

The theory of Berzelius, however, of the formation of basic salts of chromium which would naturally be green and uncrystallizable, offers a full and sufficient explanation of the changes, and is in accord with the observations so far as they have been verified by us. It accounts quite plausibly for the partial withholding of the sulphuric acid from precipitation by barium chloride in the cold, and is strongly confirmed by the experiments with alcohol. This theory is also in accord with the facts that the green coloration may be brought about by the addition of alkaline substances, and that it is retarded by the addition of sulphuric or nitric acid. It is also easy to apply this explanation to the cases of the nitrate, chloride, acetate, and other soluble compounds of chromium. When we have opportunity we propose examining the action of alcohol upon these other compounds.

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## A METHOD FOR THE DIFFERENTIATION OF ORGANIC MATTER IN WATER.

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AT present one of the least satisfactory determinations made in the usual course of a sanitary water analysis is that of the so-called "oxygen-consumed" or carbonaceous matter. Various methods have been proposed for estimating the organic matter in water to replace the difficult and tedious combustion process of Frankland. Probably the one most generally used is some modification of the Forchammer potassium permanganate process. The objections to this process may be briefly summarized as follows: (1) The results obtained by means of it are only comparative and do not indicate in any degree the absolute amount of carbonaceous matter present; (2) these comparative results are of value only when the organic matter in the various samples compared is practically identical in composition. As a matter of fact, this latter condition is one that is very seldom realized in natural waters from different sources. The readiness with which the organic matter is oxidized by potassium permanganate varies not only with its character and the conditions under which it is found in the water, but also with the manner in which the determination is conducted.

The fact that by means of the Forchhammer process as ordinarily carried out we are unable to distinguish the character of the organic matter contained in water, has been recognized by nearly all chemists who are authorities upon the subject of water analysis. Frankland<sup>1</sup> says in regard to this: "Reliance ought not to be placed on the Forchhammer process, for the action of the permanganate of potash test is not only liable to considerable uncertainty, but it makes no distinction between nitrogenous and non-nitrogenous organic matter, and may even confuse innocent inorganic substances with organic matters of most objectionable origin." It is true that methods have been proposed by which this distinction may be more or less satisfactorily made, but most of those which do not require an excessive amount of time and care in manipulation are matters of judgment rather than of determination. Dr. Tidy, for example, proposes to judge the character of the organic matter by an examination of the "tint and tint depth" of the water through a two-foot tube. Considerable work has been done in this laboratory and elsewhere in order to replace the potassium permanganate by chromic acid, but it was always found that the oxidation was still incomplete.

A method for distinguishing the different kinds of organic matter by the use of chromic acid in comparison with potassium permanganate has quite recently been proposed by Joseph Barnes.<sup>2</sup> He expresses the results in the form of a ratio between the oxygen consumed from permanganate and that taken from chromic acid. The results obtained show that solutions of starch and of sugar are acted upon by chromic acid to a much greater degree than by permanganate, thus giving a very low ratio. Gelatin and glycerol in dilute solutions are likewise found to give a fairly low ratio. The highest ratios were given by infusions of peat and of tannic acid. In this work the method suggested by Barnes has been applied to the determination of organic matter in water.

The method used, while essentially that of Barnes, differs from it in some important particulars, and will be described in considerable detail because the results obtained depend largely

<sup>1</sup> *Water Analysis*, 1890.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1896, 83.

upon the method of procedure that is adopted. A determination of the carbonaceous matter is first made with potassium permanganate according to Kubel's hot acid method as follows: To a measured quantity of the water, usually 100 cc., placed in a 250 cc. flask, are added eight cc. of sulphuric acid (1 : 3), and then about ten cc. of  $\frac{N}{100}$  potassium permanganate, or more if the water is highly colored, are added from a burette. The solution is heated to boiling and boiled for exactly five minutes, allowed to cool for one minute, and the pink color is then discharged by ten cc. of  $\frac{N}{100}$  oxalic acid. It is then titrated with the  $\frac{N}{100}$  permanganate to the usual faint pink color. In order to apply the chromic acid method, the following special solutions are required: (a) six and two-tenths grams of potassium bichromate are dissolved in distilled water, fifty cc. of concentrated sulphuric acid added, and the solution is made up to one liter; (b) eighteen grams of crystallized ferrous sulphate are dissolved in a mixture of 100 cc. concentrated sulphuric acid and 200 cc. water. When cool the solution is diluted to 500 cc. This solution will not keep for more than two or three weeks. Fifty cc. of the water under examination are placed in a 250 cc. flask and twenty cc. of pure sulphuric acid (sp. gr. 1.84) are added. Exactly ten cc. of the above chromic acid solution are added, the flask shaken, and heated on a boiling water-bath for one hour, being kept covered by a watch-glass. It is then removed from the bath and allowed to cool for a few minutes; ten cc. of the ferrous sulphate are added, the solution poured into 500 cc. cold distilled water, and titrated with  $\frac{N}{100}$  permanganate until the edges of the solution are a faint pink. A blank determination must always be made at the same time, using fifty cc. of water free from organic matter. If the same  $\frac{N}{100}$  solution of potassium permanganate is used in both methods, the results are at once expressed in the form of an "oxygen ratio" by dividing the number of cubic centimeters used in the Kubel method by the number of cubic centimeters required for an equal amount of the water by the chromic acid method. This ratio in general assumes the form of a fraction less than unity.

In this investigation the method as thus outlined has been applied to natural waters which give high "oxygen-consumed," but are known to be free from sewage pollution, some of them

being used as public supplies, and to filtered city sewage in various degrees of dilution. The results obtained on these "peaty waters" are tabulated below. The "ratio" is obtained in the form of a fraction as mentioned above; the colors given are based on Professor Leeds' nesslerized ammonia scale.

	Color.	Ratio.
Boston tap water (July 24, 1897) .....	0.3	0.656
" " " (Jan. 24, 1898) .....	0.7	0.646
" " " (Mar. 11, 1898).....	0.48	0.649
Color standard ( <i>a</i> ).....	5.00	0.833
Color standard ( <i>b</i> ).....	1.8	0.689
Reservoir, Orange, Mass.....	0.58	0.659
" Athol, " (full of algae).....	.....	1.132
" " " (filtered).....	1.7	0.750
Infusion of dried leaves .....	about 10.0	0.656
Solution of humus in ammonia .....	.....	0.692

The Boston tap water is a typical brown surface water. The color standards are very dark-colored swamp waters of different dilutions. The waters from Orange and from Athol were surface waters which contained so great a growth of algae, especially *Anabaena*, as to be colored distinctly green, and gave extremely high "oxygen-consumed" and albuminoid ammonia. The leaf infusion was made by treating the dried leaves with cold distilled water, the first portion, containing the sugary extract, being rejected. It had been standing about ten months.

The ratios obtained with sewage, as shown in the following table, are about the same as given by Barnes for nitrogenous substances.

	Ratio.
Sewage from Marlboro (filtered, old) .....	0.543
" " Boston (decanted, fresh).....	0.389
( <i>a</i> ) Filtered sewage, Hereford St., Boston ....	0.470
( <i>b</i> ) Sewage ( <i>a</i> ) diluted five times with distilled water .....	0.490
( <i>c</i> ) " ( <i>a</i> ) " ten " " " " " " .....	0.460
Well contaminated with sewage.....	0.449

Two things are evident from the results shown in the foregoing tables. First, the peaty waters give a ratio above 0.600; the sewage and sewage-contaminated waters give a ratio below 0.600, this apparently being the dividing line between the ratios of animal and vegetable matter. Second, the ratio for a given water is practically constant if the character of the organic

matter present does not undergo material change, no matter how much the amount present may vary. The results with Boston tap water at intervals of several months and with differing dilutions of the same sewage show this. In order to further test this, and to see if it were really possible to differentiate the organic matter in water by this means, the following experiment was made. Two samples of water were prepared, one of which (*a*) was known to be free from sewage but contained considerable coloring-matter of vegetable origin; the other (*b*) was distilled water containing a definite quantity of sewage. These gave the same amount of oxygen consumed by the permanganate process, (*a*) = 0.2387 and (*b*) = 0.2375 parts per 100,000. The ratios, however, differed widely, (*a*) = 0.827, and (*b*) = 0.372. The method was also tried on a sample of well water which gave by the permanganate test more oxygen consumed than was warranted by its color. The question to be decided was whether the organic matter was due to sewage or to the infiltration of surface water carrying vegetable substances. The ratio obtained was high, 0.957, indicating that surface water was the cause. This was confirmed later by an examination of the well. These results certainly show that the method is quite promising and deserves further study by those chemists who are especially interested in the question of sanitary water analysis.

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## AN EFFICIENT GAS-PRESSURE REGULATOR.

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IT is well known that the various types of mercury thermometers cannot cope with marked changes in the gas pressure, and for this reason it is almost impossible to maintain a constant temperature for a considerable length of time with any degree of certainty. Numerous contrivances for regulating the pressure have been proposed at various times, and several are to be had from the principal dealers, but they either fail entirely in their purpose, or are impracticable for general use owing to cost, difficulties of construction, etc. The apparatus of Moitessier, as catalogued in this country and Europe, appears