver was adsorbed from solutions when in contact with certain types of German resistant glass; Kolthoff [14] studied the adsorption of silver, copper, zinc, and lead on glass wool; Quittner [15] made studies of the migration of ions from aqueous solutions into glass; and Mulligan [16] observed this effect in his work on the electrolysis of soda-lime glass. Haber,[17] in his work on the gold and silver content of sea water, found it to be necessary to employ special procedures to prevent the adsorption of silver and gold on the surface of glass containers.

Since very dilute silver solutions were to be employed in this investigation a further study of this adsorption effect was undertaken. The effect of increased area of contact of the solution with soft-glass surfaces was first considered. Two silver solutions were prepared in soft-glass volumetric flasks, one of which contained 1 ml of a silver-

[12] Biochem. Z. **203**, 3 (1928).
[13] Sitz. Akad. Wiss. Wien [II] **134**, 355 (1925).
[14] Pharm. Weekblad **58**, 463 (1921).
[15] Ann. Physik [IV] **85**, 745 (1928).
[16] Trans. Roy. Soc. Canada [III] **19**, 35 (1925).
[17] Z. angew. Chem. **40**, 303 (1927).

nitrate solution, containing 0.3208 g/liter of silver diluted to 250 ml, and the other contained 2 ml of the same solution diluted to 500 ml (table 1, series A). The concentration of silver in the two flasks was, therefore, the same, but there was a greater ratio of soft-glass surface to volume of solution in the smaller flask. Greater loss of silver resulted from the dilution in the 250-ml flask, as was shown by comparing the colors developed in pairs of tubes containing in one tube of each pair a definite volume of the silver solution from the 250-ml flask and in the other tube the same volume of solution from the 500-ml flask. This result is consistent with the conception that adsorption should be more pronounced in the flask having the greater ratio of surface area to volume of solution; that is, in the 250-ml flask.

TABLE 1.—*Losses of silver from dilute silver-nitrate solutions through adsorption*

Series	Experiment	Concentration of silver in original solution	Volume of original solution taken for dilution	Volume of diluted solution	Type of container used for dilution	Volume of diluted solution used	Silver content: Calculated	Silver content: Found	Error	Footnote
		g/liter	ml	ml		ml	mg	mg	Percent	
A	------	0.3208	2	500	Soft-glass flask (500 ml).	4	[a]0.0051	--------	--------	--------
	------	.3208	2	500		5	[a].0064	--------	--------	--------
	1	.3208	1	250	Soft-glass flask (250 ml).	4	.0051	<0.0051	Loss	--------
	2	.3208	1	250		5	.0064	< .0064	do	--------
A_1	------	.3208	4	1,000	Silica flask (1,000 ml).	2	[a].0026	--------	--------	--------
	------	.3208	4	1,000		3	[a].0038	--------	--------	--------
	------	.3208	4	1,000		4	[a].0051	--------	--------	--------
	21	.3208	2	500	Silica flask (500 ml).	2	.0026	.0026	None	--------
	22	.3208	2	500		3	.0038	.0038	do	--------
	23	.3208	2	500		4	.0051	.0051	do	--------
B	------	.3208	2	500	Soft-glass flask (500 ml).	2	[a].0026	--------	--------	--------
	------	.3208	2	500		4	[a].0051	--------	--------	--------
	------	.3208	2	500		5	[a].0064	--------	--------	--------
	3	.3208	2	500		2	.0026	<.0026	Loss	
	4	.3208	2	500		4	.0051	<.0026	do	(d)
	5	.3208	2	500		6	.0064	<.0026	do	
C	------	.3208	2	500	do	3	[a].0038	--------	--------	--------
	------	.3208	2	500		4	[a].0051	--------	--------	--------
	------	.3208	2	500		5	[a].0064	--------	--------	--------
	------	.3208	2	500		2	[a].0026	--------	--------	--------
	13	.3208	2	500		4	.0051	.0038	−25	(g)
	14	.3208	2	500		5	.0064	.0051	−20	
	15	.3208	2	500		3	.0038	<.0026	Loss	
	16	.3208	2	500		4	.0051	<.0026	do	(e)
	17	.3208	2	500		5	.0064	<.0026	do	
	18	.3208	5	1,000	Soft-glass flask (1,000 ml).	3	.0048	<.0026	do	
	19	.3208	5	1,000		4	.0064	<.0026	do	(f)
	20	.3208	5	1,000		5	.0060	<.0038	do	
D	------	.3208	2	500	Silica dish (500 ml).	4	[a].0026	--------	--------	--------
	------	.3208	2	500		5	[a].0064	--------	--------	--------
	6	.3208	2	500	Soft-glass flask (500 ml).	4	.0051	.0018	−65	--------
	7	.3208	2	500		5	.0064	.0030	−53	--------
E	------	.2959	1	500	do	4	[a].0024	--------	--------	--------
	------	.2959	1	500		5	[a].00295	--------	--------	--------
	------	.2959	1	500		6	[a].0035	--------	--------	--------
	------	.2959	1	500		7	[a].0041	--------	--------	--------
	8	.0963	1	500		15	.0028	.0028	0	
	9	.0963	1	500		20	.0038	.0036	−5	(b)
	10	.0963	1	500		20	.0038	.0040	+5	
	11	.0963	1	500		15	.0028	<.0024	Loss	(c)
	12	.9963	1	500		20	.0024	<.0024	do	

[a] Arbitrarily taken as a standard and assumed to have no adsorption losses.
[b] Evaporation of the 15- and 20-ml portions of silver solution was made in fused-silica dishes.
[c] Evaporation of the 15- and 20-ml portions of silver solution was made in Pyrex-glass beakers.
[d] 200 g of untreated soft-glass beads were added to the solution.
[e] 200 g of soft-glass beads previously treated in a 25-percent NaOH solution were added.
[f] 200 g of broken Pyrex-glass beakers were added.
[g] 200 g of soft-glass beads previously treated in dichromate cleaning solution were added.

The same experiment was repeated later by using 1,000- and 500-ml silica flasks instead of soft-glass flasks. In this case, a comparison of the color in one tube of each pair, containing a definite volume of silver solution from the 500-ml flask, with that in the second tube, containing the same volume of solution from the 1,000-ml flask, showed that there was no loss of silver (see section A_1 of table 1).

Further experiments were made in which the surface area exposed to the solution was increased by the addition of soft-glass beads (table 1, series B). A rhodanine color series was prepared from a dilute silver solution (0.00128 g Ag/liter) contained in a 500-ml soft-glass volumetric flask. A portion of this solution was then removed and approximately 200 g of soft-glass beads, which previously had been cleaned and dried, were added to the remainder of this solution. After the solution containing the beads was shaken thoroughly, and let stand for ½ hour, a rhodanine color series was prepared from this solution and compared with a color series made from that portion of the solution which was removed before the addition of the beads. Large differences in color were again obtained for those portions not containing the glass beads and those with the glass beads, the difference amounting to as much as approximately 50 percent.

The amount of silver adsorbed on the beads varied, depending upon their previous treatment. Beads that stood in a dichromate cleaning solution overnight and then were thoroughly rinsed with water and dried, adsorbed less silver than a similar quantity of beads which had been kept in a 25-percent sodium-hydroxide solution for the same length of time (table 1, series C—experiments 13 and 14 and 15 to 17). No determinations were made to ascertain whether these differences in color were due to a change in the surface of the beads, due to adsorbed alkali, or to a slight amount of sulphuric acid from the dichromate cleaning solution which might not have been removed from the surface by repeated washing. Sulphuric acid was subsequently found to increase the depth of the rhodanine color.

Similar trials of increased adsorption resulting from the larger amount of glass surface exposed to the solution were made, using approximately 200 g of broken Pyrex glass in one case (table 1, series C; experiments 18 to 20), and the same weight of broken soft glass in the other. The results were similar to those obtained when glass beads were used, with the exception that broken Pyrex glass adsorbed less silver than broken soft glass.

Further experiments on the adsorption of silver on the walls of silica containers were made by diluting 2-ml portions of the silver-nitrate solution to 500 ml in a silica dish and in a soft-glass volumetric flask (table 1, series D). A comparison of the colors in the rhodanine color tubes made from these dilute solutions showed a very large loss of silver in the solution made up in the soft glass; that is, there was, at the most, much less adsorption by the silica container.

Kolthoff [18] reported that the adsorption of silver on glass wool is increased with a rise in temperature of the silver solution. A similar

[18] Pharm. Weekblad 58, 463 (1921).

effect was observed in the present study in that larger losses of silver were observed when attempts were made to concentrate a dilute silver solution by evaporation in Pyrex-glass beakers. On the other hand, evaporation in fused-silica dishes produced little or no losses (table 1, series E). It may be assumed that there is also very little or no adsorption on silica at room temperature.

The data secured thus far indicate that: (a) Soft glass was quite unsuitable for use at any point in handling the silver solutions in determining silver in the concentrations in question; (b) Pyrex glass had less adsorptive power toward silver than soft glass at room temperatures, but should not be used for evaporation of very dilute silver solutions; and (c) fused-silica ware had little or no adsorptive power for silver during evaporation of dilute silver solutions and probably was also free from serious adsorption of silver at ordinary room temperatures. The adsorption of silver was increased when alkali was used for treating soft-glass surfaces, but it was decreased when the alkali was replaced by acid dichromate cleaning solution.

2. ACCURACY AND SENSITIVITY OF METHOD

Solutions for rhodanine color tubes, used in the determination of the accuracy and sensitivity of the method, were prepared and handled throughout in fused-silica ware, such as volumetric flasks, pipettes, and color tubes. It was assumed that by using silica glass there was no serious adsorption of silver from the solutions during any stage of the procedure.

TABLE 2.—*Colorimetric determination of silver*

Experiment	Volume of dilute silver solution	Silver content		Error	Type of flask used for dilution
		Calculated	Found		
	ml	mg	mg	*Percent*	
1	2	0.00107	0.00107	0.0	Pyrex glass.
2	4	.00214	.00214	.0	Do.
3	6	.00321	.00332	+3.4	Do.
4	2	.00107	<.00107	(c)	Soft glass.
5	4	.00214	.00193	−9.8	Do.
6	6	.00321	.00289	−9.9	Do.
7 [a]	4	.00219	.00214	−2.3	Pyrex glass.
8 [a]	6	.00329	.00332	+0.9	Do.
9 [a]	3	.00454	.00450	−0.9	Do.
10 [a]	3	.00454	.00442	−2.6	Do.
11 [a]	12	.00482	.00482	0.0	Do.
12 [a]	12	.00482	.00466	−3.3	Do.
13	4.5	.00681	.00675	−0.9	Do.
14	4.8	.00726	.00723	−0.4	Do.
15	5.0	.00757	.00771	+1.9	Do.
16	[b] 12	.00482	.00487	0.0	Do.
17	[b] 12	.00482	.00466	−3.3	Do.
18	[b] 12	.00482	.00498	+3.2	Do.

[a] The silver content of the solution was not known before test.
[b] After being diluted to 50 ml, the silver solutions were evaporated in fused-silica dishes to about 5 ml, transferred to color tubes, and treated to produce the rhodanine color.
[c] Not determined.

It was found that silver solutions made by diluting in soft-glass volumetric flasks had lost appreciable quantities of silver as judged by comparing with color standards prepared entirely in silica glass (table 2, experiments 4 to 6). On the other hand, silver solutions diluted in Pyrex-glass volumetric flasks showed no loss of silver when compared with the same standards (table 2, experiments 1 to 3). This is in agreement with Horovitz and Zimmerman's results.[19]

The results obtained with various dilute solutions, the concentrations of which were not known previous to test, are given in table 2, experiments 7 to 12. These and all solutions made subsequently were prepared in Pyrex-glass volumetric flasks. The accuracy of the method, as indicated by the results obtained for experiments 7 to 18 of table 2, was ± 3 percent of the quantity of silver determined in solutions of concentrations ranging from 1 to 8 mg/liter of silver. Further, no appreciable loss of silver occurred when the dilution and evaporation of the solution were carried out in fused-silica dishes, as the results for experiments 16 to 18 of table 2 will show.

It was also observed that the color comparisons could be made most easily where the concentration of the solution was between 1 and 6 mg/liter of silver.

IV. FACTORS WHICH MAY INTERFERE WITH THE RELIABILITY OF THE METHOD

Chlorides present in very small amounts in the solution decrease appreciably the sensitivity and accuracy of the rhodanine reagent for silver. The chlorides cause a fading of the color, and consequently low results for silver content are produced. This difficulty may be overcome by repeated evaporations of the solution to dryness with concentrated nitric acid. Definite amounts of chlorides ranging between 10 and 65 g/liter were effectively removed by two evaporations with 20-ml portions of concentrated nitric acid.

Acetic acid, acetone, formaldehyde, ether, alcohol, and ethyl acetate react with the rhodanine reagent to give colors.

Ammoniacal solutions of silver react with the rhodanine reagent to give colors similar to those produced in nitric acid. Greater amounts of silver, however, are required to produce the same depth of color in these solutions.

Kolthoff[20] reported that cuprous copper and mercurous mercury react with rhodanine to give colors similar to those produced by silver.

Calcium carbonate in amounts less than 1 mg/liter has no effect on the rhodanine color, though the color is deepened if the quantity of the carbonate exceeds this value.

Sodium nitrate has no effect on the depth of the rhodanine color if it is present in amounts less than 1 mg/liter but greater amounts of this salt increase the depth of the rhodanine color. Ammonium nitrate decreases the sensitivity of the test if in amounts as much as 0.6 mg/liter.

Very small amounts of either sulphuric acid or potassium sulphate (0.6 g/liter for the latter) increase the depth of the rhodanine color.

[19] Sitz. Akad. Wiss. Wien. [Ü] **134**, 355 (1925).
[20] Pharm. Weekblad **58**, 463(1921).

V. SUMMARY

A sensitive method for the colorimetric determination of silver, using *p*-dimethylaminobenzalrhodanine, has been developed.

The adsorption of silver from dilute solutions is appreciable on soft glass, slight on Pyrex glass at room temperature, and negligible on fused silica. Therefore, soft-glass containers should not be employed in the procedure.

The sensitivity and accuracy of the colorimetric test may be impaired if the quantities of certain substances exceed definite values. Notable among the inorganic substances thus interfering are chlorides, sulfates, and cuprous and mercurous salts.

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