# THE ACTINIC METHOD FOR THE DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.

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Since the original publication of this method in the *Philosophical Magazine* for July, 1883, I have been frequently asked to publish further details in addition to the brief description there given, and to give some account of the results obtained by the continued use of the method. The latter will be found in the Reports to the Newark Aqueduct Board and the Water Departments of Philadelphia for the years 1883, 1884 and 1885. And since the determinations already published are very numerous, and can be studied to greater advantage in connection with the other analytical data than they can when taken by themselves, I shall refer the reader to these publications, and shall give here only a few examples as illustrative of the method.

Neutral argentic nitrate has been found to be the reagent best adapted to the purpose, and the addition of 5 c.c. of a 5 p. c. solution of this salt to 250 c.c. of the water under examination, has been found, in all cases thus far encountered, to leave an excess of the undecomposed nitrate. The water is exposed to the direct sunlight at a window with a Southern exposure, and left there until no further precipitation of reduced silver takes place. In case much chlorine is present a white turbidity may ensue immediately, but usually the water passes through many tints of color, and the reduction may be complete within 12 hours or may require 5 days. In case the reduction is accompanied by the development of a dark red color, it is slow and requires the maximum duration of exposure. I have found that tall, narrow glass stoppered half-liter bottles of white glass are sufficiently well adapted to the purpose. Stoppered comparison tubes of 2 feet in length would serve still better. The end of the reaction is known with certainty when the water clears up and becomes brilliantly pellucid, suspended matter of every kind having been precipitated to the bottom along with the finely divided silver.

The definiteness of the end-reaction is one of the most satisfactory features of the process; no further precipitation occurring after this clarification has once occurred, and the amounts of

precipitated silver obtained in duplicate analyses of the same sample of water being identical.

The water may then be syphoned off, the precipitate thrown on an asbestos filter, similar to those used in the determination of carbon in steel, washed first with water, then with strong ammonia to dissolve co-precipitated chloride, dissolved in nitric acid, the acid neutralized with excess of calcium carbonate, and the silver determined by Pisani's method. All these washings are but the work of a few minutes with the aid of a water pump. In the first determinations made by this process the metallic silver was weighed directly, but the process outlined above is equally accurate and much more rapid.

The objections against the use of the permanganate method are manifold :

1st. Both the permanganate solution and the oxalic acid used to standardize it are not permanent, and must be freshly standardized in order that one may feel certainty as to results when these solutions have stood (especially if the oxalic acid be exposed to sunlight) for a short interval.

2d. The end-reaction varies enormously, according to the conditions under which the titration is performed. If conducted at the boiling point the results are altogether different from those obtained when working at some lower temperature. At any temperature the results obtained are different according as the action of the permanganate are prolonged through 5 minutes, 15 minutes, 1 hour, 3 hours, or a day.

3d. If the operation is carried on at the boiling point the results will differ if the flask be plunged in boiling water or heated over a Bunsen burner. In the first case, using an Eilenmeyer flask of 300 c.c. capacity, and holding 100 c.c. of the water, the contents of the flask, the mouth being left open, reach a maximum temperature of 98.5°–99° in 6–7 minutes. If the flask be held in this position for 5 minutes the results are quite different from those obtained when the flask is placed over a naked flame, and after the boiling point is reached kept there for 5 minutes. And if the boiling over the lamp be prolonged 5, 10 or 15 minutes, the results vary not only for each duration of boiling, but according as the ebullition is gentle or energetic.

From objections of the above nature the actinic method is free. The neutral argentic nitrate solution, if prepared with pure distilled water free from organic matter, keeps for years without change. It is not a standardized solution, and is added always in excess. The amount of silver finally precipitated is independent of the ordinary atmospheric ranges of temperature, and of the actinic intensity of the light during the interval of exposure.

The objections against the actinic method are that sulphites, thiosulphates, sulphides and protosalts are capable of oxidation and reduce the silver. This objection is valid, but it is to be observed in the first place that these bodies are themselves usually formed by a process of reduction, and indicate a corresponding amount of organic matter originally present; and, in the second place, permanganate is quite as much affected by the same disturbing factors.

Again, it is urged that no one knows precisely what fraction and what kinds of organic matter are oxidized by this actinic method. But neither can this question be satisfactorily answered in regard to the permanganate, whatever may be the temperature or the interval of time at which its use is conducted.

Both observation and experiment appear to indicate that while there is a general similarity between the results obtained by the permanganate at the boiling point and those by the actinic method, the latter affords a more trustworthy index of the amount of readily decomposable and putrescible organic matters.

To illustrate this point I may quote from many similar ones, the analyses of two samples of the Schuylkill river, the first taken from Phœnixville at a point above where sewers enter the river, the second taken at Spring Garden, which is below the sewers of a town of 7,000 inhabitants.

| | I. Without Sewage. | II. With Sewage. |
|---|---|---|
| | Parts per 100,000. | |
| Albuminoid Ammonia | 0.0075 | 0.0105 |
| Oxygen required [Permanganate] | 0.11 | 0.15 |
| " " [Silver] | 0.19 | 0.35 |
| Nitrous Acid | 0.0001 | 0.00015 |

Etc., etc.

| | I. Without Sewage. | II. With Sewage. |
|---|---|---|
| | Parts per 100,000. | |
| Albuminoid Ammonia | 0.009 | 0.017 |
| Oxygen required [Permanganate] | 0.11 | 0.185 |
| " " [Silver] | 0.187 | 0.385 |

Etc., etc.