Separation and Determination of Microgram Quantities of Molybdenum in Natural Waters

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Despite the importance of the role of molybdenum in the biochemical cycle of nitrogen and especially in plant growth, the only accessible datum of the content of this element in an inland water is that of Ter Meulen[1] who reported 0.9 μg. Mo/l. for a canal water in the Netherlands. As for sea water, more data have been reported. However, these data are often discordant, apparently because of defects in some of the methods employed. Thus, while Ishibashi et al.[2] found 10.6 μg./l. for the North Pacific water, Ernst and Hoermann[3] reported 0.3~0.7 μg./l. for the Atlantic.

Considering these facts, the present writers have elaborated a new method of determination, applicable to both sea and fresh waters, by which they plan to conduct an extensive study of the distribution of molybdenum in various kinds of natural water.

The method consists of two steps: 1) the element is co-precipitated together with either hydrated manganese oxide or ferric hydroxide and 2) the molybdenum is then extracted by a solvent consisting of *n*-butanol and chloroform in the form of thiocyanate to be subjected to spectrophotometry. Special care is taken in adjusting the pH of the solution to 3.8 where quantitative co-precipitation of molybdenum is ensured, resulting in a nearly 100% recovery of molybdenum[4].

Of these two different kinds of coprecipitant, manganese oxide is preferred because with this element, a precipitate is obtained which is quickly and easily filtered. This precipitate is more easily soluble in dilute hydrochloric acid containing a small amount of hydrogen peroxide, and the optimal range of pH is wider where a perfect co-precipitation of molybdenum is ensured[4].

Experimental

Reagents. — *Ferrous ammonium sulfate solution.* — Dissolve 0.70 g. of the salt in 100 ml. of 0.2 N sulfuric acid. The solution thus prepared contains 1.0 mg. of ferrous iron per ml. and is good for only one week after being prepared.

Sodium hypochlorite solution. — Neutralize 7.1 ml. of alkaline hypochlorite solution having 7% available chlorine with glacial acetic acid, using *p*-nitrophenol as indicator. Then add 0.6 ml. excess of the same acid and water bringing the solution to 50 ml. The solution is 1% for chlorine and is buffered at pH 3.7.

Potassium permanganate solution. — Dissolve 0.86 g. of potassium permanganate in 100 ml. water. The solution contains about 3 mg. Mn/ml.

Manganous sulfate solution.—Dissolve 1.0 g. of hydrated manganous sulfate in 100 ml. water. The solution contains 2 mg. Mn/ml.

Bromocresol purple. — Ethanolic solution, 0.1% wt./vol.

Potassium iodide solution.—10%, reagent quality.

Sodium sulfite solution.—10%, reagent quality.

Potassium thiocyanate solution. — 10%, reagent quality.

Hydrogen peroxide solution.—1%, 30% reagent is diluted.

Stannous chloride solution.—Ten g. of hydrated salt is dissolved in 100 ml. of 1 N hydrochloric acid. It is recommended that the preparation be made each week.

Solvent mixture of n-butanol and chloroform.— One part of *n*-butanol and four parts of chloroform are mixed. The components must be previously subjected to distillation and those fractions which distil 118°C and 61~63°C respectively are separated.

Standard molybdenum solution. — An amount (0.750 g.) of reagent quality molybdenum trioxide is dissolved in 10 ml. of 0.1 N sodium hydroxide solution and diluted to about 50 ml. After being slightly acidified with hydrochloric acid, the solution is made up to 500 ml. In practice, a dilute solution is prepared each week and used as the standard. The primary standard solution containing 1.0 mg. Mo per ml. is properly diluted

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[1] G. Evelyn Hutchinson, "A Treatise on Limnology vol. 1- Geography, Physics, Chemistry", John Wily & Sons, Inc., New York, (1957), p. 824.

[2] M. Ishibashi, T. Shigematsu and Y. Nakagawa, *Memoir of Chemical Research Laboratory, Kyoto University*, 32, 199 (1954).

[3] T. Ernst and H. Hoermann, *Nach. Ges. Wiss. Göttingen Math. -Phys.* Kl., Fach. IV, N. F. 1, 205 (1936).

[4] M. Tanaka, *Mikrochimica Acta*, 1958, 204.

with 0.1 N hydrochloric acid so that one ml. of the dilute solution contains one μg. Mo per ml.

Procedure. — Depending upon the probable content of molybdenum, a sample of $1\sim5$ liters is taken. After being warmed to $70\sim80$°C, the sample is acidified with hydrochloric acid. The solution is neutralized with 4 N sodium hydroxide solution by using bromocresol purple as indicator and is buffered to approximately pH 3.8 by adding 12 ml. of glacial acetic acid and 5 ml. of 4 M sodium acetate solution per liter. Then 2 ml. of the manganous sulfate solution and 2 ml. of the potassium permanganate solution are successively added, while stirring vigorously. The solution is heated to 80°C whereby coagulation of the formed hydrated oxide of manganese is hastened. After cooling, the coagulum is filtered and then dissolved in a small amount of 2 N hydrochloric acid containing 1 ml. of 1% hydrogen peroxide. The solution is transferred into a 100 ml. beaker and boiled gently about 30 minutes until the excess of hydrogen peroxide is expelled. After cooling, 1 ml. of sodium sulfite solution is added whereby the remaining hydrogen peroxide is decomposed and ferric ions are reduced. Further addition of the potassium iodide solution ensures elimination of traces of hydrogen peroxide and the ferric iron. The liberated iodine is driven out by heating the solution for 10 minutes on a water bath. The final volume of the solution is $10\sim15$ ml. Two ml. of concentrated hydrochloric acid, 2 ml. of ferrous ammonium sulfate solution and 3 ml. of potassium thiocyanate solution are successively added. Then the whole is transferred into a 100 ml. separatory funnel. After thoroughly mixing, 3 ml. of the stannous chloride solution is added and then shaken5).

The next step is the extraction of formed molybdenum thiocyanate by the *n*-butanol—chloroform mixture6). After the addition of 7 ml. of the mixture, the contents of the funnel are vigorously shaken for two minutes. When the layers separate, the bottom oil layer is drawn out into a 10 ml. measuring flask and the remaining aqueous fraction is treated with 2 ml. of the solvent mixture. The joint extracts in the flask are made to just 10 ml. Then a few mg. of solid stannous chloride is added to protect the ferrous iron against oxidation. Otherwise, a red coloration by ferric thiocyanate may interfere with the measurement of the coloration. The absorbance measurement is made at 475 mμ. The molybdenum determination is made in reference to the standard curve previously prepared.

Checking the method and application of the method to natural waters.—1) Recovery of molybdenum by the co-precipitation procedure was checked as follows: an amount of molybdenum ranging $5\sim15$ μg. in one liter of water was co-precipitated together with hydrated manganese oxide or ferric oxide, each equivalents to 10 mg. and 100 mg. of Mn and Fe respectively. As shown in Table I, the molybdenum recovery is from 98 to 100% by the use of either manganese or iron.

2) The interferences by ordinary elements and tungsten with the final colorimetry were examined. The results proved that these elements cause no interference at concentrations as are usually found in ordinary natural waters.

3) Examples of the results of the application of the present methods to various natural waters are given in Table II.

TABLE I

CO-PRECIPITATION OF MOLYBDENUM WITH HYDRATED MANGANESE OXIDE AND FERRIC HYDROXIDE

Mn used (mg.)	Mo added (μg.)	Mo found (μg.)
10	5.0	5.1
10	10.0	10.0
10	15.1	15.0
100	10.0	10.1
Fe used (mg.)	**Mo added (μg.)**	**Mo found (μg.)**
10	5.0	5.2
10	10.0	10.0
10	15.1	15.2
100	10.0	10.2

TABLE II

EXAMPLES OF APPLICATION

Description	Sample taken (l.)	Mo added (μg.)	Mo found (μg.)
Ground water from a well on the campus of Nagoya University.	5		3.0
	5	5.0	8.2
River water from Nagaragawa, Gifu Prefecture.	5		2.5
	5	5.0	7.4
Sea water from the Antarctic Ocean.			
68°52.5'S	1		9.8
25°33.5'E	1	5.0	14.6
Pacific Ocean.			
04°14.0'N	1		10.0
128°55.0'E	1	10.0	19.8
Indian Ocean.			
12°48.0'S	1		12.2
78°03.8'E			

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5) E. B. Sandell, "Colorimetric Determination of Traces of Metals.", Interscience Publishers, Inc., New York, (1950), p. 455.

6) S. Kanamori, private communication.