

Determination of Manganese in Natural Waters

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The heretofore used methods for quantitative determination of manganese in natural waters, especially sea water, are rather slow and complicated. Therefore Prof. Kurt Buch requested the author to investigate these methods, and thus a simple analytical procedure on the basis of two works, the one by Thompson and Wilson¹ and the other by Tschuiko² has been worked out.

In natural waters manganese occurs with the valencies 2, 3 and 4. Septe-valent manganese is always reduced to a lower valency. The compounds of manganese principally form oxides, insoluble in water, wherefore they must be precipitated together with a collector. The divalent manganese salts are soluble in water but are converted into an insoluble form when the pH-value of the water is raised to about 12. Manganese hydroxide $\text{Mn}(\text{OH})_2$ is formed and this is then converted, under the influence of the oxygen dissolved in the water, into insoluble $\text{MnO}(\text{OH})_2$. At this pH-value Tschuiko uses magnesium sulfate as coagulating agent. As far as sea water is concerned the question of coagulating agent is simple, for sea salts contain so much magnesium ($\text{Mg}:\text{Cl} = 0.067$) that even such a very low salinity as 2.46 ‰ gives the necessary number of Mg-ions. Thus, the pH of the water need only be raised to 12 to bring about coagulation and to effect complete precipitation of $\text{Mn}(\text{OH})_2$.

The manganese removed from the initial volume of water concentrates in the hydroxide precipitate which, after decantation of the unnecessary supernatant liquid is dissolved in sulfuric acid and then oxidated to permanganate. Tschuiko uses the reaction of Marshall³ with alkali persulfates as oxidant in the presence of silver ions, while Thompson and Wilson use alkali periodates. In accordance with the latter alkali periodates have also been used in this research for they give a much clearer and steadier colour, than that obtained with persulfates.

The silver nitrate which has a catalytic effect in Marshall's reaction is not without importance when oxidating with alkali periodates. In the presence of silver ions the oxidation to permanganate proceeds faster than without them and even small amounts of periodates can be used. A great excess of silver nitrate, 10 ml of a 0.2 *N* solution, does not disturb the reaction, but the case is quite reverse when alkali persulfate is used as oxidant, which fact is of importance in the elimination of halide ions present, and to which reference will be made below.

A condition for oxidation to the permanganate stage is that two constituents of sea water, the halide ions and the organic matter, must be eliminated, but fortunately only the former are always present and can be removed in two ways:

1. By precipitating as silver haloides.
2. By evaporating and igniting the hydroxide precipitate dissolved in sulfuric acid.

This last mentioned method is used only when organic matter is present in great amounts and is evinced by the yellow colour of the sulfuric acid wherein the hydroxide precipitate is dissolved.

In order to check the utility of this method varying quantities of manganese, 0.001—0.01 mg were added to one liter of distilled water, which was subsequently made alkalic and then coagulated with magnesium sulfate. The precipitate was dissolved in sulfuric acid after which oxidation to permanganate took place. By comparing the results with a series of colour standards in 50 ml Nessler tubes it was found that exactly the same quantities of manganese were recovered as had been added. The method was further tested by using in stead of distilled water, sea water, freed of its eventual manganese content by coagulating with alkali and removing the precipitate as mentioned above. In this way it is possible to detect variations of 0.001 mg of manganese in a liter of sea water.

PREPARATION OF REAGENTS

- (a) *Sodium paraperiodate* is prepared by the method of Wells⁴.
- (b) *Sulfuric acid*. — Test the acid for manganese in the way suggested by Thompson and Wilson. Dilute one part of the concentrated acid with two parts of distilled water and add sodium paraperiodate so that 10 ml contains 150 mg.
- (c) *Potassium hydroxide*. — Guaranteed reagent from E. Merck shows free from manganese. Use a 0.2 *N* solution.
- (d) *Silver nitrate*. — Use a 2 *N* and a 0.2 *N* solution. To test the silver nitrate for manganese add to 10 ml of a 2 *N* solution a solution of 1.1 g sodium chloride, which has been recrystallized from water. Filter the silver chloride off and determine the manganese in the filtrate in the usual way.

(e) *Magnesium sulfate*. — Kahlbaum z. Analyse shows free from manganese. Dissolve 22.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 250 ml distilled water. 10 ml contains 90 mg Mg.

(f) *Standard permanganate solution*. — Dissolve 57.539 mg of recrystallized potassium permanganate in water add 1 ml of 2 N sulfuric acid and reduce by the addition of 0.15 g sodium bisulfite. Boil the solution until free of sulfur dioxide, cool and dilute to exactly 200 ml. Dilute 1 ml of this solution containing 0.1 mg of manganese to 60 ml and heat to boiling together with 10 ml sulfuric acid reagent and 2 ml of 0.2 N silver nitrate solution. Add 50 mg sodium paraperiodate and place in a water-bath for half an hour, cool, and dilute to exactly 100 ml. This standard solution which should be kept from contact with direct sunlight contains 0.001 mg of manganese per ml.

A liter sample of sea water to be analyzed is poured into a 1 000 ml graduated glass. Add 50 ml of 0.2 N potassium hydroxid solution while mixing well and let the now formed precipitate settle for at least 12 hours. Remove the completely clear supernatant liquid with a siphon and dissolve the precipitate in 1.5 ml of concentrated sulfuric acid. The continuation of the analysis depends on whether organic matter is present or not.

1. If the solution is colourless precipitate the halide ions with 2 N silver nitrate solution. According to this procedure a too great excess of the latter must be avoided. Filter the silver halide through a porcelain filter, Jena 3G4. Heat the filtrate to boiling with 10 ml of sulfuric acid reagent, add 50 mg of sodium paraperiodate, place in a water-bath for half an hour and cool. The total volume should now be 50 ml at the most and is transferred to a 50 ml Nessler tube and compared with a series of colour standards.

2. If organic matter is present, transfer the hydroxide precipitate dissolved in sulfuric acid into a platinum dish and heat the contents carefully until the excess sulfuric acid is expelled and the salts are fused. Raise the temperature and heat the fused salts for a few minutes over a Bunsen burner. Cool the mass, dissolve it in 10 ml of sulfuric acid reagent, heat to boiling, cool again and filter through a porcelain filter, Jena 3G4. Dilute the filtrate to about 75 ml add 2 ml of 0.2 N silver nitrate solution and treat further as described under 1.

Samples of surface sea water collected from various parts of the Gulf of Finland, the Gulf of Bothnia and the North Baltic were analyzed for their total manganese content and the results are shown in Table 1.

Table 1. Amount of manganese present in surface sea water from the Gulf of Finland and Bothnia and the North Baltic.

Date	Location	Salinity mg Mn/l	
18.11.46	Rysskär, Helsinki	6.38	0.003
18.11.46	59°06'N, 22°53'O	6.83	0.0015
27.10.46	59° N, 20°30'O	6.71	0.002
27.10.46	58° N, 18°40'O	7.02	0.0015
27.10.46	57° N, 17°30'O	7.16	0.002
28.10.46	56° N, 16°10'O	7.27	0.002
28.10.46	Snyggehuk, Denmark	7.54	0.0015
1.10.46	Helsinki harbour	5.68	0.016
27.12.46	63° 8'N, 21° 7'O	5.59	0.01
8. 1.47	60°16'22"N, 21°55'40"O	6.40	0.0075
27. 1.47	Utö	6.98	0.004

The above described method gives the total manganese content in water, but according to investigations carried out by Thompson and Wilson as well as Tschuiko a part of the manganese, especially at the seashores, exists in a suspended, insoluble form. According to Tschuiko the coagulation method offers a chance to determine the last mentioned state, that is if aluminium sulfate is used as coagulating agent in stead of manganese sulfate and the pH is about 8 the divalent manganese does not precipitate from the solution as hydroxide, for in accordance with different investigators the solubility product of manganese hydroxide is $1.3-4 \cdot 10^{-14}$ which for pH 8 gives a solubility of 7-20 mg Mn per liter, a number considerably exceeding that existent in sea water. The manganese yield obtained in spite of this only proves that a part of the same exists in a suspended or colloidal state.

SUMMARY

A method for the quantitative determination of manganese present in natural waters on the basis of two works, the one by Thompson and Wilson and the other by Tschuiko has been worked out. The manganese is isolated from the water by precipitation with potassium hydroxide. There will generally be sufficient oxygen present in the water to oxidize the precipitate to hydrous manganese dioxide which is highly insoluble. Magnesium hydroxide is used as collector. In the suggested way it is possible to detect variations of 0.001 mg of manganese in a liter of water. The halides and organic matter present in the water must be removed and care must be used to remove all suspended material. It has been found that the silver ions has a catalytic effect when oxidating of manganese to permanganate with alkali periodates.

REFERENCES

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