ON THE PRESERVATION OF THE STANDARD SOLUTION OF OXALIC ACID AND ON THE READING OF THE BURETTE.(2)

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As is generally known, the solution of oxalic acid is widely used as an important standard in volumetric analysis, though it is necessary to prepare it frequently anew on account of its tendency to decomposition, but

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(2) This paper was published in Japanese in the *Journal of the Chemical Society of Japan*, **43** (1922), 767.

very few books on analytical chemistry describe the method of preservation of this solution.

The addition of alcohol was formerly proposed by Hartly(1) and thymol by Gerland(2) as preserving agents. Riegler(3) on the other hand, described that a solution containing 50 c.c. of conc. sulphuric acid in 1 litre did not alter its titre after a year. Treadwell(4) recommended the same precaution in his famous book of analytical chemistry, and advised not to use old solutions prepared in the usual manner without any preserving agent, on the basis on his observation that an oxalic acid solution prepared according to the method of Riegler lost, after eight months' standing, only 0.07% of its original strength, while one containing no sulphuric acid lost 0.57%.

Werner(5) and Blass(6) attributed the cause of the decomposition of oxalic acid to the action of a micro-organism, Bizio,(7) Fleury(8) and Gigli(9) expressed the opinion that the concentrated solutions were not subject to the influence of the harmful micro-organism and Duclaux(10) and Jorissen(11) described about the action of light upon it.

As the degree of the deterioration observed by Treadwell and Riegler in the oxalic acid solution containing sulphuric acid was too small to be in accordance with the author's experience, it was suspected that there might have been something wrong with their observations. The author also wondered why the two investigators had used so large a quantity of conc. sulphuric acid as 50 cc. for the purpose of preservation, though as a matter of course, a small quantity of it must have exerted a sufficiently disinfecting effect.

The experiments to be here described were carried out by the present author, in order to clear up the points in question, by a thoroughly systematical investigation, with the view that the most important of the influential factors as regards the preservation of the standard oxalic acid solution would probably be the action of light.

Two series of 0.1 N solutions of oxalic acid, with and without the addition of the various quantities of conc. sulphuric acid were prepared from

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(1) *Chem. News*, **37** (1878), 9.
(2) *J. Soc. Chem. Ind.*, **10** (1891), 25.
(3) *Z. analyt. Chem.*, **35** (1896), 522.
(4) „Lehrbuch der analytischen Chemie," 7th ed. II, p. 499.
(5) *Arch. Pharm.*, [3], **2** (1873), 522.
(6) Ibid., [3], **3** (1873), 310.
(7) *Z. analyt. Chem.*, **9** (1870), 392.
(8) *J. pharm. chim.*, [5], **7** (1883), 383; *Chem. Zentr.*, (1883), 547.
(9) *Apoth. Zt.*, **7** 583; *Chem. Zentr.*, (1893), I, 11.
(10) *Comp. rend.*, **103** (1886), 1010.
(11) *Z. angew. Chem.*, (1899), 521.

Kahlbaum's purest oxalic acid ("Zur Analyse"): the one series was kept in ordinary colorless reagent bottles, while the other, in reagent bottles completely wrapped with black paper.

For the sake of studying the disparity, if any, between the degrees of the deterioration of the solutions differing in purity, the duplicates of the whole series were made from oxalic acid of the pure commercial grade.

All the bottles were kept in rows, on the laboratory shelves, which were beyond the reach of the *direct* sun light. From time to time, the rate of decomposition was measured, by titration with a standard solution of potassium permanganate, standardized against the pure oxalic acid solution, *freshly* prepared each time from Kahlbaum's preparation ("Zur Analyse").

In order not to exclude the chance of development of the microorganism, the investigation was begun in April and continued till September; the reagent bottles were simply closed with glass stoppers applying neither special sealing nor sterilization, so that the conditions would be kept the same, as far as possible, with those prevailing in the ordinary analytical practice.

TABLE 1.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
1	0	0.0991	0.0991	0.0991	0.0987	−0.0004
2	2	0.0992	0.0990	0.0986	0.0981	−0.0011
3	10	0.0990	0.0983	0.0980	0.0951	−0.0039
4	20	0.0992	0.0972	0.0941	0.0900	−0.0092
5	40	0.0992	0.0965	0.0929	0.0890	−0.0102
6	100	0.0992	0.0941	0.0887	0.0827	−0.0165

TABLE 2.

(Oxalic acid: commercial. Containers: ordinary colorless reagent bottles.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
7	0	0.0993	0.0993	0.0986	0.0982	−0.0011
8	2	0.0993	0.0987	0.0980	0.0975	−0.0018
9	10	0.0993	0.0985	0.0970	0.0955	−0.0038
10	20	0.0993	0.0978	0.0960	0.0943	−0.0050
11	40	0.0990	0.0970	0.0938	0.0908	−0.0082
12	100	0.0991	0.0960	0.0927	0.0899	−0.0092

From the figures given in Tables 1 and 2, it is clearly shown that, contrary to the general belief now prevailing among chemists, the plain aqueous solutions are comparatively most stable (Nos. 1 and 7), and the solutions become more and more unstable as the quantities of sulphuric acid added are increased (No. 12 lost more than 9%, while No. 6 even 16% or so, of the original strength). Accordingly the method, recommended by Treadwell and Riegler, of adding sulphuric acid to the standard solution of oxalic acid and keeping it in the ordinary *colorless* bottle, is altogether of no practical value as a means of preservation.

It will also be seen that in the presence of fairly large quantities of sulphuric acid, the solutions of Kahlbaum's purest oxalic acid (Nos. 4–6) are less stable than those of the pure commercial sample (Nos. 10–12).

TABLE 3.

(Oxalic acid: Kahlbaum, "Zur Analyse." Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	47th day.	90th day.	148th day.	Difference.
13	0	0.0992	0.0992	0.0992	0.0992	0.0000
14	2	0.0990	0.0992	0.0990	0.0992	+0.0002
15	10	0.0992	0.0992	0.0991	0.0995	+0.0003
16	20	0.0990	0.0992	0.0991	0.0995	+0.0005
17	40	0.0992	0.0992	0.0992	0.0995	+0.0003
18	100	0.0994	0.0992	0.0992	0.0993	−0.0001

TABLE 4.

(Oxalic acid: commercial. Containers: reagent bottles wrapped with black paper.)

No. of experiment.	Conc. H_2SO_4 in L. cc.	Normality.				
		1st day.	48th day.	91st day.	149th day.	Difference.
19	0	0.0993	0.0992	0.0992	0.0994	+0.0001
20	2	0.0991	0.0993	0.0992	0.0995	+0.0004
21	10	0.0991	0.0992	0.0992	0.0995	+0.0004
22	20	0.0993	0.0992	0.0992	0.0994	+0.0001
23	40	0.0991	0.0992	0.0991	0.0995	+0.0004
24	100	0.0993	0.0993	0.0991	0.0996	+0.0003

The results given in Tables 3 and 4 indicate, that the plain aqueous solutions of oxalic acid, kept in the bottles completely wrapped with black paper, without any precaution for excluding the influence of the micro-organism, are all strikingly stable, entirely regardless of the difference in the grades of purity of the materials (Nos. 13 and 19); even those containing large quantities of sulphuric acid are also stable when kept in the *black* bottles (Nos. 18 and 24).

The negligible increase, observed in the concentrations of these solutions, must naturally be explained to be due partly to the experimental error and partly to the slight evaporation during the extreme heat in the summer. Had the bottles, with specially well ground and perfectly fitted stoppers, instead of the *ordinary* reagent bottles, been used in the above experiment for keeping the solutions, the concentrations would doubtless have remained absolutely the same.

From the results stated thus far, it is clearly established, that the standard solution of oxalic acid should always be kept in a bottle carefully wrapped with black paper, and that the addition of sulphuric acid is entirely unnecessary.

What then was the reason which led Treadwell and Riegler to such an erroneous conclusion? It seems very plausible, in the light of the author's observation recorded above, that the two investigators accidentally kept their solutions for the experiments of preservation, in a more or less dark place—most probably inside the laboratory table.

On the Reading of the Burette.

For the purpose of making the reading of the burette easy and accurate, there have been many devices proposed, such as the use of a mirror, etc., but none of them satisfies the following five conditions at the same time, namely, (1) constancy of the background of the meniscus, (2) deep coloration of the meniscus, (3) facility of fixing the position of the experimenter's eye, (4) easy and comfortable reading of the graduations of the burette, none of them being covered from sight, and lastly (5) no necessity of holding it by hand.

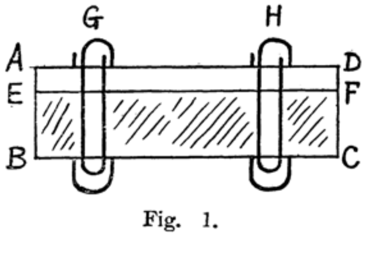

Fig. 1.

The device to be here described, is the one constantly used by numerous workers, in this laboratory of analytical chemistry for several years and found to answer all the requirements enumerated above.

A piece of paper ABCD, measuring 22 cm. × 8 cm., is cut from a name card, as shown in the accompanying figure, on which is pasted a strip of black glazed paper EBCF, measuring 1.5 cm. × 8 cm.: then a strip of transparent colorless celluloid plate, having exactly the same size as the glazed paper EBCF, is fastened by two paper clips, G and H, to the card, so that the edges of the glazed paper and celluloid perfectly coincide on the line EF, between which the burette is inserted. When it is moved until the meniscus seems to touch the line EF, the afore-mentioned conditions are satisfied simultaneously and the reading is made exceedingly easy and accurate.

Summary.

(1). The standard solution of oxalic acid should always be kept in a reagent bottle carefully *wrapped with black paper*. The solution thus preserved does not change its strength, irrespective of the presence or absence of sulphuric acid. Hence the old standard solution kept in a black bottle can as well used for titration.

(2). The method of preservation of the oxalic acid solution, described in Treadwell's "Analytical Chemistry" is not appropriate; the addition of sulphuric acid is not only unnecessary but *objectionable,* because the velocity of decomposition of the oxalic acid solution kept in a *colorless* bottle, becomes greater with the increase in the concentration of sulphuric acid added.

(3). A convenient device for the correct reading of the burette is described.

In conclusion, the author wishes to express his heartfelt thanks to Prof. M. Kobayashi for valuable suggestions during the work.

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