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V. 2. Development of Monitoring System of Aqueous Environment by PIXE VI: Quantitative Analysis for Cr(III) and Cr(VI) Ions 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 toxic effects of some chemicals in the biosphere have been pointed out previously. The 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. Chromium shows a greatly different hazardousness according to its oxidation state and in Japan the quality limit of environmental water samples is legally set to lower than 50 ppb (ng/ml) for harmful chromium of hexavalent state. However complex separation and preconcentration procedures are required in order to determine Cr(VI) concentrations below 50 ppb in environmental water samples by using the spectrophotometric method, graphite furnace atomic absorption spectroscopy or induced coupled plasma atomic emission spectroscopy. PIXE using 3 MeV protons shows high sensitivity for chromium. Chemical states of chromium 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 chromium at trace level concentrations.

In this study, an enhanced sample preparation method for PIXE analysis was developed for assaying the oxidation state of chromium ions dissolved in water samples. Trivalent Cr$^{3+}$ ions are adsorbed at pH 9 by ferric hydroxide colloids generated in the solution and PIXE targets for analyzing the total concentration of chromium in both
hexavalent and trivalent states are prepared by depositing 0.15 ml of a sample solution on a user-made thin polycarbonate film. PIXE analyses of the two kinds of targets reveal the fraction of chromium of different oxidation state. The applicability of PIXE using this sample-preparation technique was confirmed to determine the oxidation state of chromium ions for concentrations less than 50 ppb in river water samples.

EXPERIMENTAL

*Target preparation of dissolved trivalent Cr or hexavalent Cr ions*

The standard method for collecting ferric hydroxide colloids selectively adsorbing Cr$^{3+}$ ions on a thin filter was tested by investigating the pH-dependence of the recovery of dissolved chromium ions in 50 ppb concentration and ferric ions in 1 or 5 ppm (µg/ml) concentration added to solutions containing coexisting ions such as K$^+$, Ca$^{2+}$, Mn$^{2+}$, Cl$^-$, SO$_4^{2-}$ and PO$_4^{3-}$ in ppm concentrations, and the obtained calibration curve covers the concentration range from 5 to 100 ppb for Cr$^{3+}$ ions. The target preparation procedure is as follows. In a 25 ml solution containing 50 ppb Cr$^{3+}$ and coexisting ions in ppm-concentrations, in which the pH is adjusted to around 2 by adding conc. HNO$_3$, a chosen amount of ferric ions is added on a hot plate at 80°C, and then the pH is readjusted to a selected value by adding 2% NH$_3$ aq. After stirring 2 minutes on the hot plate at 80°C, the solution is filtered under suction (ca. 250 mmHg) through a Nuclepore filter of 0.2 µm pore size and 10µm thickness. In order to determine the best suitable pH value for separating trivalent Cr ions from hexavalent ones in a solution, the target preparation procedure was applied to solutions containing 50 ppb CrO$_4^{2-}$. Test solutions containing chromium of different oxidation states and typical elements of appropriate concentrations in river water were used after serial dilution of each standard solution of certified concentration (1.00 mg / ml).

In order to confirm a high sensitivity of PIXE for analyzing the total chromium concentration, targets for CrO$_4^{2-}$ were prepared by depositing 30 µl of test solution on a user-made polycarbonate film. The test solutions contained 0.5 ppm Ga as an internal standard. After drying at 60°C, the procedure was repeated four more times for a total of 150 µl dried solution on a film. As mentioned in our previous study,$^{12,13}$ a thin polycarbonate film is prepared by slowly dropping 0.25 ml of 0.5 wt% polycarbonate solution in chloroform-benzene mixture within a 20-mm aperture of Mylar target frame floating on 50 wt% sucrose aqueous solution. Rutherford backscattering spectra for the
user-made film and commercial polycarbonate film of 5 μm thickness were obtained with 3 MeV proton beams at a 135° scattered angle with respect to the incident beam axis. In order to evaluate the reliability of the quantitative PIXE analysis for samples deposited on polycarbonate films, a calibration curve was measured for 2-4 μC accumulated charges covering the concentration range from 10 to 100 ppb for CrO₄²⁻.

**PIXE analysis**

The targets prepared from test solutions were analyzed in a vacuum chamber by using the submilli-PIXE camera (3 MeV protons, 1-5 nA beam currents, 4x4 mm scanning area, irradiation time 5-10 minutes) at Tohoku University, Japan. Target X-rays were measured at 135° with respect to the beam with a Si(Li) detector (0.012 mm thick Be window, 10 mm²x3mm thick) covered with a 200-μm Mylar absorber whose high geometric efficiency allows the detection of X-rays > 4 keV. A target containing Fe³⁺ and Cu²⁺ of a known amount (40 ppb in a 25 ml solution) was prepared by a DBDTC-DBS pre-concentration technique¹, 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 laboratory². The lower detection limit was obtained based on exceeding 3σ statistical error of the background counts integrated over the width of detector resolution (FWHM) at the position of the X-ray energy characteristic of the element of interest in the PIXE sample spectrum.

**RESULTS AND DISCUSSION**

Ferric hydroxide colloids possess amphoteric ion-exchange property with the isoelectric point located in the vicinity of pH 8³⁻⁴. By changing the pH values, the collection rates of iron and chromium of trivalent or hexavalent state were examined for the filter of 0.2 μm pores (Fig. 1). In order to confirm separation of Cr in 50 ppb concentrations from other constituents of river water, test solutions were prepared containing major constituents such as K⁺, Ca²⁺, Cl⁻, SO₄²⁻ and PO₄³⁻ in the ppm-concentrations and minor ones of Mn²⁺ and Zn²⁺ in the ppb-concentrations. In test solutions with ferric scavenger added in 1 and 5 ppm concentration, Cr³⁺ ions are quantitatively recovered at pH > 5, and less than 40% of added CrO₄²⁻ ions is collected from the solution of pH 4.2 but recovery largely decreases on the alkaline side of Cr³⁺ adsorption.
Since ferric hydroxide colloids are produced in a solution of pH > 3, Cr$^{3+}$ of low concentration like 50 ppb is appreciably coprecipitated on ferric hydroxides in a wide pH region because Cr$^{3+}$ ions easily hydrolyze\textsuperscript{10).} The recovery of CrO$_4^{2-}$ decreases to 1 to 3 percent in the alkaline region of pH > 8, since the anionic adsorption capacity of ferric hydroxides appreciably diminishes. These results indicate that we can obtain thin and uniform targets of trivalent chromium ions well separated from hexavalent chromium ions in an alkaline region of pH > 8. The adsorption of coexisting ions in 100-300 times higher concentrations had no effect on the recovery of trivalent chromium in the coprecipitation with ferric hydroxide colloids generated in test solutions.

In order to evaluate the reliability of quantitative PIXE analysis of dissolved Cr ions in trivalent state, a calibration curve was measured using targets, which were prepared at pH 9.0 ± 0.1 by adding 1 ppm Fe$^{3+}$ to a 25 ml of trivalent chromium solution in concentrations ranging from 5 to 100 ppb, as shown in Fig.2-(a). A linear relationship is observed between the initial concentrations of Cr$^{3+}$ ions added to the solutions ([Cr]$_{ini}$) and the concentrations converted from PIXE analysis values of Cr$^{3+}$ scavenged on the filter ([Cr]$_{exp}$). Although a somewhat large difference of 8-14% was observed for two targets of 100 ppb, an error margin of ±6% was obtained for five targets prepared from test solutions of 50 ppb Cr$^{3+}$ ions. The detection limit in the present PIXE measurement setup with 0.9-2.6 μC irradiation of 3 MeV protons is 1 ppb, when the characteristics X-ray peak yield is close to the 3σ statistical error of background counts. The average recovery of ferric scavenger was 0.98 ± 0.06 for 11 calibration measurement targets, indicating no appreciable loss in filtration of ferric hydroxide colloids.

Figure 2-(b) shows the calibration measurement results of deposit targets for the purpose of analyzing the total chromium concentration in a solution. In these measurements, targets were prepared by depositing 0.15 ml solutions containing CrO$_4^{2-}$ ions with the concentrations ranging from 10 to 100 ppb. The straight line corresponds to the relation C$_{exp}$ = C$_{ini}$. The difference between the nominal and the experimentally obtained concentrations seldom exceeds ±6% in a wide concentration range, although a 26 % deviation is observed in the case of 10 ppb CrO$_4^{2-}$, which is close to the quantification limit being three times larger than the detection limit in PIXE measurements. In the case of PIXE spectra of CrO$_4^{2-}$ deposit targets, the detection limit was estimated to be 3.4 ppb Cr in a solution based on the 3σ statistical error of background counts. It is clear that the limit of quality of environmental water sample relevant to human life can be assessed for harmful
hexavalent chromium (< 50 ppb) by means of PIXE measurement for deposit targets onto a thin polycarbonate film with low continuum X-ray background. In Fig. 3, the RBS spectra are compared for a commercial polycarbonate film in 5 μm thickness and an user-made polycarbonate film. In the case of user-made film, two narrow peaks appear in the recorded energy spectrum, indicating a thin target with a higher energy peak of oxygen atoms and a lower energy peak of carbon atoms. Based on the chemical composition, (C₁₆H₁₄O₃)ₙ, and the density of polycarbonate, 1.2 g/cm³, the commercial film of 5 μm thickness should contain a layer with 4.7x10¹⁹ atoms / cm² of carbon and oxygen atoms and the fitted curve area of the commercial film (upper graph) indicates a layer with 4.6x10¹⁹ atoms / cm². In the case of the user-made film (lower graph), the experimental fitted curves show a surface atomic density of 5.7x10¹⁸ atoms / cm², indicating a much thinner film of 0.6 μm.

In order to confirm the applicability of PIXE using these sample-preparation techniques to determine the distribution of chromium oxidation states in environmental water samples, ferric hydroxide scavenged targets and deposit targets were prepared from 25 ml river water samples containing 50 ppb chromium in trivalent or hexavalent state. The river water sample was collected from Natori river at the outskirts of Sendai city. The sample had a pH value of 7.78 and an oxidation-reduction potential of 414 mV at 21.8°C, indicating a reducing condition in comparison to 480 mV of the standard oxidation-reduction potential at the same pH value for the pair of Cr₂O₃ and CrO₄²⁻. Chromium was added to the filtrate of river water, and elements, either collected on the filter or contained in the filtrate, were analyzed by PIXE. It was revealed that the river water sample contained much iron, 0.581 ± 0.005 ppm, as an insoluble constituent and also much calcium, 9.0 ± 0.8 ppm, as a soluble constituent. Figure 4-(a) shows the PIXE spectrum of ferric hydroxide target for a 25 ml river water sample containing 50 ppb of trivalent chromium ions and chromium K X-ray peaks are clearly observed. For three iron scavenged targets separately prepared at pH 9 from a 25 ml solution containing trivalent chromium ions in 50 ppb, the average analyzed value was 49 ± 3 ppb, indicating quantitative coprecipitation of added Cr³⁺ ions on ferric hydroxide colloids generated in the solution. In Fig. 4-(b), a small but clear K X-ray peak of Cr is observed in the PIXE spectrum for a ferric hydroxide target prepared from a river water sample containing 50 ppb CrO₄²⁻ ions. The PIXE analysis for three targets prepared at pH 9 under identical solution condition indicated that around 12% of CrO₄²⁻ ions added to river water samples was
precipitated with ferric hydroxide scavenger. In comparison to the recovery of a few percents of CrO$_4^{2-}$ ions in test solutions over pH 8 (Fig. 1), an appreciable increase of chromium recovery can be ascribed to a pre-existing reducing condition for CrO$_4^{2-}$ in river water. For the deposit target of the sample added by both Cr$^{3+}$ and CrO$_4^{2-}$ ions in 50 ppb in Fig. 4-(c), the concentration of chromium was analyzed to be 99 ± 3 ppb, which is fairly close to the total Cr concentration in the original solution. In a 25 ml sample of river water to which both Cr$^{3+}$ and CrO$_4^{2-}$ ions were added at 100 ppb, the K X-ray peak of Cr in the ferric hydroxide target corresponded to 113 ± 2 ppb of the original Cr$^{3+}$ concentration in the solution, and the deposit target indicated the total Cr concentration to be 209 ± 5 ppb which is close to the total Cr concentration in the original solution. Although lead chromate is a compound with low solubility ($K_{sp}$=1.6 x 10$^{-4}$), lead ions in high concentration to precipitate hexavalent chromium in < 10$^{-8}$ mol/dm$^3$ were not detected in a river water sample. These findings reveal that around 13% of added chromium of hexavalent state is reduced to the trivalent state in river water with somewhat reducing condition for CrO$_4^{2-}$ ($E_{SHV}$ = 414 mV) at pH 7.78 and 21.8°C. Light elements like carbon, nitrogen and sulfur contained in an organic such as humin in river water is thought as a cause of the reduction of hexavalent chromium. Note that the lower detection limits for Cr in river water were estimated in PIXE analysis to be 1 ppb for ferric hydroxide scavenger and 7 ppb for deposit target, respectively. When compared with the detection limit of 3.4 ppb for deposit targets prepared from test solutions of CrO$_4^{2-}$, the coexistence of Ca in high concentrations like 9 ppm in river water deteriorates the detection limit of Cr(VI), but the 50 ppb limit in environmental water samples is easily detected by the PIXE analysis of 0.15 ml water sample deposited on a thin polycarbonate film.

CONCLUSION

The techniques developed for the preparation of PIXE targets from water samples were successfully applied to examine the distribution of oxidation states of chromium in water. The target preparation and the PIXE measurements are not time-consuming and suitable for environmental monitoring. The PIXE analysis using two kinds of targets, that is, ferric hydroxide target scavenging trivalent chromium and a target where a small volume of solution is deposited onto a thin polycarbonate film, is sufficiently sensitive to reveal the oxidation state of chromium in concentrations lower than the 50 ppb quality limit of drinking water for harmful chromium of hexavalent state. Hence, the method developed in
this study shows that PIXE analysis is an effective technique for monitoring the harmful chromium(VI) ions entering the primary pathways of human metabolism.

REFERENCES

Figure 1. The pH-dependence of filtration scavenging for trivalent and hexavalent chromium with ferric hydroxide colloids. The precipitates were filtered under suction (~250 mmHg) with a Nuclepore filter of 0.2 μm pores. In a 25 ml solution containing 15 ppm K⁺, 5 ppm Cl⁻ and 5 ppm SO₄²⁻, □: 50 ppb Cr³⁺ and 1 ppm Fe³⁺ added, ●: 50 ppb Cr³⁺ and 5 ppm Fe³⁺ added, □: 50 ppb CrO₄²⁻ and 1 ppm Fe³⁺ added, ■: 50 ppb CrO₄²⁻ and 5 ppm Fe³⁺ added, ∆: 50 ppb Cr³⁺, 1 ppm Fe³⁺, 5 ppm Ca²⁺, 0.1 ppm Mn²⁺, 0.025 ppm Zn²⁺ and 3 ppm PO₄³⁻ added.

Figure 2. Experimental results ([Cr]exp / ppb) versus nominal concentrations ([Cr]ini / ppb), (a):trivalent chromium ions collected on ferric hydroxides targets using 1 ppm of Fe³⁺ scavenger, filtration at pH 9.0 ± 0.1, 0.8-2.6 μC irradiation in PIXE measurements, (b):hexavalent chromium ions deposited on a user-made thin polycarbonate film. 0.15 ml deposition, 2.4-4.1 μC irradiation in PIXE measurements.
Figure 3. RBS energy spectra obtained with 3 MeV protons for thin polycarbonate films. The scattering angle is 135°. (a): a commercial polycarbonate film of 5 μm thickness, (b): user-made polycarbonate film.

Figure 4. PIXE spectra for deposit and ferric hydroxide scavenge (pH 9) targets of river water samples with Cr added. (a): ferric hydroxide target of 25-ml river water added Cr³⁺ in 50 ppb, (b): ferric hydroxide target of 25-ml river water added CrO₄²⁻ in 50 ppb, (c): deposit target of 0.15-ml river water added both Cr³⁺ and CrO₄²⁻ in 50 ppb, PIXE measurement: 1.4-2.6 μC of 3 MeV protons, 200 μm Mylar absorber.