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Determination of Organically-bound Iron in Fresh and Coastal Sea Waters

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Abstract

Analytical conditions for the determination of organically-bound iron in natural waters were examined and the procedure was applied to river, lake and coastal sea waters. By using the method, organically-bound iron was found in fresh and coastal sea waters.

Introduction

Iron and manganese are considered to be very important elements for the growth of phytoplankton. Dissolved heavy metals in natural waters are present in the forms of cations or as complexed compounds with inorganic or organic ligands. The main organic substance in river and lake waters is humic substances which closely resemble soil fulvic acid.¹⁻³⁾ It has been reported that humic substances in natural waters combine with metals.^{4,5)}

Iron in natural waters was associated with organic materials⁶⁾ and humic acid-Fe complex was formed at a indoor experiment.⁷⁾ Figueres et al.⁸⁾ reported that iron passed through a filter with a 0.025 μm pore size in river water diffuses by only physical water mixing into coastal water and assumed that the iron complex was organically-bound iron.

Humic substances have many carboxyl groups with a dissociation constant of $\text{pK}_a=4.2$.⁹⁾ Thus, the substances almost dissociate in natural waters at about pH 6 and then the substances and their metal complexes possess negative charge. The iron complex with negative charge would be exchangeable with an anion exchange resin. By using the resin, about half of copper in Lake Ohnuma was found to be associated with fulvic acid and also this result was in good accordance with thermodynamic calculations¹⁰⁾.

In this paper, the analytical conditions for the iron complex are investigated and the method was applied to natural waters.

Experimental

Analytical procedure

Reagents

Ferrozine solution: Dissolve 0.514 g of 3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2,4-triazine (ferrozine) and 10 g of hydroxylamine hydrochloride in a small amount

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of water. Add 50 ml of conc. hydrochloric acid and dilute to 100 ml with water. Buffer solution: Dissolve 40 g of sodium acetate in 35 ml of 25% ammonium hydroxide and dilute to 100 ml.

Analytical procedure

Filter a sample through a Membrane filter with a pore size of $0.45 \mu\text{m}$. Pass 50–200ml of the filtrate through a column of the anion exchange resin (Dowex 1 \times 8) with a flow rate less than 5 ml/min. After washing out the column with water, elute the iron complex with 40 ml of 1 M hydrochloric acid solution. After neutralizing the solution with aqueous ammonia to pH 6–8, measure iron by the method of Stookey¹¹⁾. The outline is as follows. Add 1 ml of the ferrozine solution to the neutralized solution and boil at 100°C for 10 min. Add 1 ml of the buffer solution and dilute to 50 ml with water. Measure the absorbance at 562 nm with a spectrophotometer.

Analytical conditions

Effect of a flow rate

Analytical conditions were examined with filtered river water. 200 ml of the filtrate was passed through the column with various flow rates. As shown in Fig. 1, a constant absorbance was obtained in the flow rate range between 1 and 5 ml/min.

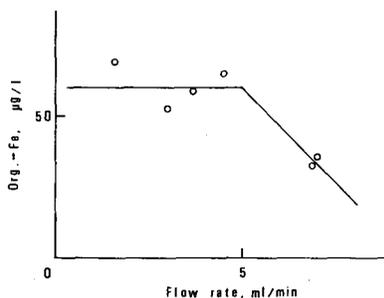


Fig. 1 Effect of flow rate

Effect of salt

The river water was passed through the column and 0.6 M sodium chloride solution was passed the column. If the iron complex was exchanged by chloride ion, the iron complex would be detected in the sodium chloride solution. However, the iron was not detected in the solution. Thus, there is no effect of salt on the exchange of the complex by using the resin.

Precision

The reproducibility of the method was determined by using river water (Table 1). The relative standard deviation for 6 replicate determinations was 15% at 95% confidence limits.

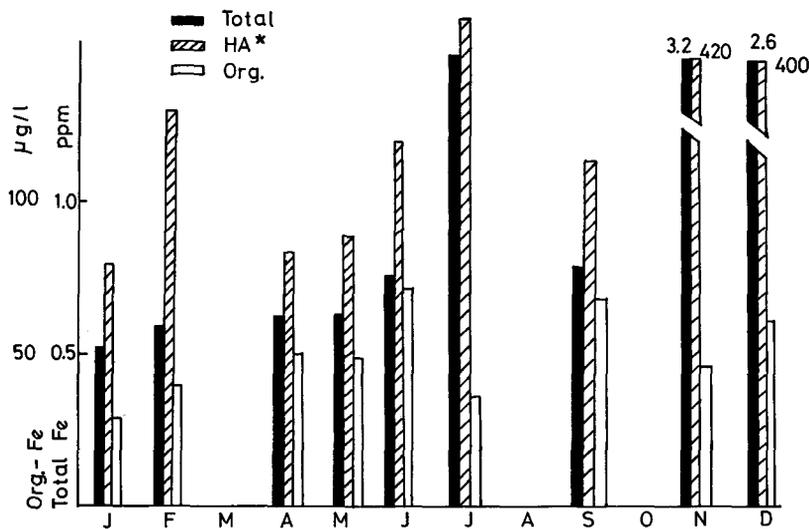
Application to river water

River waters were sampled from the Kunebetsu River thorough a year and some forms of iron were determined. Total iron in raw sample, soluble

Table 1. Precision of the determination of the iron complex

Column No.	Absorbance	Org.-Fe ($\mu\text{g/l}$)
1	1.34	135
2	1.26	127
3	1.61	163
4	1.68	170
5	1.23	124
6	1.36	137

$\mu = 143 \pm 20 \mu\text{g/l}$
(confidence limits at 95%)



* Iron in filtrate passed through an HA type filter

Fig. 2 Seasonal variations in the concentration of some forms of iron in the Kunebetsu River

iron (passed through the filter) and the iron complex were determined according to the analytical procedure. Total and soluble iron changed considerably but the iron complex concentration showed a nearly constant value, 50 $\mu\text{g/l}$ (Fig. 2).

Application to lake water

The iron complex in Lake Ohnuma and the Shukunohe River which flows into the lake was measured through a year. The iron complex concentration in the lake shows a lower concentration, almost zero, during a period from spring to autumn than that in the river. On the other hand, in winter which has an almost zero primary productivity, the iron complex concentration becomes equivalent to that in the river. The iron complex shows the same behavior as nitrate in the lake.

Fig. 3 shows the ratios of the iron complex, nitrate in the lake to those in the river. Their concentrations in the lake are near to that in the river if their loss in the lake does not occur. In the lake, however, nitrate decreases from spring

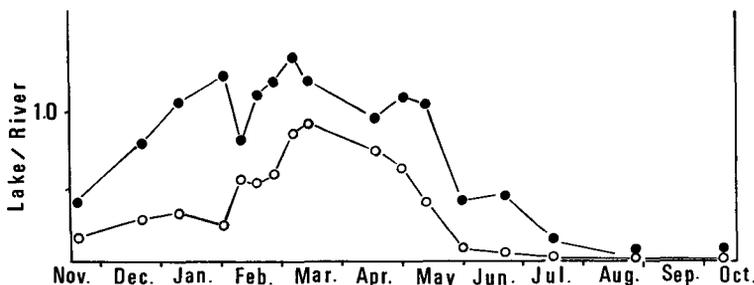


Fig. 3 Ratios of the iron complex, nitrate in Lake Ohnuma to those in the Shukunohe River

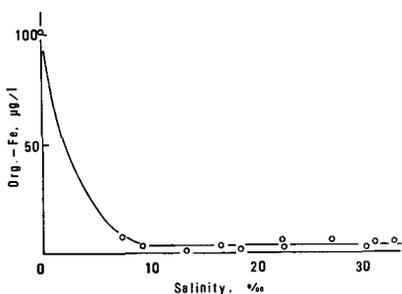


Fig. 4

Fig. 4 Relationship between the iron complex and salinity

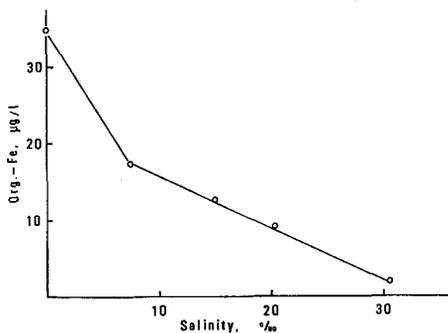


Fig. 5

Fig. 5 Relationship between the iron complex and salinity

because of consumption by phytoplankton and increase again from early winter, that is, the iron complex shows the same behavior as nitrate. From a growth rate of phytoplankton and these results it is assumed that the iron complex is utilized by phytoplankton¹²⁾.

Coastal sea waters were sampled from the estuary at the Kunebetsu River. Immediately samples were filtered through the filter and the iron complex was analyzed by the above analytical procedure. Figs. 4 and 5 show the relationship between the iron complex and salinity. In the case of Fig. 4, the iron complex considerably decreases at 10‰ salinity, but the iron complex diffuses with physical water mixing from 10‰ to higher salinity. There are two patterns in the relationship, but its reason is not clear. Next, the behavior of the iron complex in coastal sea must be studied.

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