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# Studies of Lead-complex Formation in Sea Water by Anodic Stripping Methods

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**Synopsis.** For the purpose of the determination and chemical speciation of trace lead in sea water by the use of an electrolytic concentration technique, the effects of the pH on the reduction potential of lead ions in the presence of various organic and inorganic ligands were investigated. In the pH range below *ca.* 5, the lead–chloro complex is dominant in sea water. Even in the presence of organic model ligands such as nitrilotriacetic acid (NTA), the electroactive species of lead was also its chloro complex when the sample solution was acidified enough below pH 2.

From the viewpoint of the electroanalytical studies of trace metals in natural waters, much attention has been paid not only to the total metal concentration, but also to the chemical speciation of the respective metals.[1] Particularly, for the direct identification of the metal complex in a very dilute solution *via* estimations of the ligand number and the complex stability constant, so-called "pseudo-polarography"[2,3] is one of the most promising methods; that is, the anodic stripping peak currents plotted as functions of the cathodic deposition potentials. The complexation of trace metals with organic ligands in natural waters has come to be of great interest in recent years.

We have developed an automatic coulopotentiographic analyzer system by utilizing several flow-electrolysis cells, and applied it to the analysis of trace lead and copper in sea water.[4] It was confirmed, by this method, that these metals at sub-ppb levels in sea water could be determined without any standards, and that the amounts of these metals determined depended remarkably upon the pH of the acidification of the sample sea water. This effect of pH seemed to be attributable to the distribution of the chemical species of these metals.

In this paper, we studied the relationships between the half-wave potential ($E^*_{1/2}$) of the pseudo-polarogram of lead and the pH of the solution in the presence of various organic and inorganic ligands in order to confirm the analytical conditions for the stripping coulopotentiographic determination of total lead and in order to clarify the distribution of chemical species of lead in sea water.

## Experimental

*Apparatus.* The stripping voltammograms were recorded with a Yanagimoto voltammetric analyzer, model P-1000, and a National Pen-Recorder, model VP-654A. A three-electrode system was used; the working electrode was a hanging mercury drop electrode (Princeton Applied Research HMDE), and the potentials were controlled against an Ag/AgCl (saturated NaCl) reference electrode, with a platinum wire as an auxiliary electrode. During the pre-electrolysis stage, the sample solution was stirred for 5 min with a Yanagimoto magnetic stirrer, model MS-60, with a Teflon-covered stirring bar.

*Reagents.* The sodium perchlorate and humic acid were purified by the use of chelate or ion-exchange resins respectively. All the other chemicals used were of an analytical-reagent grade. Deionized water, after having been distilled from an all-quartz distillation apparatus, was used throughout for all the reagents. The sea-water sample was taken from the surface region of the Pacific Ocean off Wakayama and was filtered with conditioned 0.4 μm Nuclepore membrane filters.

*Procedures.* The pseudo-polarographic measurement consisted of the following stages, as usual: (1) to a 20 $cm^3$ base solution with adjusted pH in the electrolysis cell, we added 0.01 $cm^3$ of $1\times10^{-4}$ mol $dm^{-3}$ lead standard solution; (2) we passed nitrogen gas into the solution for 10 min (30 s for each subsequent run); (3) after renewing a mercury drop and setting the deposition potential, we pre-electrolyzed the solution for 5 min; (4) after stopping the stirrer and letting the solution equilibrate for 10 s, we recorded the anodic stripping voltammogram of lead ions at the scan-rate of 5 mV $s^{-1}$; (5) after changing the deposition potential, we repeated the procedures from Stage (2). Finally, each stripping current was plotted as a function of the corresponding deposition potential; that is, a pseudo-polarogram of lead was obtained. This pseudo-polarogram was then analyzed analogously to the classical d.c. polarogram, and its half-wave potential ($E^*_{1/2}$) was estimated.

## Results and Discussion

In order to investigate the effects of the anions of the supporting electrolyte on the reduction potential of lead, the pseudo-polarogram of lead was measured in model solutions containing different supporting electrolytes at the ionic strength of 0.7, such as sodium perchlorate ($ClO_4^-$ system), sodium chloride ($Cl^-$ system), and sodium acetate plus acetic acid ($CH_3COO^-$ system). Figure 1 shows the shift in $E^*_{1/2}$ with the pH of a lead solution containing a different supporting electrolyte. In the $ClO_4^-$ system, the free lead ion is a dominant species in the pH range up to *ca.* 4. The negative shift of the half-wave potential with an increase in the pH is attributable to the formation of lead-hydroxy complexes. In the case of the $Cl^-$ system, the lead ion preferentially forms chloro complexes ($K_1=10^{1.6}$, $K_2=10^{0.8}$) up to pH *ca.* 5, and then the half-wave potential shifts remarkably toward the negative side. The lead ion also forms weak complexes with the acetate anion in the pH range between 4 and 8 ($K_1=10^{2.4}$, $K_2=10^{1.5}$). The difference in the half-wave potentials between the $Cl^-$ system and the $CH_3COO^-$ system, −46 mV, was in good accordance with that calculated, *ca.* −44 mV, from the difference in the stability constants between the two complexes.

Figure 2 shows the shift in $E^*_{1/2}$ as a function of

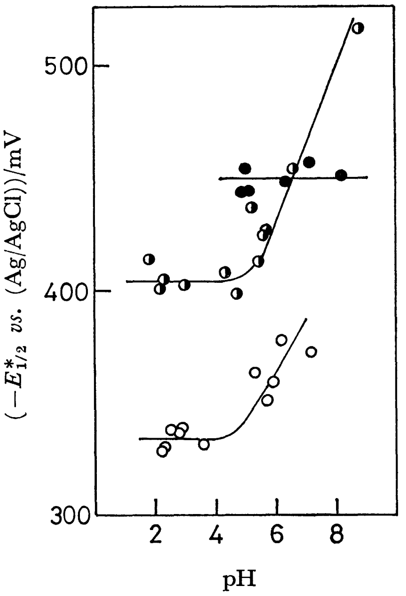

Fig. 1. Effect of pH on the $E^*_{1/2}$ values for the lead stripping peaks in model solutions (ionic strength= 0.7).

○: Sodium perchlorate, ◑: sodium chloride, ●: acetic acid+sodium acetate.

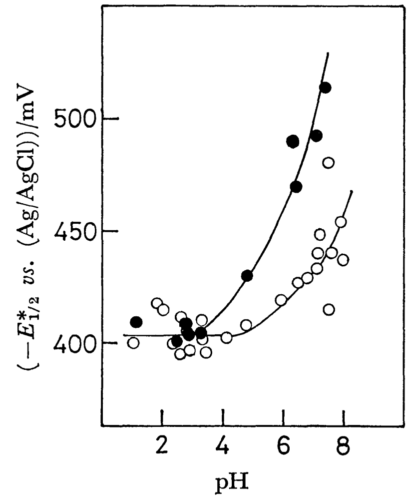

Fig. 2. Effect of pH on the $E^*_{1/2}$ values for the lead stripping peaks in sea water.

○: Sea water, ●: sea water with $5\times10^{-5}$ mol dm$^{-3}$ NTA.

the pH of sea water with or without the co-presence of the organic model ligand. The half-wave potential of lead in sea water was close to that in the $Cl^-$ model system. However, the negative shift of the former was not so much as the latter at pH values greater than about 5. When the sea-water sample was pretreated with acetic acid, no notable shift of the half-wave potential was observed, not even in the presence of 0.1 mol dm$^{-3}$ of acetic acid. For a detailed discussion of these phenomena, a more complicated metal complexation equilibrium should be taken into consideration for that complicated multicomponent system, sea water.

The complex-formation effects with organic ligands on the half-wave potential of lead were investigated in the same way using model ligands, such as NTA, cysteine, ethylenediaminetetraacetic acid (EDTA), and humic acid. As is shown in Fig. 2, in the co-presence of NTA, the electroactive species of lead also consisted of lead–chloro complexes when the pH of the sea-water sample was adjusted to below *ca.* 3. Cysteine behaves in a manner similar to NTA, while in the presence of EDTA, no definite stripping peak of lead was observed, not even by acidification to pH 3. Because of the stability constant of lead–EDTA ($K_1=10^{17.0}$), larger than those of lead–NTA ($K_1=10^{10.6}$) and lead–cysteine ($K_1=10^{13.2}$), this method is inapplicable to the study of lead–EDTA complexes.[5] However, the quantitative electrolysis of lead–EDTA can be performed by acidification with hydrochloric acid to pH 1.0. Concerning humic acid, the half-wave potential of lead was similar to that with NTA in a pH range up to *ca.* 3. In the higher pH range, however, no well-defined pseudo-polarogram of lead was obtained, though the stripping peaks were observed. The electrode process of lead reduction in the presence of humic acid seems to become rather complicated, as a result of the adsorption effect of humic acid on the electrode surface, *etc.*[6]

In conclusion, various chemical species of lead are distributed in sea water, and most of the organic and inorganic ligands of lead complexes can be replaced by chloride anions by acidification to pH 1.0. As a result, the pretreatment of the sea-water sample by acidification with hydrochloric acid to pH 1.0 is effective for the electrochemical determination of the total lead concentration in sea water at sub-ppb levels. For a quantitative discussion about metal complexation, it will be necessary also to take into account such effects as the reversibility of the electrode reaction and adsorption phenomena.

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