THE PRECIPITATION OF THE GOLD AND THE SILVER FROM THEIR DILUTE SOLUTIONS.

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It is well known that the precious metals precipitate from their solutions by contact with the base metals. It is also known that the metallic couples such as zinc-copper, zinc-lead and others were studied as reducing agents(1) and lead-aluminium couple was used to precipitate gold for analytical purposes.(2) It seems probable that the higher electric potential difference between the metals is more favourable to precipitate the precious metals from their exceedingly dilute solutions such as sea water. As was described in the former paper(3), I believe that the gold and the silver in sea water exist in ionic states, thus $Au^{\cdot\cdot\cdot}$, $Au^{\cdot}$ and $Ag^{\cdot}$. The metallic couples, therefore, may apply to precipitate the precious metals in this case.

The fact that the precious metals exist in sea water was known very early times, and since then many works were published on this subject.(4)

Since two years I have studied the chemical properties of metallic manganese, and found that this metal is suitable to precipitate the precious metals from exceedingly dilute solution such as sea water, because of its close resemblance to the metallic magnesium, and its chemical reactions is much slower in the sea water than the latter.

At first I tried with a couple of manganese and lead. It is, however, very difficult to obtain the couple directly by dipping the metallic manganese in the solution of lead, for the adhered lead on the manganese has spongy appearance and is easily detached therefrom. I, therefore, made an alloy by mixing the manganese and the lead. The purpose of the metallic couple or alloy is to utilize the galvanic current which occurs between these metals, the easily oxidizable metal, the manganese, being anode, and the nobler

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(1) J. J. Hood, *J. Soc. Chem. Ind.*, **14** (1895), 808; Christy and Butters, *Chem. News*, **75** (1897), 309; H. Becker, *Chem. Zeit.*, **21** (1897), 296.

(2) *Proc. Chem. Met. a. Min. Soc. South Africa*, Sept. 1913.

(3) M. Yasuda, this journal, **2** (1927), 322.

(4) Malaguti and Durocher, *Compt. rend.*, **49** (1859), 463; Liversidge, *Chem. News*, **74** (1896), 146; A. Münster, *J. Soc. Chem. Ind.*, **11** (1892), 351; Liversidge, *Proc. Roy. Soc. New South Wales*, **29** (1895), 335; Liversidge, *J. Chem. Soc.*, **71** (1897), 298; J. R. Don, *Tran. Am. Inst. Min. Eng.*, **27** (1897), 615; L. Wagoner, *Trans. Am. Inst. Min. Eng*, **31** (1901), 807; F. Haber, *Z. angew. Chem.*, **40** (1927), 303; J. W. Pack, *Min. and Sci. Press*, **77** (1898), 154; P. de Wilde, *Arch. Sci. phys. Nat.*, 4th ser. **19**. 559; A. Wiesler, *Z. angew. Chem.*, **19** (1906), 1795; H. Koch, *Kolloid Z.*, **22** (1918), 1.

metal, the lead, cathode. The galvanic current will continue until the anode is oxidized and is covered by the film of mangano-manganese oxide. By this galvanic current the precious metals in sea water will deposit on the cathode metal, lead.

As above stated, the gold which is able to effect the galvanic current is the ions, $Au^{\cdots}$ and $Au^{\cdot}$. The chlorine ion oxidizes the manganese and the gold deposited on the lead. The silver will behave the same as the gold. The manganese can changes its valency in several stages, and form many oxides, some of which are soluble and others insoluble as was described by Spring and be Boeck(1). If we put the manganese-lead couple into the sea water, no perceptible change in the solution was found at begining, but after some hours the soluble hydroxide is oxidized, and hydrated black mangano-manganic oxide adhered on all parts of the vessel.

It may be also supposed as J. M. Stuart and G. D. Bengough(2) stated, the manganese hydroxide which is formed from the manganese charged positively in colloidal state and neutralized the ion $AuCl_4'$ and changes to single salt $AuCl_3$ or $AuCl$, and the metallic ions $Au^{\cdots}$ or $Au^{\cdot}$ neutralized again with negatively charged metal and is deposited on the lead. Here the passivity of the metallic manganese which is known to be very unstable, and soon recover its electric potential and the reactions go on.(3) In general it is recognized that the metal resemble to zinc or magnesium in its behaviors.

At first, I have carried out the experiments on several couples of metals, such as copper-manganese, manganese-lead and lead-aluminium. The preparation of the alloys of lead and aluminium(4) or lead and manganese(5) are very difficult, but the mechanical or heterogeneous mixtures of lead and aluminium or lead and manganese can easily be prepared. The experiment on lead-manganese couple was carried out in the following manner.

The powdered lead and manganese are put together in a steel case and are strongly hammered with an air hammer as hard as possible, and at last a thin plate of 0.07 mm. thickness was obtained. The plate thus made was then cut into rectangular sheet and hang into a beaker in which two or three litres of sea water being contained, and stir the water with a appropriate stirrer. After some hours, the plate is taken out and rolled to a small volume and put in a crucible. Then 2 or 3 grammes of lead oxide are added and heated to a fused state to oxidise the remaining manganese in the alloy,

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(1) Spring and de Boeck, *Bull. soc. chim.*, [2] **48** (1887), 170.

(2) J. M. Stuart and G. D. Bengough, *Chem. News*, **161** (1922).

(3) H. Küssner, *Z. Elektrochem.*, **16** (1910), 758.

(4) A. G. C. Gwyer, *Z. anorg. Chem.*, **57** (1908), 149.

(5) R. S. Williams, *Z. anorg. Chem.*, **55** (1907), 91.

and obtained a button and cupelled. The gold or the silver-gold bead thus obtained is weighed, and then dissolved in nitric acid (specific gravity, 1.18), and the remaining gold is washed with water, dried, heated and weighed as usual manner. It was confirmed that the initial lead-manganese couple contains no silver or gold by cupellation four times.

To test the accuracy of the method, artificially made sea waters were used, which contained some sodium chloride, potassium chloride, magnesium sulphate and potassium sulphate as well as known quantities of gold chloride. The results are given in the following table.

TABLE 1.

Solution	Gold added gr./l.	Temp.	% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Duration of exp. hr.	Gold obt. gr.	% of gold obt.	Gold calc. for 1000 kg. alloy gr.
Aq. sol.	2.7×10^{-4}	15°	2	18.00	1.3749	5	1.15×10^{-4}	19.7	81.7
Aq. sol.	,,	28°	2	17.96	1.4087	28	0.65 ,,	11.6	42.2
Sal. wat.	,,	18.5°	,,	53.90	4.2940	69	3. ,,	53.8	64.3
Sal. wat.	3×10^{-4}	18.5°	,,	27.72	1.4824	69	3. ,,	50.0	20.2

The volume of solution used in the experiment = 2 litres.
Aq. sol. = aqueous solution.
Sal. wat. = saline water.

Next, the natural sea water was tested which had been obtained at a point four miles off the coast of Kominato Bay, south eastern sea from Tokyo. The results are as follows.

TABLE 2.

% of Mn in alloy	Surface of alloy sq. cm.	Wt. of alloy gr.	Total duration of exp. hr.	Gold-silver bead obt. gr.	Gold obt. gr.	Gold calc. for 1000 kg. alloy gr.
8%	28.50	2.0284	641	27×10^{-6}	0.68×10^{-6}	3.4
8%	28.42	2.1000	641	77×10^{-6}	——	——
9.05%	34.40	4.9255	467	85.5×10^{-6}	——	——

Three litres of sea water was used each time, and after some hours it was thrown away and fresh sample of three litres of sea water was introduced into the vessel, and so on. By this manner the water was changed six times in each experiment, so in total eighteen litres of sea water was used. The weight of the bead, therfore, was obtained from 18 litres of the sea water.

Next, some excess gold was added to the Kominato Bay sea water and the gold content was raised to 37 mg. per one cubic meter, and the experiments were done using couples of various contents of manganese. The results are as follows.

TABLE 3.

% of Mn in alloy.	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Wt. of Au-Ag bead gr.	Wt. of gold gr.	Gold adhered on 1 sq. cm. of alloy gr.
			Before exp. gr.	After exp. gr.			
1	0.193	24.38	1.3384	1.3280	10 $\times 10^{-6}$	——	——
2	0.100	20.30	2.0307	1.9994	10.7 "	3.4 $\times 10^{-6}$	0.17 $\times 10^{-6}$
2	0.100	40.80	2.1191	——	16.5 "	6.6 "	0.16 "
3	0.075	36.40	1.5621	1.4984	31.7 "	9. "	0.27 "
4	0.113	26.40	1.6998	1.7109	390. "	18. "	0.68 "
4	0.156	30.32	2.7317	2.7552	770. "	30. "	0.97 "
4	0.130	99.76	7.5199	7.5656	113. "	43. "	0.43 "
5	0.060	46.00	1.6604	1.6649	80. "	15. "	0.32 "
6	0.096	42.78	1.8518	1.8396	34.2 "	10. "	0.25 "

The durations of these experiments were 100 hours, the temperatures, 10–20° C., and the volumes of the sea water, three litres. From these experiments it seems that the 4% alloy gives best result. The weight of alloy decrease in some cases, for the manganese oxidized and removed as oxide or hydroxide from the plate. I have collected the precipitate settled down to the bottom of the vessel, and obtained two samples, about 0.5 gr. in each case, and wrapped with a lead foil and heated with lead oxide in a crucible, and obtained a button and cupelled. In this way, a bead of gold or silver was not obtained. So it is clear that the gold or silver does not precipitate with the oxide or hydroxide of manganese.

Next, another experiment was done with sea water taken at Atami Bay which contained 3 mg. of gold in a cubic meter. And moreover, the experiments were extended to the waters which were made by adding some gold chloride to the Atami Bay water. The results are as follows:

TABLE 4.

Gold content mg. in cb. meter	Thickness of alloy mm.	Surface of alloy sq. cm.	Weight of alloy		Gold adhered gr.	Gold adhered on 1 sq. cm. gr.	Water
			Before exp. gr.	After exp. gr.			
3	0.07	37.4	2.6074	2.5232	2.3 $\times 10^{-6}$	0.06 $\times 10^{-6}$	Natural sea water
7	0.055	47.32	2.5440	2.5215	5. "	0.1 "	$AuCl_3$ was added
7	0.075	56.40	2.3453	2.3375	5.8 "	0.1 "	"
10.5	0.055	60.52	2.7027	2.6843	38. "	0.6 "	"
10.5	0.075	54.88	3.3650	3.3635	19.6 "	0.35 "	"
17.5	0.055	36.64	2.0430	2.0180	30.7 "	0.85 "	"
17.5	0.075	74.46	4.1990	4.1950	17.5 "	0.32 "	"
22.9	0.055	56.48	2.3032	2.3000	12.3 "	0.22 "	"
22.9	0.075	89.60	5.7268	5.7068	29. "	0.33 "	"
37	——	——	——	——	——	0.69 "	"

In these experiments an alloy of 5% manganese was used. Three litres of the waters were taken, the temperature of which was 23°C., and the duration of each experiment was 122 hours.

Theoretical Considerations. We will assume that an alloy plate is moving in the undisturbed solution containing some gold atom. The number of the gold atoms can be calculated as follows. It is known that 6×10^{23} atoms (Avogadro's number) exist in 179.2 grammes of gold. So the number of gold atoms in the sea water which contains a mg. of gold in one cubic meter is $6\times10^{23}\times a\times10^{-3}/197.2=3.07\times10^{18}\times a$. It becomes, therefore, in one cubic centimeter, $3.07\times a\times10^{12}$, and the gold atoms come to one square centimeter, or one side of the cube are,

$$(3.07\times10^{12}\times a)^{\frac{2}{3}}=1.486\times10^{8}\times a^{\frac{2}{3}}.$$

This is the number of gold atoms sweep over the metallic surface of one square centimeter and adhere on the surface. On the other hand, the weight of the single atom of gold is, $197.2\times1.66\times10^{-24}=0.33\times10^{-21}$ gr., where 1.66×10^{-24} is the weight of one atom of hydrogen. So the weight of gold sweep over the unit area of alloy surface is

$$0.33\times10^{-21}\times1.486\times10^{8}\times a^{\frac{2}{3}}=0.49\times a^{\frac{2}{3}}\times10^{-13}\text{ gr.}$$

If we suppose that the sea water contains 32 mg. gold in one cubic meter, or $a=32$, then the above quantity becomes 4.94×10^{-13} gr.

Assume the metallic surface moves in the water with the velocity of n centimeter per second and there precipitated b gr. of gold during h hours, then,

$$b=4.94\times10^{-13}\times n\times h\times3600\text{ gr.}$$

Now taking $n=3$, and $h=100$, it becomes,

$$b=0.54\times10^{-6}\text{ gr.}$$

This number approximately agrees with the experimental results. In the present experiment the water was stirred constantly with a stirrer, so the concentration of the gold decreases with time. Moreover, the factors such as the free path of ions, hydrodynamic conditions of flowing water on the surface and the influence of temperature must be considered. The above calculations, therfore, by no means an exact one, but only rough approximation.

It is probable that the colloidal gold in the sea water adheres also on the metallic plate for the particles have electric charges.

Summary.

It has been pointed out that the metallic alloy of manganese and lead is suitable to fish the gold from its very dilute solution such as sea water. The method of preparation and the composition of the alloy have been described. The efficiency of its action has been studied.

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