Semi-continuous Monitoring of Cr(VI) and Cr(III) during a Soil Extraction Process by Means of an Ion Transfer Device and Graphite Furnace Atomic Absorption Spectroscopy

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Electrodialytic separation of Cr(VI) and Cr(III) followed by graphite furnace atomic absorption spectrometry for monitoring of soil extraction was studied. The sensitivity was improved by in-line purification of the solutions and bi-polar pulse cleaning. The detection limit for both Cr(VI) and Cr(III) was 0.01 $\mu\text{g L}^{-1}$. The system was successfully used to monitor the concentration change during soil extraction with dual solution line filtration. The results demonstrate the difference in concentration changes with the different sources of Cr(VI).

Keywords Chromium, soil extract, ion transfer device, GFAAS

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Introduction

Chromium (Cr) is well-known as a toxic heavy metal. Cr(VI), present in chromate or dichromate, is a strong oxidant and is classified as a carcinogen. However, Cr(III) is essential for the metabolism of lipids and sugar. Recently, the improvement of sucrose accumulation in rice by exposure to Cr(III) or Cr(VI) was reported.¹ Cr in soil is important not only for environmental protection but also to control plant growth. Many analytical methods are used to separately measure Cr(III) and Cr(VI). The Cr(VI) selective colorimetric method using diphenylcarbazide (DPC), coupled with total Cr analysis with induction coupled plasma/mass spectrometry (ICP/MS) is widely used, and new approaches have been reported, including a dual-electrochemical detector,² Au nanoparticle-based colorimetry,³ a microfluidic paper-based analytical device (μ PAD) with electromembrane extraction,⁴ carboxylic group functionalized mesoporous silica as a solid phase for selective extraction⁵ and 2,6-pyridinedicarboxylic acid (a ligand for Cr(III)) as an eluent for LC-ICP/MS.⁶ Chromatographic separation is a reliable method but difficult to measure on site even though the chemical forms can be changed easily. We previously developed a method for the electrodialytic separation of Cr(III) and Cr(VI). The cationic Cr(III) and anionic Cr(VI) were separately transferred into acceptor solutions using an electric field. The separation was continuous and rapid (~ 5 s), and the acceptor solutions can be directly analyzed by ICP/MS.⁷ The acceptor solutions were also analyzed with a DPC-based flow injection analysis system

coupled with chemical conversion of Cr(III) into Cr(VI) by alkaline H_2O_2 to detect Cr(III) with DPC chemistry.⁸ Graphite furnace atomic absorption spectrometry (GFAAS) is sensitive for metal analysis even though single analysis can be achieved with ~ 20 μL of sample. Also, the instruments itself and consumables are much lower in cost than ICP/MS. In the present study, GFAAS has been used for elemental analysis of Cr.

Cr(VI) contamination occurs not only anthropogenically but also naturally.^{9,10} Cr(VI) is formed by oxidation of Cr(III) with a suitable oxidant such as MnO_2 .¹¹ Different sources of Cr(VI) contamination may cause differences in the elution of Cr from soil. In the present study, we monitored Cr(III) and Cr(VI) concentrations separately during the extraction procedure to discover differences in the elution profile with the source of Cr(VI). The Cr concentration in non-contaminated soil extracts during the extraction procedures are sometimes less than 0.10 $\mu\text{g L}^{-1}$ based on our preliminary experiments. For the differentiation of the contamination sources, trace levels of Cr species need to be analyzed. An improvement in sensitivity from the previous reports⁷ is required for the present purpose. Even though the ITD separation can be achieved simultaneously with enrichment, the sample amounts are limited in the present study. Thus, the background concentration caused by reagents and ITD itself was carefully considered for the trace Cr speciation analysis.

Experimental

Reagents and chemicals

A stock solution of 1000 mg L^{-1} Cr(III) was prepared by dissolving $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (www.nacalai.co.jp) in 10 mM HNO_3 ,

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Fig. 1 Schematic diagram of the extraction system used in this study. ITD, Ion transfer device; E, electrode; CC, purification column filled with cation exchange resin; CM, purification column filled with mixed-bed resin; SP, syringe pump; PP, peristaltic pump; IF, in-line filter.

diluted from 70% HNO_3 (ultra-trace analysis; www.labchem-wako.fujifilm.com). A stock solution of 1000 mg L^{-1} Cr(VI) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (www.labchem-wako.fujifilm.com) in ultra-pure water (UPW). Standard solutions of various concentrations were made daily by further dilution with HNO_3 or UPW.

Ion transfer device, flow system, and detector

A schematic diagram of the current Cr(III)/Cr(VI) separation system is shown in Fig. 1. The electrodiolytic ion transfer device (ITD) used in this study is the same as previously reported.^{7,8} The ITD consists of five thin solution channels, which are separated by ion-permeable membranes (dialysis or ion exchange membranes). The sample solution was pumped through the center channel at 0.1 mL min^{-1} with a peristaltic pump (Minipuls 3, www.gilson.com). The acceptor solutions (30 mM HNO_3 and UPW for Cr(III) and Cr(VI) , respectively) were flowed continuously at 0.1 mL min^{-1} using selection valve integrated syringe pumps (Versa 3, www.imi-precision.com). Isolator solutions were flowed at 3 mL min^{-1} with unimol pumps (UPS112E, www.nitto-kohki.co.jp). The isolator channels were separated from the acceptor channels by cation and anion exchange membranes (Selemion CMV, and DSV, www.aged.co.jp) for the anode and cathode sides, respectively. An electric field ($\sim 15 \text{ V DC}$) was applied with a DC power supply (PMC-35-1A, www.kikusui.co.jp). The effluents from the acceptor channels were collected into vials and analyzed with a graphite furnace atomic absorption spectrometer (GFAAS, iCE3400, www.thermofisher.com). The manufacture recommended conditions were used for the analysis of Cr species with GFAAS.

Speciation analysis during the soil extraction procedure

We monitored the concentration of Cr(III) and Cr(VI) during a soil extraction procedure. The soil extraction procedure was performed according to the Japanese Environmental Agency Notification No. 46. Soil samples were collected and dried in a desiccator to 25 – 30% RH. The dried soil sample was crushed in a mortar to achieve a particle size appropriate to the analysis, homogenized, and sieved with 2.00 mm pore size. The soil sample ($\sim 50 \text{ g}$) was added to 500 mL UPW, pH adjusted to 5.8 – 6.3, and shaken at 200 rpm with 45 mm of amplitude. During the extraction, the extract solution was pumped by a peristaltic pump at 8.7 mL min^{-1} through an in-line glass fiber filter (GA-55, www.advantec.co.jp) placed in the cartridge (Swinnex SX0001300, www.merckmillipore.com). A subsample of the filtrate was introduced into the ITD for analysis.

Results and Discussion

Sensitivity improvements and system performance

The speciation analysis of Cr(III) and Cr(VI) has been previously successful using ITD and ICP-MS. The detection limit of a flow injection analysis method was $0.1 \text{ } \mu\text{g L}^{-1}$ and the separation at mg L^{-1} levels of a concentration was also demonstrated. However, the blank response caused a loss of sensitivity. In the present study, Cr is analyzed with GFAAS, which has relatively higher sensitivity than ICP-MS and uses less argon gas and electricity. In the initial test, under the same conditions as reported previously, the detection of Cr with GFAAS had detection limits of 0.5 and $0.01 \text{ } \mu\text{g L}^{-1}$ with and

without ITD, respectively. Previously, 10 mM HNO_3 was used for both the acceptor solutions. To decrease the blank response, a cation exchange resin-(Dowex 50w-x8) filled column (#7733, www.chemites.co.jp) was connected just before the ITD. The column effectively decreased the blank response to one-tenth, caused by impurities in the HNO_3 . The blank response was further decreased with bi-polar pulse cleaning of the ITD. The typical polarity of the applied voltage for ITD transfers the ionic solutes in the sample. If the opposite polarity is applied, the ions adsorbed on the ion exchange membranes are released into the solution. The bi-polar pulse cleaning was applied with a square wave of 50 V_{p-p} and 0.5 Hz for 1 min. The blank response was further decreased to one-fifth. This bi-polar pulse cleaning procedure was performed before every analysis to improve repeatability. The repeatability of the analysis of a sample containing 2.0 $\mu\text{g L}^{-1}$ Cr(III) and 0.5 $\mu\text{g L}^{-1}$ Cr(VI) was improved from 7.9 and 10.8% to 4.0 and 6.4% ($n = 5$) for Cr(III) and Cr(VI), respectively (Fig. S1 in Supporting Information).

During preparation of the calibration curve, it was noted that the Cr(VI) response at concentrations less than 1.0 $\mu\text{g L}^{-1}$ was initially ~50%. This may be caused by the reduction of Cr(VI) by organic compounds in the ITD under acidic conditions (using 10 mM HNO_3 as acceptor), which were then transferred to the opposite acceptor or adsorbed onto the membrane surface. The transfer efficiency for Cr(VI), calculated from the slope of the calibration curve, was dramatically improved from 60.8 to 90.1% by using UPW as the Cr(VI) acceptor and passing the sample through a mixed-bed ion exchange resin column before the ITD step (Fig. S2 in Supporting Information). The transfer efficiency was also evaluated with IC-ICP/MS analysis of the acceptor solutions (Fig. S3). The chromatograms obtained indicate that the anionic Cr(VI) and cationic Cr(III) were transferred effectively (>90%) into the anion and cation acceptors, respectively. Under the optimized conditions, the detection limit was 0.01 $\mu\text{g Cr L}^{-1}$ and the linear range extended to 10 $\mu\text{gCr L}^{-1}$ for both Cr(III) and Cr(VI). The linear range was the same as GFAAS without ITD, and this range is sufficient to detect both Cr species in soil extracts.

Simultaneous determination of Cr(III) and Cr(VI) in soil extract

In the present study, a method for monitoring the concentrations of Cr(III) and Cr(VI) in soil extract during the extraction processes is proposed. The elution profile, the time-based concentration change of Cr species in a soil extract, may depend on whether the contamination source is anthropogenic or natural.

To monitor the concentration of Cr(III) and Cr(VI) in soil extract, a flow system that continuously samples the soil extract and introduces it into the ITD was developed. Initially, the soil extract solution was directly introduced into the ITD with peristaltic pump at 0.1 mL min⁻¹. However, problems were encountered, such as a time delay and clogging of the ITD channel by particulates. Furthermore, long residence time (>4.4 min with 0.75 mm i.d. $\times$ 1 m length) in small diameter polytetrafluoroethylene (PTFE) tube caused loss of Cr(VI), which was partly converted to Cr(III) and adsorption of Cr(III) even with the standard solutions. Thus, a dual solution line system was applied. The soil extract solution was pumped at a higher flow rate (8.7 mL min⁻¹) and passed through a glass fiber filter. The sample solution introduced into the ITD was taken from the in-line filter effluent just after the in-line filter at 0.1 mL min⁻¹, and the rest of the effluent was returned to the soil extract bottle. This sampling method resulted in a time delay of less than 1 min, and channel clogging was not observed.

Fig. 2 Elution profile with the results obtained with ITD and SPE. Inset shows the direct comparison of the results of ITD and SPE for Cr(III) and Cr(VI).

The separation of Cr(III) and Cr(VI) is achieved within ~10 s, although the GFAAS requires at least 0.5 mL of sample. Therefore, the cycle was set to determine soil extract every 5 min.

The obtained elution profile is shown in Fig. 2. The concentrations of Cr(VI) and Cr(III) were measured every 5 min. The concentrations of both species were initially high and then gradually decreased. It was expected that the concentrations would gradually increase as the Cr species were released from the soil sample, however, the concentrations gradually decreased to a stable concentration after 2 h. The same phenomenon has been observed for other soil samples, likely because ionic solutes are released when the soil sample is immersed in the extractant, and these ionic solutes accelerate the release of the Cr species. The solution conductivity was ~1 mS cm⁻¹ after soil extraction because of salts released from the soil samples. Furthermore, the soil extraction with 1 mM KNO_3 caused the release of Cr species released with two times the concentration from the soil sample. The details of this phenomenon are under investigation and will be published in the future.

Cr species were also analyzed with a solid phase extraction (SPE) method during the soil extraction procedure. Soil extract (1.0 mL) was collected every 30 min then filtered with 0.45 μm syringe filter (Minisart® SRP 17574K, www.sartorius.com). The filter effluent was passed through a cation exchange resin (Dowex 50w-x8, 100 – 200 mesh, labchem-wako.fujifilm.com) to selectively remove Cr(III), and the effluent was analyzed for Cr(VI). Then, 15 mL of 0.01% HNO_3 was passed through the SPE cartridge to elute Cr(III). The results of the SPE and ITD separation methods are compared in Fig. 2 (inset). The results are in close agreement even though the concentrations were ultra-trace, sub $\mu\text{g L}^{-1}$. The correlation of the results obtained with SPE and ITD ($n = 7$) had slopes of 0.980 and 0.952 for Cr(III) and Cr(VI), respectively. Additionally, a recovery test was performed by adding a standard solution to the soil extract to add Cr(VI) back at a concentration of 2 $\mu\text{g L}^{-1}$. The observed recovery was 98.7% ($n = 24$). These results also suggested that there were no significant effects of particulates collected on glass fiber filter. Because the results obtained with ITD and SPE methods are well agreed.

Fig. 3 Elution profile of Cr(VI) during the soil extraction process for three different soil samples.

Because the ITD method for soil extract analysis was well evaluated, the method was applied to several kinds of soil samples. Soil samples were collected from (a) Kumamoto University (KU, as a reference), (b) Indonesian park near a leather factory (IND, using Cr(VI) for tanning), and (c) a road side near a steel mill (which may release Cr(VI) from manufacturing). The elution profiles of these samples are shown in Fig. 3. The Cr concentration in the soil samples obtained by acid digestion on a hot plate¹² were 0.011 – 0.013 w/w%. However, the concentrations of eluted Cr species were significantly different, caused by the different chemical forms in soil samples. In addition, the elution profiles were different. The Cr(VI) concentration in the soil extract from samples collected near the anthropogenic sources increased gradually then decreased. However, the elution profile of Cr(VI) in the soil extract from samples collected further from a source of contamination sharply increased then decreased. This profile difference may be related to the contamination sources, however further research is required to confirm this hypothesis.

Conclusions

The electrodynamic separation of Cr species was used to measure the changes in Cr concentration during a soil extraction procedure. In the IC-ICP/MS analysis, the sample required filtration through a filter with a pore size <0.5 μm even though a glass fiber filter was sufficient for the ITD separation. In ITD,

simultaneous matrix isolation and separation of each Cr species can be achieved. One benefit of ITD separation compared with IC separation is that passing the extract through a small-pore filter required relatively larger pressure and a pump (such as a plunger pump). Additionally, the current separation system can be used for on-site separation of the Cr species. The chemical forms of Cr species are easily changeable, so on-site separation followed by highly sensitive lab analysis is effective to accurately detect Cr species.

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Supporting Information

Reproducibility data, IC-ICP/MS chromatograms and calibration curves are listed in supporting information. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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