Proceedings of the Iowa Academy of Science

Volume 8 | Annual Issue Article 12

1900

The Influence of Chlorine as Chlorides in the Determination of Oxygen Consumed in the Analysis of Water

J. B. Weems

J. C. Brown

THE INFLUENCE OF CHLORINE AS CHLORIDES IN THE DETERMINATION OF OXYGEN CONSUMED IN THE ANALYSIS OF WATER.

J. B. WEEMS. J. C. BROWN.

One of the most valuable determinations in the analysis of water and sewage is the determination of the oxygen consumed. In the deep well waters of the state, the amount of chlorine in the form of chlorides in many cases is very high, as may be seen by the investigations of the Geological Survey,* on the artesian waters.

In this investigation it was found that chlorides were present in the following amounts, as shown in the analysis of water from the places named:

McGregor	967.	parts	per	million.
Manchester	80.	"	"	"
Boone	152.	"	"	"
Davenport	273.	"	"	"
Centerville	388.	"	"	"

The selections made contain large amounts of chlorine as chlorides, and while there are many other waters which contain only small quantities of chlorides, it is readily seen that the deep well waters vary between wide limits in the amounts of this substance present in them. It may be said in a general sense, that the amount of chlorine found in the analysis of the deep well waters of the state varies from a small quantity to 1000 parts of chlorine as chlorides per million.

It has been recognized for some years that the presence of chlorine in combinations in the form of chlorides has a certain effect upon potassium permanganate when boiled in the presence of sulphuric acid; and the problem which naturally presents itself is, to what extent is the

* Iowa Geological Survey, Vol. 6.

permanganate solution effected by the presence of a certain amount of sodium chloride in the water with which it is desired to make the determination of oxygen consumed.

The next considertion given was that of selecting the methods which are in general use for the determination of the oxygen consumed. As a result of an investigation of the literature on the subject it may be said that the four following methods are those which are most generally used:

I. KUBEL METHOD.* 100 c.c. of the solution is taken and placed in a flask; 5 c.c. of sulphuric acid (dilute 1.3) is added with a quantity of standard potassium permanganate solution. The contents of the flask are boiled for five minutes; then 10 c.c. of standard oxalic acid solution is added and the solution titrated to color with standard permanganate.

II. SCHULZE METHOD. 100 c.c. of the sample is taken and placed in a flask to which there is added 1-2 c.c. of sodium hydrate (one part of sodium hydrate to two parts of water) and a quantity of standard potassium permanganate which will insure a permanent color to the solution. The contents of the flask are boiled for ten minutes, allowed to cool to a temperature of 50-60°, and 5 c.c. of dilute sulphuric acid is added; 10 c.c. of standard oxalic acid is then placed in the flask and the contents titrated with standard potassium permanganate.

The permanganate solution used in both the Kubel and Schulze methods is a 1-100 normal.

III. THE ASSOCIATION METHOD† as recommended by the chemical section of the American Association for the advancement of science.

To 200 c.c. of the water to be examined in a 400 c.c. flask, add 10 c.c. of dilute sulphuric acid (1.3) and such measured quantity of the permanganate as will give a persistent color; boil ten minutes; add, if necessary, more permanganate in measured quantities so as to maintain the red

* Konig, Landwirstschafttiche und gewerblichewichtiger Stoffer. 2nd auf. p. 607.
† Leffmann & Beam, Examination of Water, p. 41.

color; remove the flask from the lamp, add 10 c.c. of oxalic acid solution to destroy the color, or more if required by the excess of permanganate, and then add permanganate, drop by drop, till a faint pink tint appears. From the total quantity of permanganate used deduct the equivalent of the oxalic acid used, and from the remainder calculate the milligrams of oxygen consumed by the oxidizable organic matter in the water.

IV. THE ENGLISH METHOD.* This method is the one generally used in England by the Society of Public Analysts.

"Two determinations are made, the amount of oxygen absorbed during fifteen minutes and that absorbed during four hours; both are to be made at a temperature of 80°F. It is most convenient to make these determinations in 12oz. stoppered bottles, which have been rinsed with sulphuric acid then with water. Put 250 c.c. or 3,500 grains in each bottle, which must be stoppered and immersed in a water bath or air bath until the temperature rises to 80°F. Now add to each bottle 10 c c. or 100 grains of the dilute sulphuric acid, and then 10 c.c. or 100 grains of the standard potassium permanganate solution. Fifteen minutes after the addition of the permanganate, one of the bottles must be removed from the bath and two or three drops of the solution of potassium iodide added to remove the pink color. After thorough admixture, run from a burette the standard solution of sodium hyposulphite until the blue color is just discharged. If the titration has been properly conducted, the addition of one drop of the solution of potassium permanganate will restore the blue color. At the end of four hours remove the other bottle, add potassium iodide, and titrate with sodium hyposulphite as just described. Should the pink color of the water in the bottle diminish rapidly during the four hours, further measured quantities of the standard solution of potassium permanganate must be added from time to time so as to keep it markedly pink."

It will be noticed that the method of the Association is very similar to the Kubel method and only differs from it in using double the quantity of water and reagents in the determination, and boiling for ten minutes.

It would naturally be expected that the results from an investigation of these methods, that the action of the chlorine as chlorides would be very little if any in the Schulze and English methods, for in the first there is an alkaline condition present and in the second the temperature is so low that it is only slightly above ordinary temperature.

*Analyst. 1881, p. 136; also Leffmann & Beam, Examination of Water, p. 39.

In the Kubel and Association methods, however, a reaction would be expected and the permanganate acted upon to a certain extent. As the results from the investigation of these two methods were the same the following table will give the amount of permanganate decomposed for both methods in terms of oxygen consumed.

Parts per million of chlorine as sodium chloride in sample.	Oxygen consumed in parts per million.
5	.03
10	.08
15	.10
20	.13
25	.15
50	.18
100	.23
200	.28
300	.33
400	.38
500	.48
600	.63
700	.72
800	.80
900	.83
1000	.98
1100	1.08
1200	1.24
1400	1.44
1600	1.56
1800	1.68

From these results it is seen that in waters that contain large quantities of chlorides, it is well to give consideration to the action due to the presence of chlorides on the permanganate solution where the Kubel or the Association method is used, for the determination of oxygen consumed.