Metal-Organic Complexes in Seawater Pumped up from under the Ground*

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Abstract: Metal-organic complexes of transition elements removed by Amberlite XAD-2 resin from seawater pumped up from under the ground were determined. The proportions of iron, copper and zinc retained on the resin to dissolved forms of these metals were about 70, 40 and 5%, respectively, while manganese, cobalt and nickel were not retained on the resin. These results suggest that although iron may be retained in colloidal form, a significant fraction of copper is present in some organic forms.

1. Introduction

In a previous paper (Takematsu et al., 1981), the distribution coefficients of transition metals between manganese oxides and seawater were measured in the seawater supply system of the Marine Science Museum, Tokai University, Miho, Shimizu City, Shizuoka Prefecture, Japan. The observed distribution coefficients were comparable to those obtained in laboratory experiments (Takematsu, 1979), except for copper for which the distribution coefficient of the former was much smaller than that of the latter. This discrepancy may be due to the presence of copper-organic complexes in the seawater. In this paper, metal-organic complexes of transition elements in the same seawater are investigated in order to understand their influence on sorptive behavior of metals to manganese oxide phases.

2. Materials and methods

2.1. Sampling

The water supply system for the aquarium of the Marine Science Museum, Tokai University (Fig. 1) includes a tank with four compartments for removal of manganese oxides formed in the seawater.

Seawater was sampled from each compartment using a polypropylene bellows pump connected to Tygon tubings with a plastic holder containing a prewashed Whatman GF/F glass fiber filter attached to the outlet tubing. Water samples were analyzed immediately after sampling without addition of acid, except for those measured by the APDC-DDDC solvent extraction method, which were stored for more than 2 months at pH 2 after addition of 6 M HCl.

2.2. Reagents and columns

The reagents used, unless otherwise stated, were guaranteed ones for harmful metal measurement (Wako Pure Chemical Industries). Water purified by a Milli-Q (Millipore Corp.) and Pyrex glass columns (26 mm in diameter and 20 cm in length) were used in the experiments.

Amberlite XAD-2 resin columns were prepared by loading 75 ml aliquots of the resin in the columns. After removal of the finer fraction by decantation in water, the resin was cleaned in a large column by successive treatment with acetone, 2 M HCl, water, 2 M NH₄OH and finally with water until the pH of the washings dropped below 9.

Chelex-100 resin columns were prepared according to Bruland et al. (1979), except that the diameter of the column (26 mm) and the volume of the resin (75 ml) differed.

2.3. Procedures

Metal-organic complexes were determined using a slight modification of the method of Sugimura et al. (1978a). Twenty liters of filtered seawater (pH ca. 7.8) were passed through the two successive XAD-2 resin columns at a flow rate of 5-6 ml min⁻¹ for the adsorption of metal-

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organic complexes. After thorough rinsing with water, the adsorbed metals were eluted first with 2 M HCl (100 ml) and then with 2 M HNO₃ (150 ml). After addition of perchloric acid (2 ml), the effluent was evaporated almost to dryness. The residue was dissolved with 0.3 M HNO₃ (10 ml) and analyzed for transition metals by atomic absorption spectrometry.

To determine dissolved metal concentrations, the following three methods were used for comparison: (1) oxine-XAD-2 method (Sugimura et al., 1979); (2) Chelex-100 method (Riley and Taylor, 1968; Kingston et al., 1978) and (3) (APDC-DDDC)-chloroform extraction method (Bruland et al., 1979).

Oxine-XAD-2 method: Ten ml of 3% oxine in dilute acetic acid (1:1) (which was prepared from Merck guaranteed oxine and Merck Suprapur acetic acid) was added to 20 liters of filtered seawater, and the pH of the seawater was adjusted to 8 with dilute ammonia water (1:1). After this, procedures were the same as those in the XAD-2 method described above.

Chelex-100 method: Twenty liters of filtered seawater without pH adjustment were passed through the duplex resin column at a flow rate of 5-6 ml min⁻¹. The Chelex-100 column was subsequently rinsed with 1 M ammonium acetate (which was prepared from Merck Suprapur acetic acid and ammonia water) to remove large amounts of Ca and Mg from the column (Kingston et al., 1978). Subsequent procedures were the same as those for the XAD-2 method described above.

(APDC-DDDC)-chloroform extraction method: Two liters of acidified seawater (pH 2) were transferred to each of four 3-liter separatory funnels and buffered to pH 5 by addition of 30 ml of 5.5 M ammonium acetate. After addition of 20 ml of a complexing agent solution (1% each of APDC and DDDC), metal complexes were extracted first with 50 ml and then with 30 ml of chloroform. The combined chloroform extracts from the four separatory funnels were evaporated to dryness in a quartz beaker, and 5 ml of HNO₃ and 2 ml of HClO₄ were added to decompose organic matter. On almost reaching dryness, the residue was dissolved with 0.3 M HNO₃ and analyzed.

2.4. Precision

Duplicate analyses were made for each sample in the case of the Chelex-100 and the solvent extraction methods and pooled relative standard deviations (Bruland et al., 1979) were calculated. The pooled relative standard deviation of the Chelex-100 method was 14, 11, 8.3, 18 and 13 %, and that of the solvent extraction method 12, 9.5, 6.8, 15 and 7.5% for Fe, Co, Ni, Cu and Zn, respectively. Estimation of the precision of the XAD-2 method could not be made due to the lack of duplicate analyses. However, the precision of Cu and Zn may be estimated to be within 25%, if the four samples analyzed (i.e., PT 1 to PT 4) are regarded as one sample.
3. Results and discussion

3.1. Blanks

The blanks given in Table 1 include all of the metals in the reagents and introduced during operational procedures.

In the column methods, two columns were always connected in series and the lower one was used to determine the blanks. After the passage of sample water through the duplex column, the lower column was disconnected and processed in the same way as the upper sample column. In the case of the oxine-XAD-2 method, however, 10 ml of 3% oxine solution and 6 ml of dilute ammonia water (1:1) were added to the effluent from the lower column in order to determine the reagent blank. In the solvent extraction method, blanks were determined by extracting previously-processed seawater following the normal extraction procedure.

There is a possibility that the metals in sample water escape from the first column or remain after the first extraction and that they are captured on the second column or are extracted by the second extraction for the determination of the blanks. The increase in the blanks due to this effect is difficult to estimate but will have little influence on our results, although the high blanks for iron relative to those for copper may...
Table 3. The retention and recovery of transition metals by the oxine-XAD-2 method*.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention (%)</td>
<td>95</td>
<td>—</td>
<td>99</td>
<td>98</td>
<td>99</td>
<td>95</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>110</td>
<td>—</td>
<td>6.5</td>
<td>94</td>
<td>85</td>
<td>99</td>
</tr>
</tbody>
</table>

* Retention (%)=(A0−A1)×100/A0; Recovery (%)=A2×100/A0, where A0, A1, and A2 are the amounts of metals loaded on the column, those found in the solution passed through the column and the rinse, and those found in the effluents of 2 M HCl and 2 M HNO3, respectively. Average of 4 replicate determinations are given.

be due to this effect.

The meaning of the blanks in the XAD-2 method for the determination of organic metals is somewhat different from the others, since the blanks in the XAD-2 method include inorganic metals in the sample water, which are trapped by polar impurity groups in the XAD-2 resin (Mackey, 1982a, 1982b). This problem is discussed later in section 3.3.

3.2. Comparison of the results
As shown in Table 2, the concentrations of dissolved transition metals obtained by the three preconcentration methods almost coincide with each other, except for cobalt. In order to investigate the cause for the lower concentration of cobalt obtained by the oxine-XAD-2 method, the following experiment was carried out. A 200 ml Milli-R/Q water solution containing known amounts of transition metals (0.025 mg in dilute hydrochloric acid) and oxine (0.3 g in dilute acetic acid) was buffered to pH 8 with dilute ammonia water and passed through a XAD-2 resin column (75 ml). The column was rinsed with 250 ml of water. The solution that passed through the column and the rinse were combined. After addition of 2 ml of concentrated HClO4, the solution was evaporated to dryness. The residue was dissolved in 0.3 M HNO3 (10 ml) and determined for metals by atomic absorption spectrometry. The metals retained on the resin were determined as described before. The results (Table 3) revealed that cobalt on the resin was not eluted quantitatively with 2 M HCl or 2 M HNO3, hence the method was not suitable for the determination of cobalt.

3.3. Metal-organic complexes
The proportions of iron, copper and zinc determined by the XAD-2 method to dissolved ones were about 70, 40 and 5%, respectively. Manganese, cobalt and nickel were not retained on the resin. These percentages are lower than those reported by Sugimura et al. (1979), but their order (Fe>Cu>Zn) is the same, with the exception of cobalt. The great discrepancy in cobalt may be due to the deficiency in the oxine-XAD-2 method used by Sugimura et al. (1979), as described above.

Whether all the metals obtained by the XAD-2 method are present in organic form or whether all the metals in organic form are retained on the resin is a matter in dispute (Mantoura, 1981). Mackey (1982a; 1982b) reported the unsuitability of XAD-2 resin for extracting organic complexes of trace metals quantitatively because of the presence of polar impurity groups in the resin itself, which are capable of removing inorganic ions from aqueous solutions. His experiments, however, seem to show that inorganic copper and zinc can be retained in equal efficiency on two columns connected in series, suggesting that the inorganic ions adsorbed on the upper column can be corrected for by those adsorbed on the lower one. In the present experiment, the blank correction was made on the basis of the amount retained on the second column, hence the results of copper given in the column headed XAD in Table 2 may be present in organic form. Some organic matter such as humic substances are not adsorbed on XAD-2 resin at neutral pH. If copper is bound to such organic compounds, the actual amounts of organic copper in the seawater may be higher than those obtained here.

Sugimura et al. (1978b) regarded the iron retained on XAD-2 resin as organic iron, while Mantoura (1976) showed that colloidal iron particles might be trapped by XAD-2 resin. Until this problem is resolved, it is not certain whether the iron retained on XAD-2 resin is present in organic form. The presence of organic zinc is not certain because of error in the determination.
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沿岸の井戸から汲み上げられた海水中の有機態遷移元素

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要旨: 地下から汲み上げられた海水における有機態遷移元素の存在状態をアンバーライトXAD-2樹脂を用いて調べた。

XAD-2樹脂に捕捉された鉄、鈷および亜鉛の溶存態のそれらに対する割合は、それぞれ、約70, 40および5パーセントであった。一方、マンガン、コバルトおよびニッケルはこの樹脂に捕捉されてなかった。XAD-2樹脂に捕捉された元素のうち、鈷の場合にはコロイド状態の鉄が捕捉されている可能性があるが、鈷のかなりの部分は有機態で存在しているものと考えられる。