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MANGANESE IN IOWA CITY WATERS

EDWARD BARTOW AND W. T. BAILEY

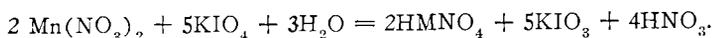
More than thirty years ago Proskauer reported the presence of manganese in many ground waters. For a long time afterward little attention was paid to the subject because it had not been proved that manganese imparted any bad qualities to water. But in 1906, the sudden appearance of iron and manganese in the Breslau water supply (1) in such quantities as to cause it to be abandoned, forced the recognition of the fact that iron and manganese produce like qualities in water. The first water in this country in which manganese occurred in sufficient quantity to cause trouble was from a well supplying a New England mill in 1898. The supply was abandoned. However water supplies containing manganese were regarded as uncommon in the United States previous to 1911, when the attention of the Illinois State Water Survey was called to a serious incrustation which had formed in the city water system of Mount Vernon, Illinois. (2) An analysis showed this to contain 4.4 to 8.8% and the original water to contain 0.6 ppm. manganese. Even at the present time manganese is seldom considered in the selection of a supply.

Manganese in a water supply is objectionable because it deposits a dark incrustation, which is sometimes so extensive as to cause complete stoppage in water pipes. The separation of the dioxide stains plumbing fixtures a dark color, and if a water containing manganese is used for laundry, it stains clothes yellow or brown. It is in these respects that waters containing manganese resemble those containing iron, but the deposits are darker, and more difficult to remove than those produced by waters containing iron.

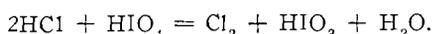
The present investigation was suggested by the finding of a deposit in the water pipes from University of Iowa well No. 2, which is located at the laundry. This deposit showed quantities of MnO_2 as indicated by the evolution of chlorine from HCl. The purpose of the investigation was to determine, if possible, whether or not the manganese occurred in any definite strata, and whether or not it could be eliminated from wells by casing out manganese-bearing waters.

The quantitative methods for determining manganese when present in small quantities are based on the color of the permanganate ion, and are made by the oxidation of the manganous salts as they occur in the water. This was first suggested by W. Crum (3) but P. Pichard (4) was the first to work out the details

for a complete method. The fact that ammonium persulfate oxidizes manganous salts in the presence of silver nitrate was discovered by Marshall (5) about 1901, and was used as a quantitative method for the determination of manganese in iron and steel. In 1915, Corson and Bartow (6) made a comparative study of the quantitative determination of manganese by oxidation with lead peroxide, sodium bismuthate, and ammonium persulfate, and recommended that Standard Methods adopt the persulfate and bismuthate methods. These methods were adopted by Standard Methods and have been generally used. In 1917 H. H. Willard and L. H. Greathouse (7) made a study of the reactions between periodate and salts of manganese,



It was found that if sufficient acid were present, the permanganate ion was always formed, even when considerable amounts of manganese were present. The reliability of this reaction led to the adoption of it for the determination of manganese in iron and steel, and a comparison with the persulfate and bismuthate methods showed slightly better results in quantitative determinations. The chief advantage of the method is the ease with which small amounts of chloride may be removed from solutions containing chlorides by the oxidation of HCl by the periodate.



Since this eliminates the necessity for the removal of chloride by precipitation with silver nitrate and filtration, which is necessary for the persulfate method, and the repeated evaporations in the bismuthate method, we adopted this method for our work. A true permanganate color was always obtained which did not disappear on standing if sufficiently acidic and slight excess periodate were used.

Samples containing known amounts of manganese were prepared for us by W. L. Denman and results were obtained as follows:

TABLE I. MILLIGRAMS MANGANESE PER LITER

THEORETICAL CONTENT	DETERMINED	EXCESS OF DETERMINED OVER THEORETICAL CONTENT
0.40	0.385	- 0.015
0.40	0.390	- 0.010
0.11	0.120	+ 0.010
0.11	0.115	+ 0.005

A comparison with the sodium bismuthate method was also made, using actual samples of water containing manganese, with results as shown in Table II.

TABLE II. MILLIGRAMS MANGANESE PER LITER

PERIODATE	SODIUM BISMUTHATE
0.8	0.8
0.48	0.48
0.55	0.58
0.20	0.190

Method of analysis. 200 cc. of each sample was concentrated to about 10 cc.; after acidifying with 5 cc. concentrated HNO₃, free from oxides of nitrogen. 5 cc. sirupy phosphoric acid, to prevent iron color interfering, and 5 cc. of concentrated nitric acid were added and the solution boiled a few minutes in an erlenmeyer flask. Then about 0.3 gram KIO₄ was added, and the solution boiled until the maximum color appeared, which usually required but a few minutes. The solution was then cooled, placed in a Nessler jar, diluted to 50 cc. and compared with tubes containing a known amount of permanganate which had been prepared by treating standard solution in the same way. The standard solution was prepared by titrating pure sodium oxalate with permanganate solution until a faint pink color remained, and was allowed to stand until this color disappeared, and was then oxidized with KIO₄ in the same way as the sample. This standard solution when so treated will retain its color two or three months if sufficiently acidic and a slight excess of periodate is used.

Samples from about fifty wells in Iowa City and the immediate vicinity were analyzed and practically all were found to contain small amounts of manganese.

TABLE III. WELLS ENTERING LIMESTONE

LOCATION	DEPTH	PARTS PER MILLION			
		MANGANESE (Mn)	IRON (Fe)	CHLORIDES	ALKALINITY
S. U. I. No. 1	200'	0.04	0.1	8	446
S. U. I. No. 2	150'	0.48	0.2	8	331
S. U. I. No. 3	400'	0.04	0.1	7	311
Jefferson Hotel	185'	0.15	0.2	10	330
Teeters'	180'	0.08	0.1	8	385

The three university wells, the well at the Englert Ice Plant, the one at the Jefferson Hotel, and the one at Dean Teeters' home are all drilled wells extending some depth into the underlying limestone, and located only a few blocks apart. Two of the S. U. I. wells show .04 ppm. manganese, the one at the Teeters' residence

.08 ppm., the Jefferson Hotel well and the Englert well 0.14 and 0.15 ppm., while the other university well shows 0.48 ppm., or more than three times as much manganese as the Englert well and twelve times as much as the other two University wells.

TABLE IV. WELLS IN GLACIAL DRIFT LOCATED IN EAST IOWA CITY

DEPTH	PARTS PER MILLION			
	MANGANESE (MN)	IRON (FE)	CHLORIDES	ALKALINITY
85'	0.13	6.0	10	245
62'	0.18	1.2	7	260
56'	0.15	2.4	9	220
60'	0.15	4.0	14	245
60'	0.25	1.4	4	250

The next five wells located on the lower Muscatine road are only about one hundred yards or so apart, and all are in the glacial drift. With one exception the manganese content is very nearly the same. This well contains 0.25 ppm., whereas the others contain .13 to .18 ppm. Since these waters come from the same source, the glacial drift, this would be an indication that manganous salts were present in greater quantities near this particular well. The fact that the iron content of these wells varies from 1.4 ppm. to 6.0 ppm. would also indicate that the distribution of metallic salts in the soil was not uniform.

Analyses of samples from dug wells from 28' to 45' showed no manganese. In such wells manganese, if present, would be subjected to oxidation and would be precipitated as manganese dioxide.

TABLE V. ALLUVIAL DRIFT AND RIVER

SOURCE	PARTS PER MILLION MANGANESE (MN)
Infiltration gallery	1.8
Low lift pump	1.6
Entrance to mains	0.8
River	0.2

The water supply of the city water company was next analyzed. This supply is taken partly from an infiltration gallery along the river, partly from ten flowing wells 150' deep, and the rest from the river. The infiltration gallery showed a content of 1.8 ppm. manganese, the river 0.2 ppm., but no sample could be secured from the wells.

The fact that wells located in the glacial drift contain a fairly large amount of manganese together with the extremely large amount found in the infiltration gallery would indicate that the

manganese occurs largely in glacial and alluvial drifts. H. P. Corson (6) found not more than 0.08 parts per million manganese in wells entering limestone in Illinois. The presence of fairly large amounts of manganese in such wells in Iowa City might be explained by the fact that the limestone is not solid, but contains many large crevices through which soil waters may be carried into wells.

Our results indicate that manganese may be concentrated in pockets, as is true of iron, and that it would be impossible to predict where a well might be located to secure a water free from manganese except perhaps in deep wells in rock. Inasmuch as five wells penetrating limestone to depths of from 180' to 400' show less than 0.1 ppm., it might be possible to prevent manganese-bearing waters from entering such a well by having a good junction of the casing to shut out the waters from the drift.

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