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Beryllium in Sediments of Nagoya Harbor Estuaries

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Beryllium occurs naturally in minerals and soils. Other than the natural sources, considerable quantity of beryllium has been discharged from its smelting industry. Soil pollutants caused by beryllium in the circumference of its smelting industry on the banks of Nagoya harbor estuaries were reported by Asami & Fukazawa (1981). Adam et al. (1952) and Shigematsu & Tashiro (1959) reported the spectrophotometric determination of beryllium using chloroform extraction of an acetylacetone complex. Merill & Honda (1960) applied this method to the determination of beryllium in sediments. Willis (1965) and Amos & Willis (1966) reported a much more sensitive method for the determination of beryllium by atomic adsorption spectroscopy in nitrous oxide acetylene flame. However, Fleet et al. (1970) showed the considerable influence of aluminum and other metals, and Matsuzaki (1975) proposed the introduction of the organic phase into nitrous oxide acetylene flame by using methylisobutylketone extraction with acetylacetone for the elimination of the interferences. This method has been widely used for the determination of beryllium in soils (Asami 1975) and biological samples (Yamanobe et al. 1977) and geological samples (Terajima 1982).

However, several methods mentioned above can not eliminate the interference caused by fluoride ion which remains in the digestion solution when hydrofluoric acid is used to degradate the silicate lattice. Accordingly, we attempted to improve the pretreatment in order to eliminate the effect of fluoride ion, and to make the procedure simpler and faster with high precision. A simple and sensitive method is presented for the determination of beryllium in sediments by atomic absorption spectroscopy using methylisobutylketone extraction with acetylacetone. We have carried out an extensive investigation on the pollution of sea water and sediments of Nagoya harbor estuaries, which is located in one of the most active industrial areas in Japan. We applied the method described above to the determination of beryllium in the estuarine sediments in Nagoya harbor.

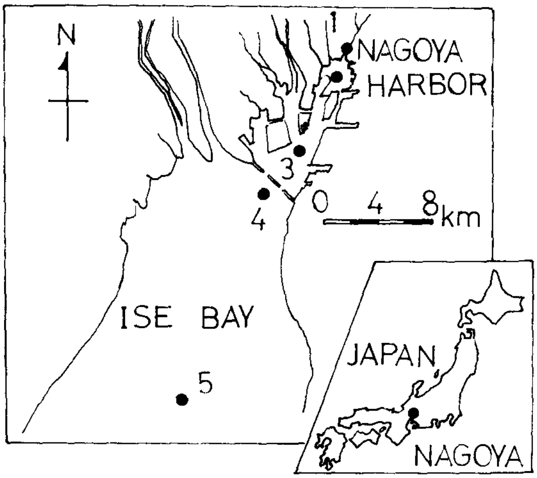

Figure 1. The sampling location for sediments in Nagoya harbor estuaries.

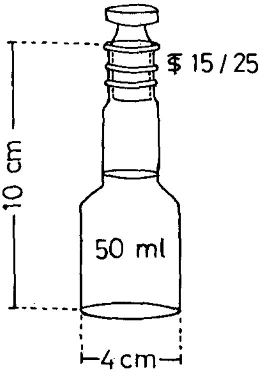

Figure 2. Volumetric flask.

MATERIALS AND METHODS

The sampling locations for the sediments in Nagoya harbor estuaries are shown in Figure 1. Sedimentary cores about 50 cm long and 10 cm in diameter were collected from a site (No. 1) in Nagoya harbor. The core samples were cut vertically into 1 cm sections immediately after the collection for chemical analysis. Sediment samples No. 2-4 were taken by using an Ekman grab sampling device on a boat in estuaries, (Summer 1984), and sediment sample No. 5 was taken from a site (35°11'N, 136°12') which is located near the central part of Ise Bay, (September 1982).

Sediment sample (1.0 g) was placed in a teflon beaker, and hydrofluoric acid (10 ml) and nitric acid (5 ml) were added and the mixture was heated mildly and evaporated to almost dryness on the hot plate. Then nitric acid (10 ml), perchloric acid (5 ml) and sulfuric acid (1 ml) were added to the mixture. The digestion was carried out until white fumes of the perchloric acid appeared and the heating was continued for further 30 minutes to remove hydrofluoric acid. The digestion mixture was heated for 5 minutes with hydrochloric acid (5 ml) and filtered through a filter paper after cooling. The digested solution was diluted to 50 ml. Then 5-20 ml of the resulted solution was transferred quantitatively in a 50 ml of volumetric flask (Figure 2). Ten ml of 20 % disodium ethylenediaminetetraacetate(EDTA) and 5 ml of 25 % ammonium acetate buffer solution (pH 8) were added to the sample solution, and pH of the solution was adjusted to 8.0-8.5 with ammonium hydroxide.

Two ml of 10 % acetylacetone and 5 ml of methylisobutylketone were added, and the mixture was shaken vigorously for 3 minutes. Beryllium extracted in the methylisobutylketone layer, was determined by atomic absorption spectroscopy, under the conditions of

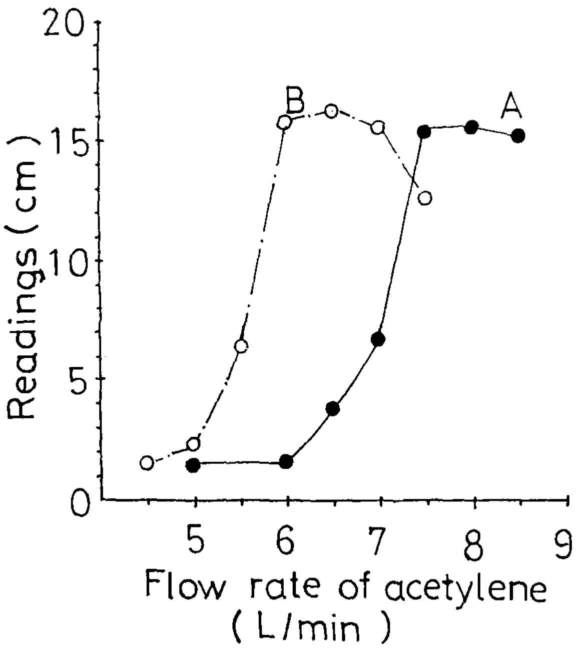

Figure 3. The effects of flow rate of acetylene on sensitivity.

A: 1.5 µg of beryllium per 1 ml of 0.1 N HCl.
B: 0.5 µg of beryllium per 1 ml of methylisobutylketone.

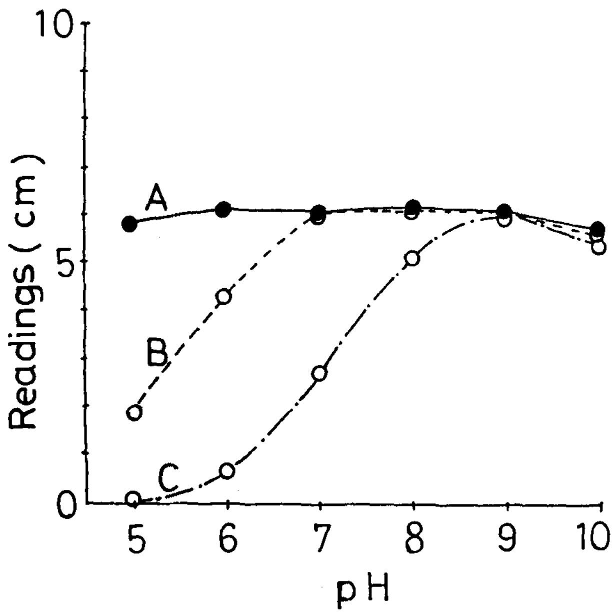

Figure 4. The effects of pH and fluoride ion on the extraction of beryllium acetylacetone complex.

A: 0.5 µg of beryllium without fluoride ion.
B: 0.5 µg of beryllium with 1 mg of fluoride ion.
C: 0.5 µg of beryllium with 10 mg of fluoride ion.

the acetylene flow of 6-7 L/min and the nitrous oxide flow of 8 L/min. A calibration curve was linear in the range of 0.01-1.0 µg of beryllium per 5.0 ml of methylisobutylketone.

RESULTS AND DISCUSSION

According to Amos & Willis (1966), for the measurement of beryllium with high sensitivity, the acetylene flow should be adjusted to give the desired flame with a 10-25 mm red feather, which is generally somewhat fuel rich. As shown in Figure 3, in the case of spraying the organic phase, the acetylene flow rate to give the desired flame, was smaller than in the case of spraying the aqueous phase. The conditions of the flame described above was found to be the best, after several examinations.

The extraction of beryllium acetylacetonate is carried out in the presence of EDTA in order to prevent the coextraction of iron and aluminum in the geological sample. It was reported by Asami (1975) and Terajima (1982) that recovery of beryllium is low in the presence of large amount of iron and aluminum which gives rise to a precipitate on neutralization of the digested solutions even in the presence of EDTA. Reported by Asami (1985), the addition of 10 g of EDTA was necessary to avoid a precipitate when ammonium hydroxide was added to the digested solution in the presence of 200 mg of iron and aluminum. However, excess of EDTA reduced the recovery, based on the complexing of beryllium with EDTA. When the amounts of iron and aluminum in sediments are in the range of 10-20 mg in the sample taken for the determination of beryllium, the interference of these metals can be eliminated by the addition of 2 g of EDTA.

Terajima (1982) reported that fluoride ion remaining in the digested solution of geological sample decreases the extractability of beryllium acetylacetonate when hydrofluoric acid is used. The effects of pH and fluoride ion on the extraction of beryllium acetylacetonate are shown in Figure 4. Without the addition of fluoride ion, the effect of pH on the extraction of beryllium acetylacetonate was slight in the range of pH 5-9. However, the effect of fluoride ion was not negligible at pH below 7, when its amount was more than 1 mg. In the presence of 10 mg of fluoride ion, beryllium was not extracted in organic phase in the range of pH 5-6. The complex of beryllium and acetylacetone increases with pH value in the range of pH 5-9, but that of beryllium with fluoride ion is not affected by pH. The interference of fluoride ion was eliminated by extracting beryllium at pH 8.0-8.5. The results in marine sediment, NRC MESS-1 (Marine Sediment Reference Materials), obtained by our analysis method were 2.11 ± 0.05 µg/g (mean ± s.d., n=3). The certified value for NRC MESS-1 is 1.9 ± 0.2 µg/g. Both values agreed with acceptable precision.

We applied the determination method described above to the determination of beryllium in the sediments of Nagoya harbor estuaries. The results are shown in Table 1. In order to investigate the

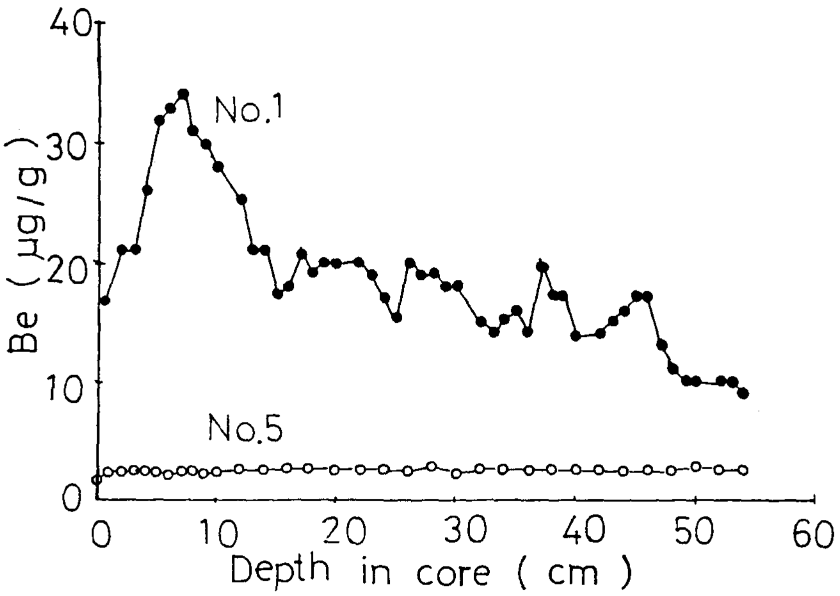

Figure 5. Vertical profiles of the concentration of beryllium in Nagoya harbor estuaries.

Table 1. Beryllium contents of sediments in Nagoya harbor estuaries.

No.	Be (μg)
1	16.1
2	3.9
3	2.5
4	2.8
5	1.9

pollution status, we have chosen five points for sampling, as shown in Fig. 1. No. 1 is located in the mouth of the most dominantly polluted river in Nagoya city and is located 4 km downstream of a beryllium smelting industry which stopped its operation in 1975. The amount of beryllium in No. 1 was the largest, whereas the amounts of other points were close to background value of beryllium in marine clay, that is generally known to be about 2.6 μg/g. Vertical profiles of the concentration of beryllium in sedimentary cores are shown in Figure 5. The core sample, No. 1 has partially irregular strata. It means that the sedimentary strata near the point, No. 1 have been agitated and mixed by physical and biological mixing processes. In fact, the point, No. 1 is located in the mouth of the river where the water current is disordered. However, the concentration of beryllium in No. 1 increases with depth till 8 cm from the surface layer. The maximum concentration was 35 μg/g at a layer of 8 cm in depth and the concentration of the surface layer was 16 μg/g. In layer deeper than 8 cm, the concentration of beryllium tended to decrease with depth. In layer deeper than 50 cm the concentration of beryllium was 9 μg/g. Whereas, the concentration in any layer of No. 5 was close to background value in marine clay. The point, No. 5 is located near the central part of Ise Bay and the current of water is moderate. The sample core consists of regular strata. These results indicate that the beryllium pollution of Nagoya harbor extuaries can be attributed to the beryllium smelting industry, and since its operation was closed in 1975, the beryllium content became lower in the surface layer. This result indicates that beryllium has been accumlated in the sediments in the mouth of the river and not spread in the estuaries and Ise Bay.

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