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# On-line preconcentration using dual mini-columns for the speciation of chromium(III) and chromium(VI) and its application to water samples as studied by inductively coupled plasma-atomic emission spectrometry

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**Abstract**

On-line preconcentration system for the selective, sensitive and simultaneous determination of chromium species was investigated. Dual mini-columns containing chelating resin were utilized for the speciation and preconcentration of Cr(III) and Cr(VI) in water samples. In this system, Cr(III) was collected on first column packed with iminodiacetate resin. Cr(VI) in the effluent from the first column was reduced to Cr(III), which was collected on the second column packed with iminodiacetate resin. Hydroxyammonium chloride was examined as a potential reducing agent for Cr(VI) to Cr(III).

The effects of pH, sample flow rate, column length, and interfering ions on the recoveries of Cr(III) were carefully studied. Five millilitres of a sample solution was introduced into the system. The collected species were then sequentially washed by 1 M ammonium acetate, eluted by 2 M nitric acid and measured by ICP-AES. The detection limit for Cr(III) and Cr(VI) was 0.08 and 0.15 $\mu g\,l^{-1}$, respectively. The total analysis time was about 9.4 min.

The developed method was successfully applied to the speciation of chromium in river, tap water and wastewater samples with satisfied results.

*Keywords:* Speciation; Chromium; On-line preconcentration; ICP-AES; Chelating resin

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## 1. Introduction

Speciation analysis of trace amounts of chromium(III) and chromium(VI) ions has become an important topic in environmental and biological sciences [1]. It is well known that the toxicological and biological properties of most elements depend upon their chemical forms. Therefore, the knowledge on the speciation of chromium is of particular necessity.

Chromium is widely used in various industries, such as plating, tanning, paint and pigment production, and metallurgy, which possibly contaminate the environment. Chromium(III) compounds are one of the essential trace nutrients in human bodies, and play an important role in the metabolism of glucose and certain lipids, whereas chromium(VI) compounds are toxic and carcinogenic [2–4]. The United State Environmental Protection Agency (USEPA) has regulated the permissible limit of 0.1 $mg\,l^{-1}$ of total chromium in drinking water. In Japan, the maximum tolerable concentration of chromium in wastewater is 0.5 and 0.05 $mg\,l^{-1}$ for total chromium and chromium(VI), respectively. However, World Health Organization (WHO) thought that the guideline value of 0.05 $mg\,l^{-1}$ of chromium(VI) is too high, compared with its high risk of carcinogenicity. Consequently, the development of sensitive method, as well as the speciation method of chromium, in environment is absolutely required.

A number of methods have been reported for the speciation of chromium in water samples. Liquid chromatography (LC) is a convenient method for the separation and determination of metal ions simultaneously. The LC methods coupled with atomic absorption spectrometry (LC-AAS) [5], inductively coupled plasma-atomic emission spectrometry (LC-ICP-AES) [6], and inductively coupled plasma-mass spectrometry (LC-ICP-

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MS) [7] were successfully applied to the speciation of chromium in water samples. Generally, the speciation of chromium is performed after the separation of one species of chromium(III) and (VI) by sorption [8–10], solvent extraction [11], and co-precipitation [12,13], followed by the instrumental analysis, and the another species is then determined after reducing or oxidizing the residual chromium contained in the sample solutions. Hirata et al. [9] used an iminodiacetate chelating resin for the collection/preconcentration of Cr(III) in seawater. Total chromium was determined after addition of the reducing agent to the sample, whereas Cr(VI) was determined by subtraction of total chromium with Cr(III). The concentration of Cr(VI) in waters is usually about one order of magnitude lower than that of Cr(III) and its determination as a difference between two much higher values may generate large errors.

Another option for the speciation of chromium is a simultaneous retention of Cr(III) and Cr(VI) by using dual column system. The dual column system can be constructed using the same sorbents [14–16] or different sorbents [17–19]. This system provide a good efficiency for the separation and preconcentration of Cr(III) and Cr(VI), which resulted in more accurate analysis when the species of chromium exist at very low level. The use of a dual column system, in which each species of chromium was retained on one column with their respective elution, was first reported by Naghmush et al. [17]. In this method, the effluent pH of the first column must be readjusted before it enters the other column, which makes the procedure somewhat complicated. This disadvantage was solved by Motomizu et al. [18] and Hashemi et al. [19]. However, the latter methods suffer from high concentration of matrix existing in water samples, which significantly reduced the sorption efficiency of chromium species on the column.

In this study, the on-line preconcentration system using dual mini-columns containing iminodiacetate chelating resin was proposed for the speciation of chromium(III) and chromium(VI). In this system, chromium(III) was collected on first column, whereas chromium(VI) was reduced to chromium(III) in the downstream and collected on the second column. Hydroxylamine was used as a potential reducing agent for the conversion of chromium(VI) to chromium(III). The collected species were sequentially eluted by 2 M nitric acid and measured by ICP-AES. The developed method permits the simultaneous measurement of both chromium(III) and chromium(VI) without need to readjust the pH of samples. The method was successfully applied to the speciation of chromium in environmental water samples.

## 2. Experimental

### 2.1. Instrumentation

The ICP-AES system (Vista Pro, Seiko Instrument, Japan) was used for the measurement of chromium. The optimized operating conditions of ICP-AES were summarized in Table 1. The flow diagram for the pretreatment of sample is shown in Fig. 1. The PTFE tubing (0.5 mm i.d.) was used for the assembling of flow lines in a flow injection pretreatment system. Peristaltic pumps (ALITEA, Sweden and SPETEC, Germany) were used to propel the solution of buffer, sample, reducing agent and eluent.

Table 1
Operating conditions of ICP-AES

| | | |
|---|---|---|
| ICP-AES:SII VISTA-PRO | | |
| Plasma condition | | |
| RF power | 1.2 kW | |
| Plasma gas flow rate | 15 l min$^{-1}$ | Ar |
| Auxiliary gas flow | 1.5 l min$^{-1}$ | Ar |
| Nebulizer gas flow | 0.75 l min$^{-1}$ | Ar |
| Sample uptake rate | 1.0 ml min$^{-1}$ | |
| Nebulizer | Concentric glass nebulizer | |
| Torch | One-piece low flow extended torch in the axial view mode | |
| Data acquision | | |
| Measurement mode | Time scan mode | |
| Emission line | 267.716 nm | |

### 2.2. Reagents and materials

A 100 mg l$^{-1}$ stock standard solution of Cr(III) was prepared by dissolving chromium nitrate nonahydrate (analytical reagent grade: Wako Pure Chemicals, Osaka, Japan) in 0.01 mol l$^{-1}$ nitric acid solution (ultrapure reagent grade: Kanto Chemical, Tokyo, Japan). A 100 mg l$^{-1}$ Cr(VI) stock standard solution was prepared by dissolving sodium chromate tetrahydrate (analytical reagent grade: Kanto Chemical, Tokyo, Japan) in ultrapure water (resistivity $\geqq$ 18 MΩ cm$^{-1}$) prepared by an Elix3/Milli-Q Element System (Nihon Millipore, Japan).

Accurately diluted solutions of Cr(III) and Cr(VI) were prepared daily using the standard stock solutions. The reducing agent was prepared by accurate dilution of a stock solution of 10 (w/v)% hydroxylamine (Wako Pure Chemical, Osaka, Japan). The ammonium acetate solution was prepared by appropriate mixing of the electronic grade acetic acid and ammonia water (Mitsubishi Chemicals, Japan).

An iminodiacetate resin (Muromac A-1, 50–100 mesh: Muromachi Technos, Japan) was used for the collection and the preconcentration of Cr(III) species. The solid-phase columns was prepared by packing the resin into the PTFE tubing (5 cm × 2 mm i.d.) equipped with the plugs of quartz wool at both ends of the tubing to keep the resin in the column. The sample solutions were filtered through the membrane filter of nitrocellulose ester (0.45 μm, Advantec, Toyo, Japan) and adjusted to pH 3.3 before being injected to the system.

### 2.3. Column separation/preconcentration procedure

The schematic diagrams for the on-line separation/preconcentration of Cr(III) and Cr(VI) are shown in Fig. 1. The procedures involve the conditioning step (0.2 min), in which the iminodiacetate chelating resin in column was washed with ultrapure water, followed by the collection step (4.2 min; 5 ml of sample solution), where the chromium in water samples (pH