

# THE STABILITY OF CERTAIN REAGENTS.

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It will have been noticed in the last Proceedings that the Committee of Chemical Control recommended for the standardisation of Iodine the substitution of Arsenious Acid for the Sodium thiosulphate, the reasons for the change being the greater keeping power of the arsenic solutions. The Committee also wished to know the stability of other solutions used, and as the literature, as far as could be seen, did not furnish the information sought, the writer undertook to carry out the work, and in the following places before this Congress the results.

The programme consisted in examining the keeping power of N/10  $\text{KMnO}_4$ ; N/10 sodium thiosulphate; N/10  $\text{As}_2\text{O}_3$ ; N/10  $\text{K}_2\text{Cr}_2\text{O}_7$ ; N/32 sodium thiosulphate and N/32  $\text{As}_2\text{O}_3$ .

Since the literature is not generally available to the chemists in the factories the data are given rather fully.

The titrations were performed using weighing burettes rather than the ordinary burettes, because the former are much more accurate. By using this type of burette there is no reading error due to the meniscus and tem-

perature effects are absent. This latter consideration is a great boon, when it is remembered that the solutions under test had to be kept and tested during the hot summer and cold winter, the temperature variations being considerable at these extremes.

All the solutions when made were placed in aspirators with glass stop-cock outlets. The top being closed with a rubber bung and in the bung a soda-lime tube was inserted.

## Potassium Permanganate, 0.1 N.

The method of preparation and of standardisation of this solution was fully described in the Proceedings of this Association, 1931, p. 15. Two lots were made up, (1) a two-litre batch and (2) a ten-litre batch.

(1) Two litres of potassium permanganate 0.1 N were made up on January 28th, 1931, allowed to stand ten days and then filtered through a sintered glass Buchner funnel. On standardising on February 9th, it was found to be exactly 0.1 N. Standardisation was repeated on the dates shown below and found to remain exactly 0.1 N up to August, when all the solution was used up.

Feb. 9th.	Mar. 3rd.	Apr. 2nd.	May 1st.	June 2nd.	Aug. 5th.
Factor = 1.0	f = 1.0	f = 1.0	f = 1.0	f = 1.0	f = 1.0

(2) Ten litres of permanganate were made up as before and after filtration were found to have a factor

0.994 to the 0.1 N. This solution gradually deteriorated from month to month as follows:—

May 1st.	June 2nd.	Aug. 6th.	Sept. 16th.	Nov. 16th.	Jan. 15th.
Factor = 0.994	f = 0.992	f = 0.988	f = 0.986	f = 0.986	f = 0.983

It will thus be seen that the smaller volume of solution kept far better than the large volume.

Treadwell, "Quantitative Analysis," says (p. 514/515, p English edition) that permanganate will keep indefinitely when protected from dust and reducing vapours. This is then added: "The addition of 10 gm. caustic potash per litre increases the stability of the solution." This sentence is *not* in the German edition, so the translator must have added it. Kolthoff shows that such an addition is definitely harmful ("Volumetric Analysis, I., pp. 228-230).

Another two litres of 0.1 N permanganate was made up five months ago and again has kept its titre unchanged. It looks as if for the period of the crop a properly made and carefully preserved small volume of potassium permanganate will be reliable.

## Sodium Thiosulphate, 0.1 N.

Kolthoff ("Volumetric Analysis, I., pp. 231-234) discusses the keeping power of this important reagent

and shows that it is uncertain whether the gradual decomposition which sets in is due to carbon dioxide, air oxidation, or micro-organisms. It appeared, therefore, that if the aspirator had a long tube filled with soda-lime and a good plug of cotton-wool to keep out micro-organisms, the best protection would be given to the solution. Two solutions, each 2-litres in volume, were made up.

The standardisation of the solution was carried out as described on page 11 of the 1930 Proceedings of this Association, using, as already said, weighing burettes in place of ordinary burettes. A 32-ounce winchester was taken and 5 ml. of 1 : 10 sulphuric acid introduced, diluted with 100 ml. of water, and the permanganate (about 25 ml.) was then run in from the weighing burette. The potassium iodide (10 ml. of 1 : 10) introduced last. By adding the reagents in this order no iodine vapour escapes into the bottle and the results are therefore accurate. After the iodine has been liberated, a reaction which is practically instantaneous,

the titration against the thiosulphate is proceeded with in the usual manner. The solution was also standardised against a 0.1 N. solution of potassium iodate.

Potassium iodate and potassium chromate, Kolthoff ("Volumetric Analysis," I., p. 231) states, do not change in the least on standing. The potassium iodate used was British Drug Houses A.R. chemical, but I found that my particular sample required re-crystallising. After crystallisation the salt is freed from water by heating to 180°, at which temperature it became slightly brown, so I feared decomposition. Another sample was obtained and heated, and it also discoloured but did not lose weight. I then wrote Prof. Kolthoff and asked his experience. He replied that he had also

found the same happen and said that the decomposition is negligibly small because the slightly coloured products gave the same values as pure white iodate. I mention this in case anyone finds a similar occurrence.

The test is carried out in exactly the same manner as when using permanganate. It must, however, be remembered that when making up a 0.1N/KIO<sub>3</sub> that the reaction with iodide is  $5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2$ , and that therefore 5/6 of the iodine set free is due to the iodine of the potassium iodide, and therefore a 0.1 N potassium iodate 1/60 of the molecular weight should be taken, i.e. 3.5671 grams in 1,000 ml.

The results of the tests were as follows:—

Standardised with	Feb. 9th.	Mar. 3rd.	May 1st.	July 8th.	Sept. 16th.	Nov. 16th.
0.1 KMnO <sub>4</sub>	f = 1.004	f = 1.004	f = 1.004	f = 1.003	f = 0.993	f = 0.988
0.1 KIO <sub>3</sub>	f = 1.004	f = 1.004	f = 1.004	f = 1.002	f = 0.992	f = 0.989

For five months the solution kept perfectly clear, but a deposit of sulphur began to settle from then on, and after a year's standing the bottom of the aspirator, in spite of the precautions taken, is covered with sulphur. Both solutions behaved similarly.

#### Arsenious Acid 0.1.

Last year the Committee of Chemical Control recommended the use of arsenious acid for the standardisation of thiosulphate. Kolthoff states in Vol. II. of his "Volumetric Analysis" (p. 363) that "Standardisation of iodine against arsenious acid has proved to be the best." Treadwell also recommends it, but different directions are given by these chemists as to the manner of preparing the solutions. Accordingly, both the solutions were made up and tested.

Kolthoff dissolves 4.95 grams of As<sub>2</sub>O<sub>3</sub> in 40 ml. of N caustic soda. Then 39-40 ml. of N HCl are added and the solution is made up to 1 litre. "The solution must react neutral to litmus or at all events not alkaline. A solution thus prepared is stable for a long time," Kolthoff states.

Treadwell dissolves 4.95 grams of As<sub>2</sub>O<sub>3</sub> in the least quantity possible of strong caustic soda, transfers to litre flask, add a few drops of phenolphthalein and then discharge the colour with pure dilute sulphuric acid. Add a solution of 20 grams sodium bicarbonate in 500 ml. water and make up to the 1,000 mark.

Kolthoff's solution is neutral, Treadwell's alkaline to litmus. These solutions were tested by means of the same solutions (0.1 N potassium permanganate and 0.1 N potassium iodate) which were used to examine the thiosulphate. Sodium thiosulphate, however, reacts quantitatively with iodine in acid solutions, but arsenious acid requires a solution neutral to phenolphthalein. The reaction  $As_2O_3 + 2H_2O + 2I_2 \rightleftharpoons 4HI + As_2O_3$  is required and only goes quantitatively from left to right when the HI is continuously removed. This is effected by using sodium bicarbonate (alkaline hydroxides are, of course, excluded as they react with free iodine).

The procedure, therefore, is as follows. Liberate the iodine as described under sodium thiosulphate, neutralise the acid used with sodium carbonate and then add a slight trace of alkali, about 3 grams.

#### Treadwell's Solution.

Standardised with	Nov. 1930.	Apr. 1931.	Aug.	Sept.	Nov. 1931.
0.1 N KMnO <sub>4</sub> .. ..	f = 1.000	f = 1.000	f = 0.996	f = 0.992	f = 0.992
0.1 N KIO <sub>3</sub> .. ..	f = 1.000	f = 1.000	f = 0.996	—	f = 0.992

#### Kolthoff's Solution.

Standardised with	Feb. 1931	Apr.	Aug.	Sept.	Jan. 1932.
0.1 N KMnO <sub>4</sub> .. ..	f = 1.000	f = 1.000	f = 1.000	—	f = 1.000
0.1 N KIO <sub>3</sub> .. ..	f = 1.000	f = 1.000	—	f = 1.000	f = 1.000

It is, therefore, quite clear that Kolthoff's method of making up arsenious acid is superior to Treadwell's, and such a solution as a primary standard for iodine solutions is far superior to sodium thiosulphate.

#### Potassium Dichromate 0.1 N.

This solution, as the authorities say, keeps unchanged. It has, however, the great disadvantage that the end point is not as sharp as that given by permanganate, the colour change being from yellow to green, and, further, an outside indicator has to be used.

#### The Dilute Solutions.

The dilute solutions are of particular interest to the factories because they are used so largely in control work. The literature, so far as could be seen, gave little assistance on their stability. Three solutions were of special interest, and these were the N/32 solutions of potassium permanganate, sodium thiosulphate and arsenious acid. They were prepared, stored and tested in a way similar to those adopted for the N/10 solutions, and it will be seen that only the arsenious acid (Kolthoff's solution) is stable. It is stable for nine months, which is long enough to cover the time of the crop.

	March.	April.	August.	November.
N/32 Potassium permanganate ..	f = 0.995	f = 0.992	f = 0.9908	f = 0.981
N/32 Sodium thiosulphate .. ..	f = 1.000	f = 0.9998	f = 0.993	f = 0.979
N/32 Sodium arsenite .. .. .	f = 0.997	f = 0.997	f = 0.997	f = 0.997

Another solution which kept remarkably well was a standard phosphate such that 1 ml. contained 0.1 mg. of  $P_2O_5$ . The solution was made up in November, 1930, stored in a waxed bottle and used throughout the year. It was tested at regular intervals, and in November, 1931, was found to have kept its value unchanged for a year.

Experiment Station,  
South African Sugar Association,  
Mount Edgecombe.  
March, 1932.

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CHAIRMAN: I am sure you will have here plenty of food for discussion. This has been a very able paper of Dr. Hedley's and I think you can take it as typical of the useful work which the Experiment Station can do for you in the line of Laboratory Practice. We all know what the Experiment Station does for us in the way of producing new canes, but some of us are rather apt to overlook the fact that the Experiment Station has several functions, and this paper is a very good example of the useful work they can do for us. One point Dr. Hedley mentioned and which we ought all to remember, is that information of this sort is of little value if we try to use it under different circumstances. He has given us the keeping qualities of these solutions, kept and preserved in the way they should be. If we make

them up, and keep them in a haphazard manner we must not expect the same results. This is an example again of the point I tried to make in my opening remarks that these papers will be useless to us unless we make use of them, and take the advice which has been given to us.

Mr. BECHARD: I wonder if Dr. Hedley has attempted to keep N/32 thiosulphate by means of chloroform and salicylic acid. That method was given to me by Mr. Viger some years ago and I made use of it. I found the solution kept very well, for the length of time I used it at any rate, from six weeks to two months when I make a fresh solution.

Dr. HEDLEY: I did not use chloroform now because I wanted to see if it would keep under other conditions. I think anything which will keep the air from getting at the thiosulphate, petrol for instance, provided you have boiled your water beforehand thereby killing any germs which might be there, would preserve a thiosulphate solution. Still, although it does keep, I don't think it is anywhere in the same street as arsenious acid.

CHAIRMAN: Since there seems to be no criticism of the paper I think Dr. Hedley can take it he has produced a paper above reproach, and I will ask you to thank Dr. Hedley for the work he has done in presenting this paper. (Applause.)

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