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THE USE OF PICRIC ACID AS AN ARTIFICIAL STANDARD IN THE COLORIMETRIC ESTIMATION OF SILICA

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The determination of small amounts of silica in natural waters has been shown to be of industrial value as well as scientific interest. Diénert[1] has shown the importance of the silica content of ground waters in relation to their origin. In his studies of town water supplies, Thresh[2] noted an inverse relationship between the silica content of the water and the action of dissolved oxygen on lead pipes. The possible biological importance of silica was commented on by Richter,[3] who observed that artificial cultures of marine organisms thrived in glass vessels but that very poor development occurred in paraffined containers.

Atkins[4] investigated the possibility of a lack of silica being a limiting factor in the multiplication of phytoplankton.

Since the gravimetric determination of traces of silica in water is both long and tedious, Diénert and Wandenbulcke[5] proposed a colorimetric method based on the production of a highly colored yellow silico-molybdic acid. When dilute silica solutions are treated with an acid and ammonium molybdate, a color develops which exactly matches that of dilute picric acid solutions. Diénert and Wandenbulcke proposed an artificial standard of 36.9 mg. of picric acid per liter as being equivalent to 50 mg. of silica per liter. The permanence of the picric acid solution renders it a more desirable standard than the relatively unstable silicate solutions which might be used. The procedure consists in adding 2 cc. of a 10% solution of ammonium molybdate and 4 drops of 50% (by volume) sulfuric acid to 50 cc. of solution. The yellow color which develops reaches its maximum in less than ten minutes and remains constant for some time. Appropriate dilutions of the picric acid standard are made and the solutions are compared in a colorimeter or in Hehner tubes.

Atkins[4] followed the above procedure in his studies of the silica content of natural waters and used the 36.9 mg. picric acid standard. Thresh and Beale[6] regard the colorimetric method as being as accurate as the

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[1] F. Diénert, *Compt. rend.*, **155**, 797 (1912).

[2] Thresh, "The Action of Natural Waters on Lead," *Analyst*, **47**, 459, 500 (1922).

[3] O. Richter, *Verh. Gesell. deut. Naturf. Arzte Breslau*, **2**, 249 (1904).

[4] W. R. G. Atkins, *J. Marine Biol. Assocn., United Kingdom*, **13**, 151–159 (1923).

[5] F. Diénert and F. Wandenbulcke, *Compt. rend.*, **175**, 1226–1229 (1923); *Bull. soc. chim.*, **33**, 1131–1140 (1923).

[6] J. C. Thresh and J. F. Beale, "The Examination of Waters and Water Supplies," **1925**, London.

gravimetric, but recommended the use of 40 mg. of picric acid per liter as a standard equal to 50 mg. of silica per liter.

As a result of a series of colorimetric determinations of the silica content of marine waters on the west coast of Canada, in which unusually high values were obtained, the picric acid standards used were suspected of being at fault. This led to a careful comparison of the color intensities given by picric acid and silicate solutions. For this purpose a standard solution was made containing 40 mg. of vacuum dried, C. P., picric acid per liter. This solution was found to have considerably more color than that developed in a solution containing 50 mg. of silica per liter when treated with ammonium molybdate and sulfuric acid.

Standard picric acid solutions containing 40 mg. per liter were prepared from various makes of C. P. picric acid, all of which were dried to constant weight in a vacuum desiccator. Solutions made from picric acid recrystallized from water, from ethyl alcohol and from benzene had the same depth of color as the other standard solutions. This seemed satisfactory evidence that the picric acid solutions used had a definite and constant color value.

Merck's pure silica was dried in a muffle furnace at red heat to constant weight. The material was cooled in a desiccator and weighed rapidly to avoid any possible adsorption of moisture. An excess of anhydrous sodium carbonate (Kahlbaum) was mixed in a platinum crucible with 0.2000 g. of silica and cautiously heated to fusion. The melt was cooled, dissolved in distilled water and made up to 200 cc. Five cc. of this solution when diluted to 100 cc. gave a concentration of silica of 50 mg. per liter. When treated with ammonium molybdate and sulfuric acid, a color was again obtained which was much less intense than that of the 40 mg. picric acid standard.

Pure silica was prepared by treating washed sea sand with calcium fluoride and concentrated sulfuric acid. The silicon tetrafluoride which was produced was passed into distilled water and the hydrated silica formed by hydrolysis was collected on a filter, washed and dehydrated in a muffle furnace. A silicate solution made from this material developed the same intensity of color as the former solution.

The color values of these silicate solutions when read against the 40 mg. picric acid standard in a Duboscq colorimeter are given in the accompanying table.

TABLE I

COLOR VALUES OF 50MG. SILICATE SOLUTIONS AGAINST 40MG. PICRIC ACID STANDARD

	Silicate solns. prepared from	Reading of test, mm.	Reading of standard, mm.
(1)	Commercial silica dust	10.0	6.3
(2)	Powdered quartz	10.0	6.3
(3)	Commercial silica dust	10.0	6.4
(4)	Merck's pure silica	10.0	6.4
(5)	Silica from silicon tetrafluoride	10.0	6.4

A stock solution (containing approximately 1 mg. of silica per cc.) made from Baker's C. P. $Na_2SiO_3 \cdot 9H_2O$ was tested colorimetrically. Five cc. of this solution, diluted to 100 cc., when treated with acid and molybdate developed a color of such intensity that with the test set at 10.0 mm. the standard read 6.0 mm.

Two hundred-cc. portions of the stock solution were analyzed gravimetrically with the following results: silica from 200 cc. of stock solution, (1), 0.1874 g.; (2), 0.1867 g.

Since by analysis the stock solution was only 93.6% of its stated concentration, the dilute solution prepared from it was also under strength to the same degree. Consequently, a solution containing 50 mg. of silica per liter when set at 10.0 in the colorimeter would give a standard reading of 6.0 mm. × 100/93.6 = 6.4 mm.

From the foregoing figures it would appear that a picric acid solution, to show equal color to that given by a 50 mg. per liter silica solution treated with the reagents, should contain 0.64 × 40 = 25.6 mg. of picric acid per liter. A solution of this concentration was prepared and found to have the same intensity of color as that given by the silica solution when matched in a Duboscq colorimeter or in Hehner tubes.

It was thought that the discrepancy between our results and those of other workers might lie in their having used commercial picric acids. Since considerable amounts of water are added to picric acid by the manufacturers to eliminate the possibility of explosion in transit, care must be taken to dry the material thoroughly before attempting to use it in quantitative work. Possibly the earlier workers neglected to take this precaution. To test this point crystals were taken from the top of a freshly opened bottle of Baker's picric acid. A solution of the proper color value required 36 mg. per liter of these crystals, but when dried to constant weight in a vacuum desiccator over calcium chloride only 26 mg. per liter was necessary. Samples of picric acid from different bottles had widely varying moisture contents and even in the same bottle the moisture content at different levels varied considerably. While most reputable brands of picric acid when dried to constant weight give solutions of maximum color value, recrystallization from benzene according to the method of Benedict[7] may be resorted to if the purity of the sample is in doubt.

Summary

The intensity of the yellow color given by a silicate solution containing 50 mg. of silica per liter when treated with the reagents of Diénert and Wandenbulcke is equivalent to that of a solution of picric acid containing 25.6 mg. of vacuum-dried, c. p. picric acid per liter.

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[7] S. R. Benedict, *J. Biol. Chem.*, **54**, 239–241 (1922).