Speciation Analysis of Chromium Oxidation States by Flow Injection Analysis

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Large quantities of chromium (Cr) are used in manufacturing processes worldwide. In the environment, Cr is mainly found as Cr(III) and Cr(VI). There are many differences between these species regarding their chemical and physical properties. For example, it is well known that Cr(VI) is carcinogenic because of its strong oxidation potential and ability to pass through cell membranes, whereas Cr(III) is an essential element and found in glucose tolerance factor. Methods for the determination of Cr have been widely studied. Among the available methods, flow injection analysis (FIA) is simple, rapid, and precise. In the present review, we summarize flow injection analysis methods for speciation analysis of chromium. The major approaches used for chromium speciation analysis use selective reaction with diphenylcarbazide combined with oxidation of Cr(III) to Cr(VI), solid phase extraction, and electrodialytic separation.

Keywords FIA, chromium, speciation analysis, diphenylcarbazide, oxidation state, solid phase extraction, electrodialysis

1. Introduction

Chromium was named because of the many colors with different oxidation states. For example, the color of alkali-borate glasses was also developed by Cr-doping [1]. Chromium is an important metal in engineering, and huge quantities of it are used worldwide. Approximately 1960 Gg of Cr are released into the environment each year globally [2]. It can also leach into food from cooking pans made of stainless steel and later released into an environment [3]. Cr has a wide range of oxidation states (−2 to +6) [4], but most of the Cr present in environmental matrices, such as water [5,6] and atmospheric particulate matter [7,8], is Cr(III) and Cr(VI) [9,10]. Conversion of Cr among its oxidation states can occur in the environment, and is caused by free radicals or ions produced under light irradiation [11], changes in solution pH and redox potential [12], arsenic species [13], and manganese oxide [14]. Among the common oxidation states, Cr(III) is considered an essential element and is involved in the control of glucose and lipid metabolism in mammals, whereas Cr(VI) is very toxic because of its high oxidation potential and free diffusion across cell membranes and is considered carcinogenic. Consequently, Cr(VI) is regulated at 50 μg L^{-1} in drinking water in Japan. The occurrences of Cr species and their behaviors in the environment are studied using speciation analysis and are important for routine evaluations for public health purposes.

The standard method for Cr(VI) analysis uses its chemical reaction with diphenylcarbazide (DPC), which is selective and produces a colored complex [15,16]. The formation of this complex is monitored by conventional spectrophotometry techniques. The complex has a strong red color (λ_{max} = 540 nm, ε = 3.5 × 10^4 L/mol·cm) and is formed under strongly acidic conditions [16]. This technique and elemental analysis for total Cr are widely used for speciation analysis of Cr. Chromatographic separation is also widely used with elemental analysis [17]. Because of the high toxicity of Cr(VI) and the potential for conversion between Cr oxidation states in the environment, Cr(III) and Cr(VI) have been widely studied by speciation analysis. Rapid and precise determination can be achieved with flow injection analysis (FIA). In this review, we detail recent progress in the speciation analysis of Cr(III) and Cr(VI) by FIA.

2. FIA for chromium speciation

A FIA system for Cr(VI) was first reported in 1980, and was based on DPC chemistry [18]. Solutions of 0.5 g/L DPC in a 10% aqueous acetone solution and 0.04 M H_2SO_4 were mixed in a 100-cm reaction coil before the injection of sample solution into the FIA system (Fig. 1a). After the injection, the solutions flowed into a 50-cm reaction coil, and products were detected by a photometric detector at 540 nm. This simple configuration had a dynamic range of 0.1 to 20 μg/mL and an analysis rate of 70 samples per hour. A two-line flow system, with one line for the sample solution and the other for the reagent solution, is widely used (Fig. 1b). Recently, two-line system with an improved limit of detection (5 ng/L) was

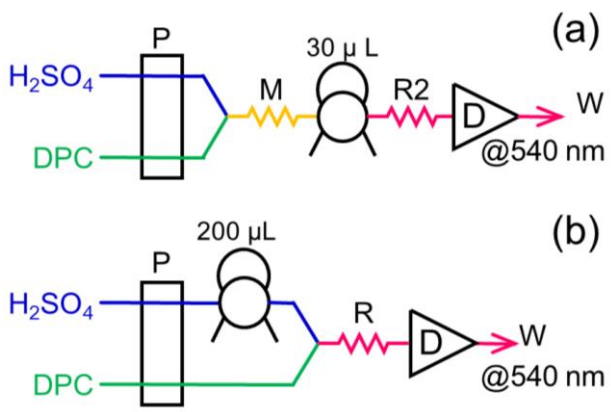

Fig. 1 Flow injection analysis (FIA) systems for chromium determination. (a) First FIA system reported for chromium [18], and (b) two -line FIA system in JIS K0170 6.3.3. P = pump, M = mixing coil, I = injector, R = reaction coil, D = detector, and W = waste

constructed using a liquid core waveguide detector with a reference wavelength [19]. FIA methods with DPC are widely used and are standard methods in many countries. These methods are used for speciation analysis along with an oxidation reaction, and are described further in Section 3.

Electrochemical Cr speciation analysis has also been reported. Potentiometric detection of Cr(VI) was achieved with Fe(III)/Fe(II) potential buffer solution contained a bromide with an oxidation-reduction potential (ORP) electrode [20]. The potentiometric method has also been applied to total Cr detection with cerium (Ce) oxidation of Cr(III) [21]. Amperometric determination of Cr(VI) with a polyaniline/polystyrene composite electrode that responded to a reduction in polyaniline when it was oxidized by Cr(VI) was used to achieve highly sensitive detection (4 ng/L limit of detection) [22]. Nanomaterial electrodes, including a flower-like self-assembly of gold nanoparticles with a limit of detection of 2.9 ng/L [23] and a sol-gel/carbon nanotube modified electrode with a limit of detection of 800 ng/L [24], were recently applied to Cr(VI) determination. An electrode integrated microchip based flow analyzer has also been prepared [25].

Only a few studies on luminescence methods have been reported. Chemiluminescence with Cr(VI)-catalyzed oxidation of gallic acid in the presence of potassium permanganate and hydrogen peroxide by FIA achieved a wide dynamic range (20 pM to 0.5 mM) and a detection limit of 4 pM [26]. In another study, Cr(III)-catalyzed luminol oxidation by hydrogen peroxide in an alkaline solution was used in a microfluidic paper-based analytical device [27]. A rhodamine derivative has been used for fluorometric Cr(III) detection with multi-walled carbon nanotubes as a solid-phase extraction (SPE) sorbent in a microfluidic FIA platform [28].

Simultaneous determination of Cr(III) and Cr(VI) has been achieved with electrospray ionization mass spectrometry using $HCrO_4^-$ (*m*/*z* 117) and [Cr(III)(*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid)]$^-$ (*m*/*z* 394) [29]. The *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*',*N*'-tetraacetic acid was carefully selected to avoid conversion of Cr(VI) to Cr(III). Direct speciation analysis by graphite furnace atomic absorption spectrometry (GFAAS) has been achieved by vaporization of Cr(III)-2-thenoyltrifluoroacetone at 400 °C after selective reaction of the chelating agent 2-thenoyltrifluoroacetone with Cr(III) [30,31]. By contrast, Cr(VI) vaporization occurs at 1200 °C.

Direct speciation analysis of Cr species can be achieved by electrospray ionization mass spectrometry or GFAAS. However, most of the FIA methods with DPC or electrochemistry are selective for one species and require conversion of Cr(VI) to Cr(III) or Cr(III) to Cr(VI) for speciation analysis of Cr(III) and Cr(VI).

3. Oxidation of Cr(III) to Cr(VI)

The DPC reaction has been widely used for Cr(VI) detection with total Cr determination by an elemental analysis method, such as atomic absorption spectrometry or ICP-MS. Oxidation methods for the determination of Cr(III) with DPC are also effective with FIA or related technologies. Speciation analysis with DPC involves determination of total Cr or Cr(III), and often uses oxidation of Cr(III) to Cr(VI). Oxidation is performed with acidic Ce(IV) [32], alkaline H_2O_2 [33], ultraviolet (UV) light [34], or sodium bismuthate ($NaBiO_3$) immobilized on a column [35]. Acidic Ce(IV) is widely used as an oxidant for the conversion of Cr(III) to Cr(VI) [32]. However, when present in high concentrations, Ce(IV) can react with DPC to produce a colored complex and false positive results. On the other hand, generated Cr(VI) oxidizes organic compounds contained in sample under acidic conditions and causes false negative results. These effects can be eliminated using calibration procedures [36] or by coupling with low pressure ion chromatographic separation [37]. Hydrogen peroxide can oxidize Cr(III) even under alkaline conditions and successfully applied for the Cr conversions [38]. Under alkaline conditions, the generated Cr(VI) from Cr(III) cannot oxidize organic compounds contained in sample and kept as Cr(VI) is. However, H_2O_2 can also be functioned as

reductant for Cr(VI) under the acidic conditions used for the DPC reaction. Thus, when the sample/H_2O_2 solution is mixed with strongly acidic DPC after oxidation procedure, the amount of Cr(VI) is reduced by H_2O_2, and this can affect the Cr(IV) response. However, in application, the concentration of H_2O_2 was constant and response decreased by 17% compared with that obtained without H_2O_2 [38]. Instead of an oxidant reagent, UV light can be used to generate hydroxyl radicals and convert Cr(III) to Cr(VI) quantitatively both pre- [34] and post-injection [39]. In the pre-injection system, the conversion was achieved with a flow irradiation system within 1.6 min for a standard and longer irradiation for a sample that contained organic matter [34]. In the post-injection system, an irradiation reactor connected to a vacuum UV lamp (185 and 254 nm) was turned on or off in response to total Cr or Cr(VI), respectively [39]. Another method uses $NaBiO_3$, which is a non-toxic solid oxidizing reagent with high oxidation potential (> 1.8 V) under acidic conditions. Immobilization of $NaBiO_3$ was achieved by mixing it with silica gel, and the column was used in a lab-on-valve format for analysis of water samples [35].

4. Solid phase extraction (SPE)

Chromium speciation analysis has been performed with a SPE column placed in-line with a FIA system [40], in an injection valve of a conventional FIA [41], 5-port injection valve [42] or a selection valve of Auto-pret system (automated pretreatment system) [43] (Fig. 2). All of these systems can effectively switch the sample and effluent passed through the column. For the further effectiveness, some of these systems passed the sample and effluent with the opposite directions. The choice of solid phase is a key to the performance of SPE with FIA. Many different solid phase materials have been applied to speciation analysis of Cr. Cationic Cr(III) and anionic Cr(VI) can be collected separately with ion exchange procedures [40]. Not only polymer based ion exchange resins, but also niobium(V) oxide impregnated on silica gel [44], and Ambrosia beetle-generated acacia polycantha frass [45] have been used for a collection of Cr in ion exchange reactions. However, in samples such as seawater, where there are many ionic species, the resin capacity is not sufficient for adsorption of Cr species. Thus, selective adsorption of Cr species with chelating resins has been widely studied. Cationic Cr(III) can form complexes with many kinds of ligands, and the following resins have been used for Cr(III) absorption: α-benzoin oxime on Amberlite XAD-16 [46], 1,10-phenanthroline on XAD-16 [47], dithizone on Dowex Optipore L493 [48], xylenol orange

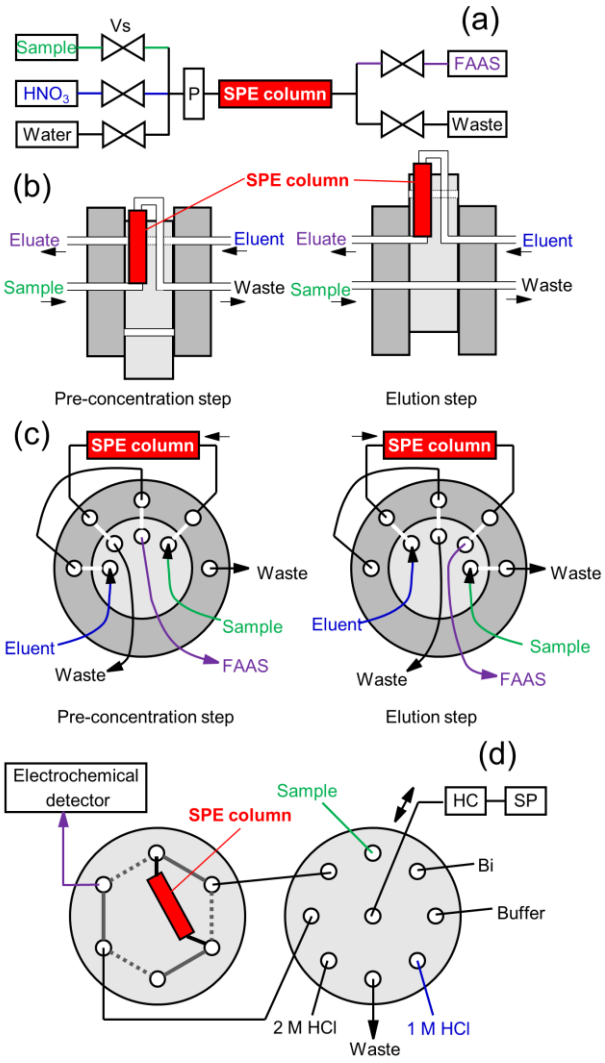

Fig. 2 Solid phase column integrated flow injection analysis (FIA) system with the column integrated in (a) a conventional FIA [40], (b) an injector [41], (c) a five-port valve [42], and (d) a sequential injection analysis (SIA) system [43].

on XAD-16 [42], and poly 2-(5-methylisoxazol)methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinyl-benzene [49]. These materials complex with Cr(III) via nitrogen or oxygen atoms. By contrast, there are few materials for Cr(VI) capture. One suitable compound is ammonium pyrrolidinedithiocarbamate (APDC), which forms complexes with both Cr(III) and Cr(VI). Cr(III) is collected directly by APDC to give a tris-[pyrrolidine-1-dithioato-S,S']-Cr(III) complex, whereas Cr(VI) is reduced to Cr(III) by APDC and forms the complex with APDC and reduced form of APDC, bis-[pyrrolidine-1-dithioato-S-S']-[pyrrolidine-1-peroxydithioato-O,S]-Cr(III) and tris-[pyrrolidine-1-dithioato-S,S]-Cr(III),

respectively [50]. An APDC has been immobilized on polychlorotrifluoroethylene resin and used for SPE [51]. Selective absorption of Cr(VI) has been achieved with poly[*N*-(4-vinylbenzyl)-*N*-methyl-D-glucamine] [52], peptoids [53], and egg-shell membrane [54]. These methods involve a reduction of Cr(VI) and complex formation with Cr(III). These SPE materials are highly selective to Cr(VI) because of its strong oxidizing properties. Speciation analysis of Cr can be achieved by comparison of the concentrations obtained with and without single or double SPE cartridges for separation of Cr(III) and Cr(VI). The methods for SPE-based speciation analysis of Cr were reviewed in 2012 [55].

5. Electrodialytic separation

The differences in the polarities of Cr(III) and Cr(VI) can be used to separate them by electrophoretic and electrodialytic separations. In electrophoretic separation, a salt bridge is used to apply a potential of 1 kV to either end of a sample tube (ø 8 mm, length 100 mm) containing the Cr species, which moves the Cr species into smaller tubes connected to either end of the sample tube [56]. In electrodialytic separation, sample and acceptor solutions are separated by ion permeable membranes, with the acceptor solutions placed in supported liquid membrane hollow fibers with Pt wire electrodes. A direct current of 30 V is applied between the electrodes for 9 min, and this moves one of the Cr species from the sample solution to an acceptor solution with recoveries of 30–50% [57].

In-line electrodialysis devices have been developed for sample pretreatment [58,59,60] and applied to speciation analysis of Cr [61] (Fig. 3). These devices can transfer ions from the sample solution to acceptor solutions quantitatively within 5–10 s. The devices contain thin layers (0.1–0.2 mm) of isolator (+), acceptor (+), sample, acceptor (−), and isolator (−) solutions. These solutions are separated by ion permeable membranes, and electrodes are placed in the isolator solution channels. The thin solution layers decrease the distance ions need to move and provide a strong electric field strength (225 V/cm), which is consistent with the electric field strength typically used in electrophoresis. Thus, rapid and quantitative transfer of ions from sample to acceptor solutions is achieved. The ions are transferred into either the acceptor (+) or acceptor (−) solutions based on their polarity. For Cr species, cationic Cr(III) and anionic Cr(VI) are transferred into the different acceptor solutions. The acceptor solutions can be analyzed by an elemental analysis method, such as ICP-MS or GFAAS, or

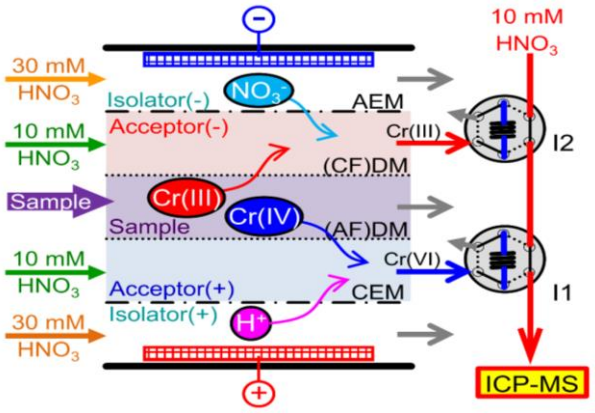

Fig. 3 Electrodialytic separation of chromium species

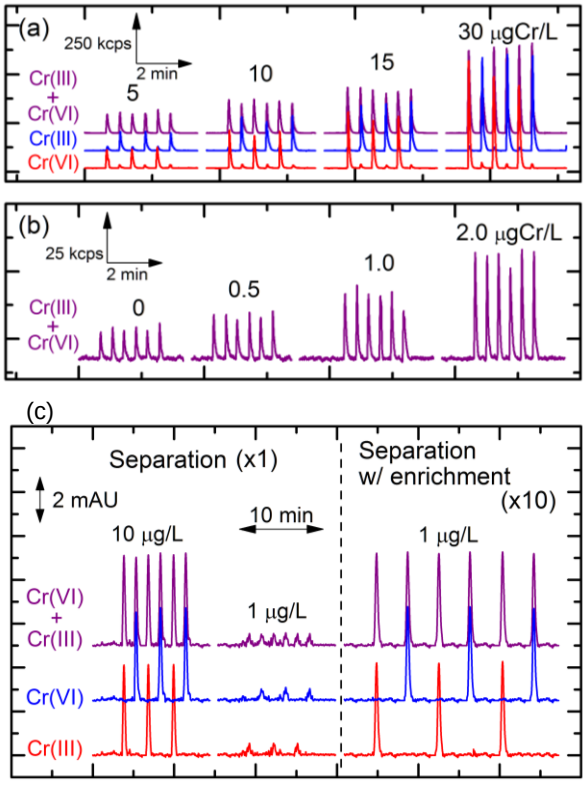

Fig. 4 Response chart obtained with (a, b) inductively coupled plasma mass spectrometry and (c) a diphenylcarbazide-based flow injection analysis system with sample/acceptor flow rate based in-line preconcentreation.

by a FIA system based on the DPC reaction with oxidation (Fig. 4a and 4b) [61]. Electrodialytic separation method can achieve real time separation of Cr species. The acceptor solutions can be continuously supplied for ICP-MS, which allows for continuous monitoring of toxic Cr(VI). This method also separates ionic species from interferences in the sample matrix, such as particulate matter, non-ionic compounds, and large molecules. For example, this pretreatment was useful for

a soil extract which contained colored materials. The materials could have interfered with the color reading for Cr(VI) determination by the DPC method, and organic matter that could have reacted with and removed Cr(VI) [38]. Furthermore, this method can concentrate Cr species. Because quantitative ion transfer is achieved, the analyte concentrations in the acceptor solutions only depend on the ratio of the flow rates of the sample and acceptor solutions. The results are in Fig. 4c. The response to 10 μgCr/L obtained by DPC-FIA with the flow rate ratio of 1 and 1 μgCr/L with the ratio of 10 is well agreed. Thus, electrodialytic ion transfer can simultaneously provide removal of interferences, separation of Cr(III) and Cr(VI), and preconcentration for continuous analysis.

6. Conclusions

FIA methods for speciation analysis of chromium oxidation states have been developed over the past four decades. Chromium species with dramatically different chemical properties can be determined simultaneously and continuously. The regulations in many countries are specific for Cr(VI), and these methods can be used to protect human health and the environment.

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(Received July 31, 2017)
(Accepted August 10, 2017)