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The Occurrence and Determination of Manganese in Sea Water

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The presence of manganese compounds in sea water was first noted by Forchhammer.¹ He evaporated a quantity of water, redissolved the resulting salts and tested the insoluble residue for manganese and iron. Murray and Irvine² failed to detect soluble manganese compounds in sea water but reported the element occurring in the suspended material in samples of water taken near the bottom at great depths. Dieulafait³ reported manganese in samples of surface water collected on a voyage between New York and Marseilles. None of these investigators gave any quantitative data.

The existence of deep sea nodules consisting largely of the oxides of manganese, the presence of the element in the suspended material in the sea, in the muds and oozes of the sea floor and its occurrence in many river waters, presuppose its presence in sea water. However, it must exist only in minute quantities because of the alkaline nature of sea water and the general chemical characteristics of the element.

The purpose of the present investigation was to study the application of the various analytical procedures for the determination of manganese and to secure quantitative data by the analysis of different samples of sea water.

(1) G. Forchhammer, *Phil. Trans. Roy. Soc. (Lond.)*, **155**, 203-262 (1865).

(2) J. Murray and R. Irvine, *Trans. Roy. Soc. Edin.*, **27**, 721 (1895).

(3) J. Dieulafait, *Compt. rend.*, **96**, 718 (1883).

Investigation of Analytical Procedures

Various methods for the estimation of minute quantities of manganese were studied. Ernyei⁴ suggested the oxidation of the manganous ion in alkaline solution and the subsequent reaction with iodide ions upon acidifying. Harry⁵ recommended the use of benzidine or tetramethyldiaminodiphenylmethane in place of iodides. Stratton, Ficklen and Hough⁶ suggested a method using benzidine, while Denigès⁷ recommended the use of formaldoxime. Clark⁸ noted the effects of dissolved salts upon the benzidine reaction. All of these methods were studied in considerable detail and found to be inapplicable for the determination of manganese in sea water.

The oxidation of the manganese to the permanganate form may be accomplished by the use of lead dioxide⁹ or sodium bismuthate,¹⁰ but the insolubility of the excess reagent is undesirable. The employment of alkali persulfates¹¹ gives a permanganate color that is not stable; furthermore, the test does not seem to be so sensitive as others. The use of hypochlorites and hypobrom-

(4) E. Ernyei, *Chem.-Zig.*, **32**, 41 (1908).

(5) R. G. Harry, *Chem. Ind.*, **50**, 796 (1931).

(6) R. C. Stratton, J. B. Ficklen and W. A. Hough, *Ind. Eng. Chem., Anal. Ed.*, **4**, 2 (1932).

(7) Denigès, *Bull. Soc. Pharm. Bordeaux*, **70**, 101-106 (1932).

(8) N. A. Clark, *Ind. Eng. Chem., Anal. Ed.*, **5**, 241 (1933).

(9) W. Crum, *Ann.*, **55**, 219 (1845).

(10) Reddrop and Ramage, *J. Chem. Soc.*, **67**, 275 (1895).

(11) Hugh Marshall, *Chem. News*, **23**, 76 (1901).

ites¹² for detecting manganese in relatively concentrated chloride solutions has serious limitations and is unsatisfactory for the study of sea water.

The method of Willard and Greathouse,¹³ in which the alkali periodates are used as oxidants, has none of the objections cited above. The permanganate color is not affected by the excess of the reagent and the color produced is very stable. Clark studied the method in detail, recommended the complete removal of chlorides and with the proper regulation of the hydrogen-ion concentration was able to determine 0.01 mg. of manganese per liter using a 100-ml. sample. In the work reported below, it was found that certain modifications of the method and using a liter sample of sea water, made it possible to detect variations of 0.001 mg. of manganese or 0.18×10^{-4} milligram atom of manganese per kilogram of sea water. All analyses were run in duplicate or triplicate, and the method thoroughly checked by adding various quantities of manganese to actual samples of sea water.

Preparation of Reagents

(a) Sodium paraperiodate is prepared by the method of Ammermuller and Magnus as reported by Hill.¹⁴

(b) Sulfuric Acid.—To test concentrated sulfuric acid for manganese, take a 50-ml. sample and evaporate to 5-ml. in a platinum dish. Upon cooling, the acid is added to 45 ml. of water, the resulting solution heated to boiling and 0.5 g. of sodium paraperiodate added. Stand in a hot water bath for a half hour. Upon cooling not more than a trace of manganese should be shown. Add 120 ml. of concentrated sulfuric acid, free of manganese, to 1880 ml. of distilled water. Introduce 2.4 g. of sodium paraperiodate, heat to boiling, allow to stand on the steam-bath for a half hour, cool, and store in a seasoned glass bottle.

(c) Standard Permanganate Solution.—Dissolve 0.1579 g. of recrystallized potassium permanganate in water, add 3 ml. of 2 *N* sulfuric acid and reduce by the addition of 0.4 g. of sodium bisulfite. Boil the solution until free of sulfur dioxide, cool and dilute to exactly 1 liter.

To 10 ml. of the standard solution, add 30 ml. of sulfuric acid reagent and 1.2 ml. of concd. sulfuric acid. After mixing, introduce 0.3 g. of sodium paraperiodate, heat to boiling, place in a water-bath for thirty minutes, cool, and dilute to exactly 1 liter. This standard, which should be kept from contact with direct sunlight, contains the equivalent of 1.0×10^{-2} milligram atom of manganese per kilogram of sea water.

Two constituents of sea water,¹⁵ the halide ions and the

(12) B. E. Dixon and J. L. White, *J. Chem. Soc.*, 1467 (1927); Denigès, *Bull. soc. chim.*, 51, 380 (1932); *Compt. rend.*, 194, 91 (1932).

(13) Willard and Greathouse, *THIS JOURNAL*, 39, 2366 (1917).

(14) A. C. Hill, *ibid.*, 50, 2678 (1928).

(15) T. G. Thompson and R. J. Robinson, "The Chemistry of the Sea." Bulletin No. 85, National Research Council, 1932.

organic matter,¹⁶ interfere with the reaction and these substances must be removed. Experiments with ammonium persulfate, after the removal of the chlorides, showed that the use of this substance would not ensure the complete removal of the organic matter. Accordingly the following procedure for the determination of manganese in sea water was found to yield the most satisfactory results.

The samples were filtered through double layers of Whatman No. 42 filter paper as soon after sampling as practicable. In several cases the samples were centrifuged but this procedure was not as satisfactory as filtration.

In order to test the effectiveness of the method of filtration used for the removal of suspended material, samples of water were analyzed as follows: (a) without filtration, (b) after filtering through filter paper, and (c) after passing through a porcelain bacteriological filter. Sample No. 1 was collected over 100 miles beyond the continental shelf and at a depth of 400 meters (Lat. 48°34' N, Long. 129° 20' W). The depth of water at this point was approximately 2750 meters and the sample may thus be considered relatively free of influences from the bottom, land drainage, and growing diatoms. Sample II was secured at a depth of 40 meters in San Juan Channel of the San Juan Archipelago where there is a marked turbulence of the waters caused by strong tidal currents. The waters about the region have a rich diatom flora, and thus the sample contained suspended material carried up from the bottom and down from the surface layers. The sample was treated the same as No. 1, and the results were as follows.

TABLE I

	Sample I	Sample II	
	Milligram atoms 10 ⁴	Mn per kilo 10 ⁴	of water (a) (b)
Unfiltered	0.4	1.8	2.0
Filtered with Whatman No. 42	.4	1.1	1.1
Filtered with porcelain filter	.4	1.2	1.1

The data show that the coastal water, either filtered or unfiltered, is richer in manganese than the water beyond the continental shelf and that the element is present in the suspended matter occurring in coastal water as shown by the difference between the filtered and unfiltered samples. The results given for Sample I indicate that the suspended matter in the ocean water was free of manganese; however, the amount of such suspended material was so exceedingly small, compared to that of the coastal water, that any manganese it may have contained would not be evident with the quantity of water taken for analysis.

A liter of the *filtered* sample of sea water to be analyzed is evaporated to dryness and the resulting salts treated with 30 ml. of concd. sulfuric acid. Heating is continued until the evolution of hydrogen chloride ceases and white fumes of sulfur trioxide begin to appear. The mixture is transferred to a platinum dish and the contents carefully heated until the excess sulfuric acid is expelled and the salts are in a fused condition. The temperature is increased and the fused salts are heated for five minutes over a Meker burner. The mass is cooled, dissolved in 50 ml. of sulfuric acid reagent, heated to boiling and filtered through asbestos that had been specially treated to ensure freedom from manganese. The solution is then

(16) T. G. Thompson, R. W. Bremner and I. M. Jamieson, *Ind. Eng. Chem., Anal. Ed.*, 4, 288 (1932).

diluted to 100 ml. with the sulfuric acid reagent, again boiled, 0.05 g. of sodium paraperiodate added and then heated for a half hour on the water-bath. The sample is cooled, allowed to stand for another half hour, transferred to a 100-ml. Nessler tube, and compared with a series of color standards.

Method of Analysis of Muds and Other Bottom Deposits.—The samples were dried at 100° for forty-eight hours, ground to a fine powder and 0.5 g. weighed in a platinum dish. Decomposition was accomplished by successive treatments with hydrofluoric and concd. sulfuric acids. The former was finally expelled, the residue ignited and then dissolved in 100 ml. of water and 10 ml. of concd. sulfuric acid. This solution was heated to boiling and 1 g. of sodium paraperiodate added. After heating on the water-bath for a half hour, the solution was cooled, diluted to exactly one liter and aliquot portions compared with measured quantities of the permanganate standard. Comparisons were made in a Duboscq colorimeter.

Analyses of Sea Water, Plankton and Bottom Deposits.—Fifteen samples of sea water collected from various parts of the northeast Pacific Ocean were analyzed for manganese, and the results are shown in Table II.

TABLE II
AMOUNT OF MANGANESE PRESENT IN SAMPLES OF SEA WATER COLLECTED IN THE NORTHEAST PACIFIC

Location	Depth in meters	Milligram atoms Mn per kilo 10 ⁴
Hood Canal, Puget Sound,		
Mouth Liliwaup River	1	0.5
Straits of Juan de Fuca,	50	1.0
off Cape Flattery	150	0.2
49°32' N, 124°26' W	1	.2
47°56' N, 125°29' W	1	1.8
48°43' N, 125°47' W	50	1.3
48°43' N, 125°47' W	100	1.5
48°43' N, 125°47' W	150	0.2
47°40' N, 126°23' W	100	.5
47°40' N, 126°23' W	400	.2
47°40' N, 126°23' W	500	.2
47°40' N, 126°23' W	750	1.0
Hecate Channel,	10	1.0
British Columbia	25	1.3
50°03' N, 128°03' W	300	1.3
		Average 0.8

Six samples of surface sea water collected at intervals throughout 1932 and 1933 in San Juan Channel, Friday Harbor, Washington, gave the following results:

Date	Manganese per kilo milligram atoms 10 ⁴
October 14, 1932	1.3
December 15, 1932	1.3
March 1, 1933	0.4
June 8, 1933	.5
July 6, 1933	1.5
July 10, 1933	1.0

A sample of plankton, particularly rich in phytoplankton, was ashed and the material found to contain 0.07% Mn on the basis of the ash weight, equivalent to 12.7 milligram atoms per kilo of ashed material.

Twelve samples of bottom muds, collected at various points in Puget Sound and Alaska, were examined for their manganese content and the results are shown in Table III.

TABLE III
AMOUNT OF MANGANESE PRESENT IN BOTTOM MUDS FROM WATERS OF PUGET SOUND AND SOUTHEASTERN ALASKA

No.	Location	Depth, meters	Av., %	Mg. atoms per kilo dry mud
32	Hoods Canal	...	0.28	50.9
35	Hoods Canal06	10.9
84	Commencement Bay07	12.7
449	Ker Point, S. E. Alaska	136	.07	12.7
446	Hammer Island, S. E. Alaska	103	.07	12.7
323	Off Shingle Island, S. E. Alaska	250	.25	45.5
397	Off Taku Glacier, S. E. Alaska	45	.11	20.0
345	False Bay, S. E. Alaska	540	.08	14.5
375	Flat Bay, S. E. Alaska	200	.07	12.7
399	Taku Harbor, S. E. Alaska	220	.09	16.3
372A	Endicott River, S. E. Alaska	150	.05	9.1
372	William Henry Bay, S. E. Alaska	385	.12	21.8
			Average 0.11	20.0

As these samples were primarily diatomaceous muds, the apparent constancy of results is not surprising and agrees fairly well with the results obtained from the analyses of phytoplankton. The two particularly high values are probably due to some peculiar local condition. The manganese content of some of the shells of organisms native to Puget Sound was found to vary from 0.003 to 0.007% of the dry weight, equivalent to from 0.5 to 1.2 milligram atoms per kilo of dried material

Conclusions

1. A method for the quantitative determination of manganese present in sea water has been devised which is sufficiently sensitive to detect variations of 0.18×10^{-4} milligram atom of manganese. The halides and organic matter present in the water must be removed and care must be used to remove all suspended material.
2. The manganese content of sea water varies from 0.2×10^{-4} to 1.8×10^{-4} milligram atoms per kilo of water.

3. Manganese may play a role in plankton growth as the element was found in the ash of these organisms, amounting to 0.07% of the ash weight. Furthermore, waters rich in plankton showed less dissolved manganese.

4. Manganese was found in various muds collected from the sea bottom, the manganese content varying from 0.05 to 0.30% of the dried sample.

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Measurement of the Interfacial Tension at a Mercury-Mercurous Sulfate Solution Interface by the Drop Weight Method

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Introduction

The purpose of this investigation was to measure the interfacial tension at a mercury-mercurous sulfate solution interface by the drop weight method. The drop weight technique developed by Harkins and co-workers is particularly advantageous for such an investigation, and it is hoped that the measurements described in this paper will be of use in clarifying the question of mercurous ion adsorption at a mercury surface.¹

Patrick measured the interfacial tension of mercury against aqueous solutions of mercurous sulfate and other substances.² In the case of mercurous sulfate, his values of interfacial tension are of the same order of magnitude as those reported in this paper, but it is doubtful whether his technique permitted equilibrium to be attained in the boundary region between mercury and solution, due to the rapid formation of mercury surface. The investigations of Harkins and others have demonstrated the necessity of slow drop formation, especially at the moment of rupture of the hanging drop from the dropping tip.

Apparatus

The drop weight apparatus was of the type developed by Harkins and Brown.¹ With the exception of a short length of 3-cm. tubing to act as a mercury reservoir, the apparatus was constructed of Pyrex capillary having a bore approximately 1.5 mm. in diameter. Since mercury does not wet glass, the drops fall from the bore of the capillary, and it is essential to have this portion of the tip uniform. By grinding the tip as recommended by Harkins, a tip free from cracks and jagged edges may be obtained. The radius of the tip was determined by measuring several diameters of the bore with a calibrated micrometer eyepiece in a microscope, and was found to be 0.0783 cm.

(1) Harkins and Brown, *THIS JOURNAL*, (a) **38**, 246 (1916); (b) **41**, 499 (1919).

(2) Patrick, *Z. physik. Chem.*, **86**, 545 (1914).

The solution under investigation was contained in a small weighing bottle, air and water being excluded by means of a tight-fitting rubber stopper. The entire apparatus was clamped in a frame, and suspended in a thermostat maintained at $20 \pm 0.1^\circ$.

To control the speed of formation of the mercury drops, a U-tube of 3-cm. tubing approximately 50 cm. high was constructed. This was filled with mercury to about half its height, and one end connected to a suction pump and the atmosphere by means of a two-way stopcock. After partial evacuation of this end of the U-tube, the open end was connected to the open end of the drop weight apparatus. By turning the two-way stopcock, the pressure exerted on the mercury in the reservoir of the drop weight apparatus may be equal to or greater than atmospheric, thus regulating the speed of formation of the drops.

In order to control further the rate of drop formation, a portion of the capillary between the reservoir and tip must be constricted. In actual practice, it was more convenient to use several comparatively large constrictions rather than one fine one, since the fine constrictions are easily clogged by small dust particles.

Experimental Procedure

The drop weight apparatus was thoroughly cleaned with warm cleaning mixture, steamed for one-half hour, and dried. The tube was then filled by suction with carefully purified mercury until the level in the reservoir was approximately 2 cm. above the ground dropping tip. A solution of mercurous sulfate of known concentration was then placed in the weighing bottle, and the apparatus immersed in the thermostat, fifteen minutes to one-half hour being allowed for attainment of temperature equilibrium.

The mercurous sulfate solutions were prepared by saturating distilled water or *N*/40 sulfuric acid solution with c. p. mercurous sulfate in the presence of mercury to prevent the formation of mercuric salts. These saturated solutions were analyzed by electrolysis, and solutions of lower concentration obtained by dilution.

The following procedure was used in all determinations of the drop weight: the partially evacuated side of the mercury-filled U-tube was opened to the atmosphere, thus building up a pressure on the reservoir end of the drop weight apparatus. In this way, approximately 90% of the drop may be formed in forty-five seconds to one min-