ART. XX. — *The Colorimetric Determination of Small Amounts of Gold*; by RALPH NELSON MAXSON.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxlv.]

APPLICATION of the colorimetric method for the estimation of small amounts of gold, based upon the purple of Cassius coloration, have been proposed by Carnot,* Rose,† Sonstadt,‡ Cassel,§ Prister,|| Moir¶ and others, but the use of this reaction for such a purpose is open to objection. According to the authority of other workers, the coloration thus produced is extremely variable, varying in intensity and shade according to the condition of the solution and precipitant. Moreover the substance is unstable, and artificial standard solutions are necessary if accurate results are to be obtained.

It has been suggested that the coloration of red colloidal gold suspensions might have a quantitative relation to the amount of metal present and a method of colorimetric estimation, free from the objections stated above, be based upon this relation. The following investigation was therefore undertaken in the hope of discovering whether such a relationship would not offer a suitable means for the estimation of small amounts of gold.

The preparation of the red colloidal suspensions was naturally the first object of interest. Blake** has shown that acetylene is the most suitable reagent for effecting the reduction of the auric salt, the treatment consisting in drying the chloride at 170°, dissolving in ether, and pouring the ethereal solution into water also containing ether and saturated with acetylene gas. The use of ether was objectionable for the purpose of this investigation and the simpler procedure described below gave good results.

The measured quantity of a standard solution of the auric salt was drawn off into a calibrated flask and treated with a suitable amount of an aqueous solution of acetylene, made by dissolving the previously washed gas in water distilled and cooled in tin. The color having developed, the solution was shaken and the flask filled to the mark. The gold solutions used in these experiments were prepared from pure gold chloride, which contained hydrogen chloride in the usual amounts, and had not been subjected to a preliminary drying. The standard of these solutions was determined gravimetrically by means of magnesium ribbon, and by the electrolytic process with the

* Compt. Rend., xcvi, 105 and 169.

† Chem. News, lxxvi, 271.

‡ Chem. News, xxvi, 159.

§ Eng. and Min. Jour., 70, xviii, 661.

|| Jour. Chem. Met. and Min. Soc. of South Africa, iv, 235, 1903.

¶ Jour. Chem. Met. and Min. of South Africa, Sept. 1903.

** This Journal, xvi, 381 (1903).

revolving cathode. Solutions of less concentration were then obtained by suitable and accurate dilution.

A preliminary series of qualitative and quantitative experiments gave evidence that the coloration was of a quantitative nature and that the suspensions were sufficiently stable under suitable conditions.

The Gallenkamp colorimeter was used in the subsequent quantitative experiments immediately following. The delicacy of the readings was increased by placing the instrument in a light-tight box pierced with suitably situated holes; the influence of external colors was avoided by admitting light to the instrument from a ground glass plate, which was found to be very efficient.

It is a well known fact that small amounts of electrolyte will rapidly change "red" gold to the "blue" modification. It is necessary therefore to conduct the comparisons in a room reasonably free from fumes, and to have all containing vessels free from soluble material. It was found that flasks which had been treated with steam for a few minutes gave the best results. Red suspensions contained in such flasks gave no trace of blue after an interval of several weeks.

Using the precautions outlined above, the results shown in the following table were obtained. The error of the personal equation was determined by means of a series of comparisons conducted with different concentrations of the same suspension, and covering a range of amounts of material identical with the amounts handled in the experiments given below.

The forty-nine analyses given in the table were made under widely varying conditions. The age of the suspensions varied from a few minutes to several weeks. In order to avoid error of measurement, new standard suspensions were prepared from time to time, and their concentrations are shown in the last column of the table.

The analyses covered a wide range in amounts of gold and were conducted under varying conditions of light. The results are seen to run with fair regularity and the errors are approximately of the same order of magnitude.

The Gallenkamp colorimeter, used in the foregoing experiments, is not only expensive but cumbersome and complicated in construction; moreover, the instrument is not suitable for the correct estimation of the most minute amounts of gold, the color becoming too faint for accurate comparison because of the shortness of the columns of liquid. A modified form of the type of apparatus proposed by Penfield for the colorimetric estimation of titanium and consisting of comparison tubes set vertically in a dark box and illuminated from below, was therefore adopted. The tubes used in these comparisons had a

TABLE I.

No.	Strength of solution. per cent.	Gold taken. grm.	Gold found. grm.	Error. grm.	Gold in 1 ^{cm} ³ of standard. grm.
1	99.6	0.00080	0.00086	+0.00006	0.000086
2	95.5	0.00077	0.00082	+0.00005	
3	90.9	0.00075	0.00078	+0.00003	
4	85.7	0.00073	0.00074	+0.00001	
5	84.3	0.00071	0.00073	+0.00002	
6	67.6	0.00062	0.00058	—0.00004	0.000086
7	63.4	0.00058	0.00055	—0.00003	
8	56.0	0.00054	0.00048	—0.00006	
9	52.0	0.00052	0.00045	—0.00007	
10	47.9	0.00047	0.00041	—0.00006	
11	98.6	0.00081	0.00085	+0.00004	
12	88.2	0.00075	0.00076	+0.00001	
13	78.8	0.00070	0.00068	—0.00002	
14	71.6	0.00065	0.00062	—0.00003	
15	66.1	0.00059	0.00057	—0.00002	
16	60.4	0.00054	0.00052	—0.00002	0.000086
17	57.8	0.00048	0.00050	+0.00002	
18	49.8	0.00043	0.00043	±0.00000	
19	44.1	0.00038	0.00038	±0.00000	
20	36.4	0.00032	0.00031	—0.00001	
21	98.6	0.00081	0.00085	+0.00004	
22	88.2	0.00075	0.00076	±0.00001	
23	78.8	0.00070	0.00068	—0.00002	
24	71.6	0.00065	0.00062	—0.00003	
25	66.1	0.00059	0.00057	—0.00002	
26	60.4	0.00054	0.00052	—0.00002	
27	57.8	0.00048	0.00050	+0.00002	
28	49.8	0.00043	0.00043	±0.00000	
29	44.1	0.00038	0.00038	±0.00000	
30	36.4	0.00032	0.00031	—0.00001	
31	87.8	0.00030	0.00030	±0.00000	0.000034
32	79.1	0.00028	0.00027	—0.00001	
33	71.7	0.00026	0.00024	—0.00002	
34	63.1	0.00024	0.00022	—0.00002	
35	57.6	0.00022	0.00020	—0.00002	
36	46.6	0.00019	0.00016	—0.00003	0.000034
37	44.6	0.00017	0.00015	—0.00002	
38	35.8	0.00015	0.00012	—0.00003	
39	28.9	0.00013	0.00010	—0.00003	
40	16.4	0.00004	0.00006	+0.00002	
41	21.9	0.00007	0.00007	±0.00000	0.000034
42	25.9	0.00009	0.00009	±0.00000	
43	36.9	0.00011	0.00013	+0.00002	
44	46.5	0.00013	0.00016	+0.00003	
45	38.3	0.00015	0.00013	—0.00002	
46	47.3	0.00017	0.00016	—0.00001	
47	Lost by accident				
48	56.8	0.00022	0.00019	—0.00003	
49	66.1	0.00024	0.00023	—0.00001	

diameter of 1^{cm} and a length of 13^{cm}, and were accurately graduated to hold 10^{cm}³.

A mirror suitably situated beneath the box containing the tubes gave efficient illumination. Such an apparatus is not only cheaply and easily procured, but if tubes of these dimensions are used it is capable of accurately determining very small amounts of gold.

The method of comparison was carried out in the following manner. A measured amount of the suspension was drawn off into the left hand tube and diluted to the mark with water; a suitable amount of water was then placed in the right hand tube and the standard suspension drawn into the tube until the colors were seen to be identical. The necessary amount of water to be used can be determined by preliminary experiment.

The positions of the tubes were always reversed before the final reading was taken.

The following experiments were made in order to determine the error and range of amounts of gold capable of accurate estimation in such an apparatus with tubes of the dimensions described above. The comparisons were made with a red suspension prepared by careful dilution of a more concentrated standard suspension which contained 0.000010175 grams of metal in one cm³.

The results obtained with different concentrations of the standard suspension just described are given in the following table.

TABLE II.

No. Ana.	Gold sus. taken. cm ³ .	Gold sus. used. cm ³ .	Gold used. grm.	Gold found. grm.	Error. grm.
1	9.50	9.05	0.000102	0.000097	—0.000005
2	8.00	7.59	0.000086	0.000082	—0.000004
3	7.00	6.89	0.000075	0.000074	—0.000001
4	6.00	5.83	0.000065	0.000063	—0.000002
5	5.00	4.84	0.000054	0.000052	—0.000002
6	4.00	3.88	0.000043	0.000042	—0.000001
7	3.00	2.47	0.000032	0.000027	—0.000005
8	2.00	1.82	0.000022	0.000020	—0.000002
9	1.00	0.93	0.000011	0.000010	—0.000001

The intensity of the color in the above experiments ranged from a deep red to a faint pink. Further comparisons made with suspensions more dilute than those described above gave errors of magnitude increasing with the dilution. The amounts handled here are, then, the minimum quantities that can be accurately estimated with the apparatus described. It is obvious that if larger amounts of the metal are to be determined, tubes of greater dimensions should be used.

The application of such a method for the determination of gold naturally starts with that element. The weighed amount of metal, contained in a clean porcelain crucible, can be readily brought into solution with the aid of chlorine water or aqua regia and the excess of the solvent evaporated off upon the water bath. Experiments have shown that a gentle preliminary heating of the solution of the auric salt hastens the rapidity of the reduction. Care must be taken not to reduce any of the gold chloride by such a procedure.

If traces of electrolyte are present the coagulation of the "red" gold may be sometimes avoided by the addition of a few drops of ether to the cold solution. When small amounts of the metal are handled the volume of the solution should not exceed a few cubic centimeters, and only a small amount of the aqueous solution of acetylene should be added; otherwise the coloration may be partially or totally inhibited.

In conclusion, it can be seen from the evidence of the experiments described above, that the colorimetric estimation of small amounts of gold is quantitatively possible if proper precautions are taken to ensure the maximum coloration and exclusion of electrolytes. The method is quick and simple in character, and for the amounts of gold used above, the results show it to possess suitable accuracy for the correct estimation of small amounts of the metal.

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