THE ESTIMATION OF GOLD AND SILVER IN SEA WATER.

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Received October 27, 1927. Published December 28, 1927.

In regard to the estimations of gold and silver in sea water, the method of Sonstadt[1] was published at the early time and at present this method is still used frequently. In recent time H. Koch[2] and F. Haber[3] have published new methods. Of course, it seems to be very excellent. But, I thought, some skillness is necessary to carry out their methods and to obtain some reliable results.

I tried to estimate the gold and the silver by an old method of Scheibler[4] by notice of Dr. S. Iimori, and modified it by adding mercuric chloride solution and reduced them with metallic magnesium and concentrated hydrochloric acid. By this treatment the mercury deposits in fine metallic particles which catch all the gold and the silver as amalgams. It seems to be very excellent in the point that the metals obtained as heavy black precipitates.

Prof. Dr. P. P. Weimarn suggested that the gold in the sea water should be exist in the following states: (1) from colloidal to suspensoid, (2) metallic state in quartz and other earths, (3) gold in the organic colloids, (4) dissolved ionic states of trivalent as $Au^{\cdots}$, (5) the same of monovalent as $Au^{\cdot}$. H. Koch thought, also, that the gold in sea water exists as ionic states, though it once changes to submicron particles by some organic reducing agents, it should be, again, convert into ionic state by oxidation. It is supposed that the cupric and the ferric ions exist in the sea water serves as the oxidising agent. My analytical method, however, can estimate all of the gold except that in the organic colloids. The detail of the method is given in the followings.

Two litres of sea water to be examined is taken into a separating funnel of 2.5 litres capacity, and add 4–5 grams of powdered or shaved metallic magnesium. The magnesium must, previously, be freed from any oily contaminations, by washing with ether two or three times, because the commercial magnesium is usually contaminated with machine oils etc. Then add 20 c.c. of 0.05 mol per litre solution of mercuric chloride, and 40 or 50

(1) Sonstadt, *Chem. News*, **74** (1896), 316.
(2) H. Koch, *Kolloid Z.*, **22** (1918), 1.
(3) F. Haber, *Z. angew. Chem.*, **40** (1927), 303.
(4) Scheibler, *Ber.*, **2** (1869), 2. Villiers and Borg, *Compt. rend.*, **116** (1893), 1524.

c.c. of strong hydrochloric acid (38% HCl). Now strong effervescence takes place with the evolution of the hydrogen gas, and deposits the white mercurous chloride at once. The deposition, however, gradually change to grey colour by the formation of the metallic mercury. The fine particles of the mercury settle down catching all of the gold and silver as amalgams.

After the reactions has finished, the heavy black precipitate is filtered. The filtration is performed in the manner shown in the accompanied figure. When emptied, the separating funnel is washed once more with water and alcohol to remove all of the black matter.

The filter paper obtained by this way contains all of the amalgam of the precious metals, it dried and burnt, and enclosed the obtained ashes with pure lead sheet and put in a small crucible. Next heat the crucible with gas flame adding two grams of gold and silver free lead oxide to oxidize the remaining carbon, and to absorb the precious metals into the lead button. The button obtained by this way is cupelled on the bone ash in the muffle, and a small bead is obtained. The bead is weighed with a balance of 0.001 mg. sensibility, and then is taken into a small glass dish of 15 mm. diameter.

If the colour of the bead is white it is dissolved directly in a drop of nitric acid (specific gravity, 1.26). If the colour of the bead is yellow or yellowish green, it is dissolved in a drop of mercury (free from gold and silver, of course), and then is dissolved in a drop of nitric acid. The gold remains in a form of black powder by such treatment. Next dip the small dish into a large white porcelain dish filled with distilled water, and moved it by means of a small pincette coated with celluloid, to dissolve out the silver and the mercury nitrate, to and fro, up and down, in the water until the black residue of gold is purified sufficiently. It happens frequently, during this treatment, that the black residue floats out from the small dish. In such a case the black residue is collected with a small dust-pan with long handle made of white celluloid and a small feather under the observation by a lens, and then transfered into the small dish.

By this way all of the gold can be collected in the small dish, which is then evaporated to dryness, and heated to 250°C. After cooled in a desiccator, it is weighed. The heating should begin slowly, for otherwise the gold residue sometimes spring out and lost.

The blank tests of the method have been carried out on three percent

solution of sodium chloride, in which the known quantities of gold chloride had been added. The results are shown in the following table.

TABLE 1.

Gold added in 3% NaCl solution (gr.)	Gold obtained (gr.)		Content of gold in the solution (mg. per cubic meter)
	I	II	
0.0000140	0.0000157	0.0000139	4.6
0.0000320	0.0000316	0.0000300	10.6
0.0000512	0.0000507	0.0000522	17.0

By this method I have estimated the gold and the silver in Japanese sea waters, and obtained the following results.

TABLE 2.

Place where the water was taken	One cubic meter of sea water contains	
	gold	silver
Kominato Bay	10. mg.	70. mg.
Kagoshima Bay	20. mg.	20. mg.
Sagami-Nada	3. mg.	—

Kominato Bay, a small sea port of Pacific coast south eastern way from Tokyo, 74 km. apart.

Kagoshima Bay, a gulf of south part of Kyûshû and there are city of Kagoshima and the volcano of Sakurajima.

Sagami-Nada, entrance sea of Tokyo Bay.

I am now endeavouring to estimate the precious metals in sea waters of the vicinity of Japan by the present method.

October 1927.

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