

# Quantitative Determination of Tungsten and Molybdenum in Sea-water

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The amounts of molybdenum in sea-water obtained by Ernst and Hörmann<sup>1)</sup>, Bardet, Tchakirian and Lagrange<sup>2)</sup> as well as by the authors<sup>3)</sup> are about 0.3, 3 and 10  $\mu\text{g}$  per kg of sea-water respectively. Tungsten has been detected in sea-water, but the amount of it is not yet quantified. From the regularities of the amounts of elements dissolving in sea-water, Ishibashi and Shigematsu<sup>1)</sup> presumed the amount of molybdenum and tungsten in sea-water as about 10  $\mu\text{g}$  Mo per L, and 0.4  $\mu\text{g}$  W per L.

The authors determined the amount of molybdenum and tungsten in sea-water, and found that the molybdenum content is almost the same as that previously obtained by our thiocyanate method<sup>3)</sup>, and the tungsten content is about 0.1  $\mu\text{g}$  per L of sea-water.

## COLORIMETRIC DETERMINATION OF TUNGSTEN AND MOLYBDENUM

The authors studied on the colorimetric procedure for trace amount of tungsten and molybdenum by dithiol (toluene-3,4-dithiol) and established the conditions necessary and satisfactory to obtain an accurate result.

Reagent :

Dithiol solution : 0.2 g dithiol (prepared by the authors) dissolved in 100 ml of n-NaOH, freshly prepared, or stored under  $\text{H}_2$  atmosphere. The solution is stable for 2 months under hydrogen.

Standard solutions of tungsten and molybdenum :

Solution of sodium tungstate and ammonium molybdate, respectively 1.0 and 10.0  $\mu\text{g}/\text{ml}$ .

Procedure :

The solution containing W and Mo was diluted to 50.0 ml. The 25 ml aliquot of the solution was acidified with 2 ml of n-HCl, then 1 ml of 0.2 % dithiol solution was added and heated on boiling water for about 10 minutes. After cooling, the resultant dithiol complexes were extracted with 10 ml of butylacetate. The color intensity of butylacetate solution (extinction:  $E_2$ ) was measured by using Pulfrich

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photometer with the cell of 2 cm length and the filter  $S_{61}$ . To the another 25 ml aliquot, 1 ml of 10 % citric acid solution and 2 ml of n-HCl were added, then 1 ml of dithiol solution was added and heated on boiling water for about 10 minutes. Then the molybdenum complex was extracted with 10 ml of butylacetate. The color intensity (extinction:  $E_1$ ) was measured as above.

The amount of tungsten and molybdenum was calculated from the following equation.

$$\mu\text{g W} = 58.8(E_2 - E_1) \quad \mu\text{g Mo} = 83.0(E_1 - 0.040)$$

It was found that through this procedure 1~40  $\mu\text{g}$  of Mo and W can be determined within the error of  $\pm 0.5 \mu\text{g}$ , and this method is only interfered by the presence of iron and copper.

#### CONCENTRATION OF TUNGSTEN AND MOLYBDENUM IN SEA-WATER

For the purpose to separate and concentrate the tungsten and molybdenum in sea-water, the authors utilized the coprecipitation method as follows.

To 0.5~15 L of artificial sea-water<sup>9)</sup>, 1~3 ml of  $\text{HNO}_3$  and 200 mg of ferric iron as ferric nitrate solution were added. Then 50~100 ml of 1 mol hexamethylenetetramine solution was added, and allowed to stand overnight to settle the precipitate. The precipitate was filtered, dried and ashed in a platinum crucible at the temperature lower than 500°C. The residue was fused with small amount of the fusing mixture ( $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 = 1 : 1$ ). The fused mass was taken up with 10~20 ml of hot water, and filtered. The filtrate was just neutralized with 4n- $\text{H}_2\text{SO}_4$  to litmus.

The solution was diluted to 50.0 ml, and the amount of tungsten and molybdenum was determined in the forgoing section.

The results obtained are shown in the table 1, No. 1~9.

Determination of tungsten in the presence of large amounts of molybdenum: - In the presence of large amounts of molybdenum ( $>10 \times \text{W}$ ), tungsten was determined inaccurately by the above procedure. In sea-water, the amount of molybdenum may be about thirty times larger than that of tungsten<sup>9)</sup>, so should be separated as sulfide from tungsten. To the neutral solution, 1 ml of 50 % citric acid solution and 5 drops of 4n- $\text{H}_2\text{SO}_4$  were added, then  $\text{H}_2\text{S}$  was streamed vigorously for a few minutes. The sulfide was filtered through a small filter, and washed with  $\text{H}_2\text{S}$  water. The filtrate was evaporated to a few ml, and filtered again, if necessary, then washed with hot water. The solution was dried up on a platinum crucible. The residue was ashed with a small amount of sodium carbonate and fused. The fused mass was taken up with hot water and just neutralized with  $\text{H}_2\text{SO}_4$ . The solution was diluted to 50.0 ml, and then the tungsten and residual molybdenum was quantified as mentioned above.

The results obtained are shown in Table 1, No. 10~16.

Quantitative Determination of W and Mo in Sea-Water

Table 1. Recovery of Mo and W.

No.	W added	Mo added	W found	Mo found
1	0.0 $\mu\text{g}$	0.0 $\mu\text{g}$	0.0 $\mu\text{g}$	0.0 $\mu\text{g}$
2	30.0	0.0	29.1	0.0
3	0.0	30.0	0.0	29.3
4	5.0	10.0	4.9	9.3
5	10.0	10.0	8.9	8.0
6	10.0	20.0	12.5	18.3
7	10.0	30.0	8.7	28.0
8	20.0	20.0	18.5	18.3
9	30.0	30.0	28.0	26.9
10	0.0	1000	0.2	13.2 <sup>a</sup>
11	20.0	1000	18.0	7.1 <sup>a</sup>
12	30.0	1000	30.6	3.5 <sup>a</sup>
13	30.0	1000	27.1	10.6 <sup>a</sup>
14	30.0	1000	27.8	6.8 <sup>a</sup>
15	30.0	1000	26.8	10.8 <sup>a</sup>
16	30.0	1000	26.4	10.6 <sup>a</sup>

<sup>a</sup> Residual Mo.

The recovery of molybdenum and tungsten in this procedure are both about 90 per cent.

DETERMINATION OF MOLYBDENUM AND TUNGSTEN IN SEA-WATER

About 50 liter of the sample water was taken, and acidified with 6 ml of nitric acid, then added 400 mg of ferric iron as ferric nitrate and thoroughly mixed. To the solution, 200 ml of hexamine solution (containing 100 g of hexamine) was added and allowed to stand for 2 days. The precipitate was treated as mentioned above, and the amount of tungsten and residual molybdenum was determined.

Molybdenum sulfide in the filter was ashed at low temperature and dissolved in sodium hydroxide. Then the amount of molybdenum was determined colorimetrically by the dithiol method.

The results obtained are shown in Table 2.

Table 2.

Sea water taken (L)	W found ( $\mu\text{g}$ )	Mo found		
		residual ( $\mu\text{g}$ )	sulfide ( $\mu\text{g}$ )	sum ( $\mu\text{g}$ )
40	3.64	11.6	340	351.6
60	7.90	15.8	598	613.8
40 (+5.0 $\mu\text{g}$ W)	8.97	—	—	—

The sea-water was sampled on June 13th, 1952, at offshore of Shirahama,

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As seen from Table 2, the molybdenum content of the sampled sea-water is 9.8 and 11.4  $\mu\text{g}$  per liter, in the average 10.6  $\mu\text{g}$  per liter, and the tungsten content is 0.10, 0.15 and 0.11  $\mu\text{g}$  per liter, in the average 0.12  $\mu\text{g}$  per liter.

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