V. 5.   Development of Monitoring System of Aqueous Environment by PIXE VII: Identification of Oxidation States of Trace-Level Arsenic in Environmental Water Samples

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Introduction

A large amount of hazardous chemicals is discharged into the environment in the process of industrial activities.   Thus water quality monitoring becomes increasingly important as we must use new water resources such as deep underground water.   The environmental degradation due to inclusion of a harmful element into flora and fauna strongly depends on the element's oxidation state.   In monitoring pollution, it is thus necessary to determine both the quantity and the chemical state of a harmful element in environmental samples.   Arsenite is more toxic than arsenate to the metabolism of flora and fauna and in Japan the quality limit of environmental water samples is legally set to lower than 10 ppb (ng/ml) for arsenic irrespective of the valence state[1].   However complex separation and pre-concentration procedures are required in order to determine arsenic concentrations below 10 ppb in environmental water samples by using the spectrophotometric method, graphite furnace atomic absorption spectroscopy or induced coupled plasma atomic emission spectroscopy[1-5].   PIXE using 3 MeV protons offers high sensitivity for arsenic[6]. Chemical state analysis of elements in percent-level concentrations can be determined by using the wavelength-dispersive PIXE technique, but this technique cannot be applied to assay the oxidation state of arsenic at trace level concentrations[7-8].

Experimental

An enhanced sample preparation method for PIXE analysis was developed for assaying the oxidation state of arsenic ions dissolved in water samples.   Trivalent AsO_3^{3-} and pentavalent AsO_4^{3-} ions are separately adsorbed at pH 4 with indium hydroxide colloids,

generated in the solution by adding competing ions of the sorption reaction such as sulfates and phosphates. PIXE analyses of the two kinds of targets reveal the fractions of arsenic of the different oxidation states. This technique is combined with a 3-step target preparation method, previously developed for soluble and insoluble constituents in trace concentra- tions[9-11]. The multi-element analysis capability of PIXE provides information on elements that are discharged from an arsenic pollution source. These sample preparation techniques are then applied to analyze the arsenic concentration in a river basin, where hot springs are located upstream being a possible source for emitting arsenic.

The targets prepared were analyzed in a vacuum chamber by using the submilli-PIXE camera (3 MeV protons, 0.5-4 nA beam currents, 4x4mm scanning area, irradiation time 5-10 minutes) at Tohoku University, Japan[12]. A target containing AsO_4^{3-}, Fe^{3+} and Cu^{2+} of known amounts (40 ppb in a 25 ml solution) was prepared by a DBDTC-DBS pre-concentration technique[11] and used as an external standard for normalization of PIXE spectra from the filtration targets. In PIXE-spectrum analysis, we used a least-squares fitting computer code based on the pattern analysis method, which has been developed in our laboratory[13].

Results and discussion

Hydroxide colloids of trivalent or tetravalent metals are produced in a solution of pH > 3.5 and possess anion-exchange property on the acidic side of the isoelectric point located at pH 7 to 8. By changing the pH value, the collection rates of arsenic of AsO_3^{3-} or AsO_4^{3-} in 100 ppb concentrations were examined for hydroxides of Fe^{3+},Ga^{3+},In^{3+} and Zr^{4+} under the condition of coexisting representative constituents of river water like K^+, Cl^- and SO_4^{2-} in ppm-concentrations. In order to confirm separation of arsenic from lead that may cause an error to PIXE spectrum analysis of arsenic, test solutions were prepared containing Pb^{2+} in 50 ppb concentrations. None of the four sorbents showed perfect separation for arsenic of different oxidation states, but indium hydroxide colloids quantitatively adsorbed arsenates separating them from lead ions in the pH region of 4 to 5. The adsorption of coexisting ions in excess of more than 50 times higher concentrations had no adverse effect on the recovery of pentavalent arsenic with metal hydroxide colloids generated in test solutions. The detection limit was estimated to be 0.3 ppb As in a 25 ml solution based on exceeding the 3σ statistical error of background counts. It is clear that the quality of environmental water samples relevant to human life can be assessed for harmful arsenic at the limit < 10 ppb by means of PIXE measurement using indium hydroxide targets

scavenging arsenic selectively in a solution.   The PIXE analysis's high sensitivity for arsenic is attributable to the high pre-concentration factor of 10^5 in preparation of indium hydroxide targets scavenging arsenate in solutions.

In order to improve separation of arsenic ions of different oxidation states, indium hydroxide targets were prepared for arsenic in 100 ppb concentrations by adding SO_4^{2-} and PO_4^{3-} in ppm-concentrations, as shown in Fig. 1.   These anions compete with arsenate and arsenite ions when they are adsorbed with indium hydroxide colloids in a solution of pH 4. Figure 1-a reveals that sulfate cannot depress sorption of arsenite even in 50 ppm concentration but 1 ppm phosphate completely controls the arsenite sorption onto indium hydroxide colloids.   The sorption of arsenate ions is not sensitive to addition of competing ions and the arsenate recovery decreases by 15% only in the case of coexistence with 5 ppm phosphate ions.   As shown in Fig. 1-b, addition of 25 ppm sulfate and 1 ppm phosphate controls the arsenite sorption within 11% in a wide concentration region of 4 to 50 ppb arsenite, while almost all of arsenate is collected with hydroxide colloids of indium of 10 ppm concentrations in original solutions.   These results indicate that thin and uniform targets of pentavalent arsenic ions are obtained well separated from trivalent arsenic ions under acidic condition at pH 4.   The separation of AsO_4^{3-} from AsO_3^{3-} is ascribed to the fact that metal hydroxides possess an anion-exchange property with higher affinity for PO_4^{3-} than for CrO_3^{3-}.   A complete separation of arsenic of different oxidation states was also confirmed under the same experimental condition in solutions containing 1ppm arsenate or arsenite ions.   In the case of separation without coexistence of sulfate, more than 60% of indium hydroxide colloids were lost in filtration even after aging of colloids in a solution heated to 80 ^{o}C.   It is suggested from these findings that coexistence of sulfate is indispensable to coagulate fine colloids of indium hydroxide into filterable particulates.

In order to confirm the applicability of the sample preparation technique to monitoring arsenic pollution in the environment, we collected 0.5 dm^3-volume samples at 7 places in the Natori river valley at a length of 35 km, where five different spas are located upstreams (Fig.2).   Samples were also collected at five spas in upstream locations and at one place in a branch of this river where no spas exist.   Four kinds of PIXE targets were prepared from each water sample using the indium hydroxide coprecipitation for arsenic and the three-step method developed previously, that is, the Nuclepore filtration target for insoluble constituents, the preconcentration target for trace amount of heavy metal ions using a combination of chelation by dibenzyl-dithiocarbamate (DBDTC) ions with subsequent condensation into dibenzylidene-*D*-sorbitol (DBS) gels, and the deposit target of

soluble major constituents.

Indium hydroxide scavenged targets with and without the oxidation reaction of arsenic ions by permanganate ions were prepared from four river water samples (P4, P6-P8) and five spa water samples.   That is, the As(V) fraction is determined by PIXE analysis for indium hydroxide targets of non-oxidized samples containing sulfate and phosphate ions inhibiting arsenite sorption, and the total (As(III) +As(V)) fraction is determined by PIXE analysis for samples oxidized by permanganate ions.   No appreciable difference is observed in arsenic concentrations analyzed for two kinds of targets prepared from each sample of spa water and river water, indicating that pentavalent arsenic is contained in soluble fractions of spa water samples and river water samples.

In PIXE analyses for three kinds of targets, filtration, deposit and preconcentration targets, fifteen elements were detected in samples collected along the 35-km valley of Natori river and hot springs located upstream of the river.   Figure 3 shows concentrations of elements whose change is correlated with the As concentration change.   Arsenic concentra- tions are largely different in five spa water samples and at the two furthermost downstream hot springs the concentration is beyond 100 ppb, the legal discharge limit of As to the aqueous environment.   As a whole, arsenic concentration in the river rises gradually by influx from these spas and saturates downstreams of the hot springs.   It is found that the arsenic concentration is quite low at the branch (P5) where no hot springs exist upstream. The highly sensitive PIXE analysis of arsenate scavenged by indium hydroxide precipitation allows to identify the source of arsenic at ultra low concentrations below the legal limit.   In addition, a chemical back-ground concerning the distribution of arsenic in river water was also clarified by the PIXE analysis for the three kinds of targets.   That is, concentrations of S, K, Mn, Ca and Sr are quite high in spa water samples collected at S2, S4 and S5, which results in the gradual increase of these elemental concentrations along the valley of Natori river.

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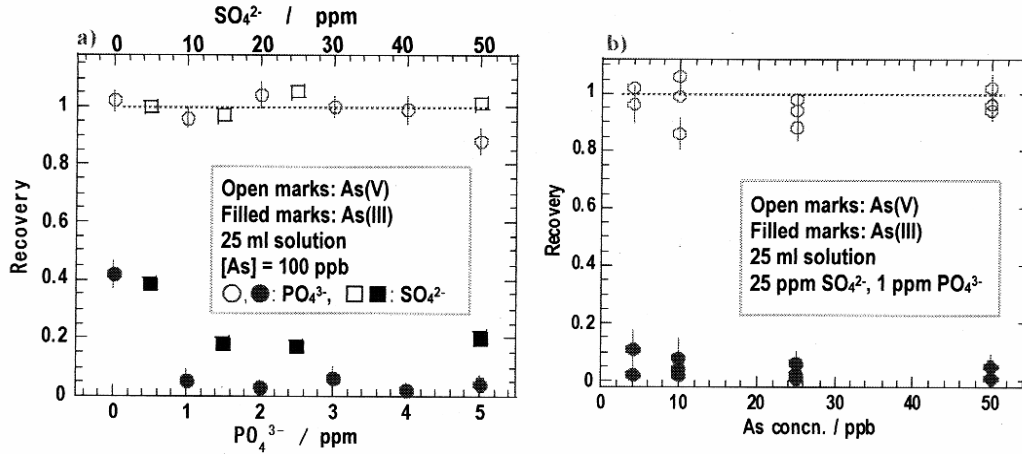13) Murozono K., et al., Nucl. Instrum. Meth. **B150** (1999) 76.

Figure 1. Separation of arsenic ions of different oxidation states by 10 ppm indium hydroxide scavenger prepared at pH4. PIXE measurement: 0.8-1.5 μC irradiation, Si(Li) detector with Mylar absorber of 200 μm thickness; a): Improvement of As separation by adding sulfate and phosphate ions; b) As separation in trace-level concentrations·
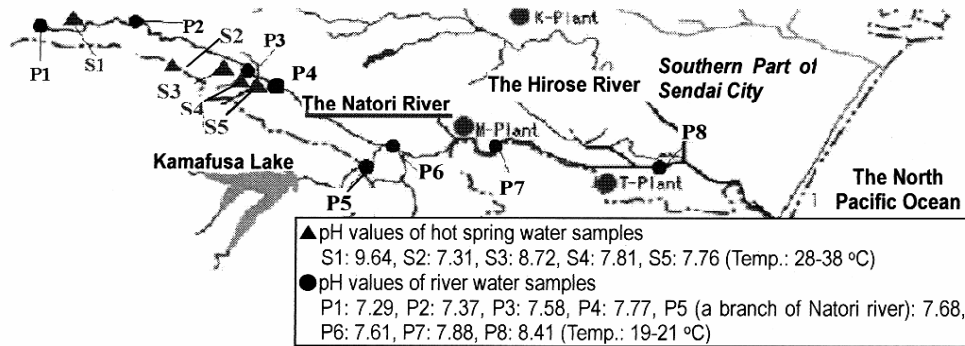

Figure 2. Location of sampling points in the Natori river basin over 35 km and pH values of water samples.
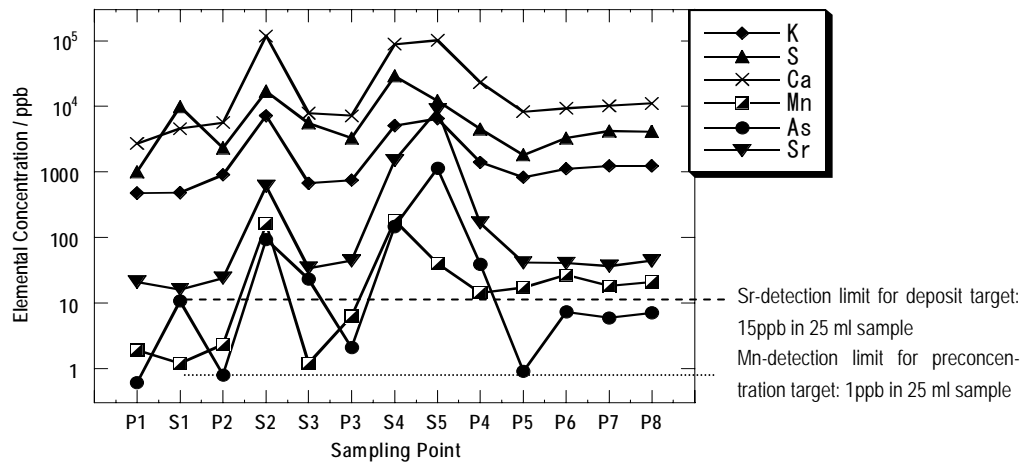
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Figure 3. Elemental concentrations in river water and hot spring water samples. Sampling points of river water (P) and sampling points of upstream hot spring water (S) are the same as those in Fig. 1, 0.5-3 μC irradiation in PIXE measurements.