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A simple method for chromium speciation analysis in contaminated water using APDC and a pre-heated glass tube followed by HPLC-PDA

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ABSTRACT

In this study, a simple sample preparation method was developed for the determination of tri-and hexavalent chromium in water samples. It utilizes a pre-heated customized glass tube (CGT), to supply the heat energy required for the reaction of Cr(III) with ammonium pyrrolidinedithiocarbamate (APDC). The products of the Cr complexes, tris(1-pyrrolidinecarbodithioato)chromium(III) and bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbodithio(thioperoxoato)]chromium(III) were chromatographed with Shimadzu LC-20AT and Zobax Eclipse C18 (150 mm × 4.6 mm, 5 μm) column using ACN: Water, (7:3, v/v) as the mobile phase. The concentration of Cr(III) ranged from 0.06 mgL^{-1} to 0.09 mgL^{-1} and that of Cr(VI) was between 0.02 $mg\,L^{-1}$ to 0.04 mgL^{-1} in the samples. Percentage recoveries from spiked real samples were between 87% (tap water) to 110% (wastewater) for Cr(III) and 92% (pond water) to 117% (tap water) for Cr(VI). The limits of detection (LODs) were 0.0029 $mg\,L^{-1}$ and 0.0014 mg/L^{-1} for Cr(III) Cr(VI) respectively. While the limits of quantitation (LOQs), were 0.0098 $mg\,L^{-1}$ and 0.0047 $mg\,L^{-1}$ for Cr(III) and Cr(VI) respectively. Method precision (RSD (%)) was 3.3% and 3.5% for Cr(III) and Cr(VI) respectively. The developed method was applied for the speciation analysis of chromium in drinking water, tap water, wastewater, river water, and pond water samples. Our findings proved the method is simple and inexpensive. The method was validated by the analysis of a certified reference material (CRM) SLRS-4. The percentage recovery and RSD(%) from the spiked CRM were 91% and 115% and 0.32% and 1.4% for Cr(III) and Cr(VI) respectively.

1. Introduction

The physiological effects of a metal in biological systems have been linked to its chemical forms rather than the total concentration. The fact leads to prioritizing speciation analysis over the total concentration of metals in matrices [1–4]. Although Cr exhibits −2 to +6 oxidation states, the tri-and hexavalent chromium species are of interest. They symbolize the beneficial and the detrimental roles respectively, associated with the element [2,5]. Although Cr(III) is an essential element to humans, there is currently little or no records of the nutritional benefits of chromium to plants [5–7]. Nonetheless, Cr(III) plays a crucial role in the metabolism of glucose and lipids, which is important in the management of diabetes [1,4,5,8–10]. It also aids the synthesis of nucleic and amino acids in mammals and some organisms, thus enabling the formation of DNA, which bears and transfer genetic information to offspring [11–13].

Conversely, the hexavalent chromium is a class 1 human carcinogen in addition to other known toxic effects [2,3,14–17]. In some reported instances, inhaling dust, dermal contact and ingestion of substances contaminated with Cr(VI) have been linked to nasal septum, asthma, inflammation of the larynx and liver. In addition, dermatitis, skin ulceration, and mutagenic and genotoxic effects in humans and experimental animals have also been associated with interaction with the hexavalent chromium [2,3,14,16,18–22].

The danger of exposure to Cr(VI) is inevitable due to the numerous industrial applications of the element which lead to the generation and disposal of Cr contaminated waste into the environment. Notable applications of Cr in leather tanning, wood preservation, artistic and anticorrosion paints, electroplating, steel alloy and stainless-steel welding as well as metal plating, refractory and metallurgy are on record [2,11,16,23–28].

In a study conducted by Pacyna and Nriagu on the global emission of chromium through anthropogenic and natural sources, it was found that about 7.5×10^3 t to 5.4×10^4 t of chromium are introduced annually into the atmosphere. But an approximate 4.5×10^4 t to 2.3×10^5 t are discharged into aquatic systems, while an estimated 4.84×10^5 t to 1.3×10^6 t of Cr find their way into the soil. According to the report, an estimated one-third of this emitted chromium is the Cr(VI)

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species. Through the rain and gravity, the atmosphere is cleaned up and the contaminants containing Cr are flushed by runoff into water bodies. Thus the atmosphere and aquatic systems serve as pathways for long-range chromium transport [11,25,29]. This has prompted the need for continuous monitoring of Cr species in water and the environment in general.

Methods for the speciation of Cr species involving derivatization by ammonium 1-pyrrolidinecarbodithioate (APDC) have been reported [1,30–33]. Sample preparation is planned to ensure minimal or no conversion of labile Cr(VI) to Cr(III) and decomposition of ammonium pyrolidinedithiocarbamate. As depicted in Reaction (i), Cr(III) species reaction with APDC results in tris(1-pyrrolidinecarbodithioato)chromium(III), or [Cr(III)$(PDC)_3$], **(A).** While Cr(VI) is reduced to Cr(III) during the reaction and in the process forms bis(1-pyrrolidinecarbodithioato)[1-pyrrolidinecarbodithio(thioperoxoato)]chromium(III) or [Cr(III)-$(PDC)_2$(OPDC)], **(B)** and [Cr(III)$(PDC)_3$], **(C)** as the byproduct as shown in Reaction (ii). A study by Honna indicates that the oxygen in the [Cr(III)$(PDC)_2$(OPDC)] complex originates from the chromate ion while the insertion of the oxygen atom takes place before the rate determining step [34].

Recently, Shirkhanloo, Ghazaghi and Eskandari [5] carried out speciation of Cr in human blood by the cloud point extraction (CPE), based on isopropyl 2-[(isopropoxycarbothiolyl)disulfanyl] ethane. And [35] use Triton –X45, and graphene in a CPE for the speciation of Cr in water samples. The electrothermal atomic absorption spectroscopy (ETAAS), detection was employed. The concentration of species was based on the difference. In human inhaled breath condensate, Leese, Morton, Gardiner and Carolan [4] carried out the speciation analysis of Cr using micro liquid chromatography coupled to inductively coupled plasma mass spectroscopy (μLC-ICP-MS) hyphenated system.

Nevertheless, the present work described a simple sample preparation procedure for chromium speciation analysis in water and contaminated water samples. The new sample pretreatment method developed used a customized glass tube (CGT), designed to serve as a reactor with the purpose of speeding up the formation of [Cr(III)$(PDC)_3$] when APDC and sample containing the analyte are introduced into the preheated tube. A locally fabricated insulating system served to check rapid heat loss during the pretreatment, whereas speciation analysis was achieved by HPLC-PDA. A combination of the sample preparation and analysis makes the method inexpensive. Parameters including temperature, time of reaction and heat equilibration of the glass tube, pH, separation conditions, and effects of metals and sodium sulfide were optimized in this study.

2. Materials and methods

2.1. Reagents

Standards of Cr(III) for ICP-MS (999 ± 4 mg/l Trace CERT), Cr(VI) for ICP-MS 1000 ± 2 mg/L trace CERT and ammonium pyrrolidinedithiocarbamate (APDC) (99.0% Trace metal basis) were supplied by Sigma-Aldrich, USA. Acetonitrile (HPLC grade) was purchased from Fisher Scientific, UK. Acetate buffer was prepared from acetic acid (HPLC grade) and sodium acetate trihydrate (99.0% BioXtra) from Sigma–Aldrich, USA, as described by Ruzin [36] and adjusted with 0.1 M acetic acid. Ultra-pure water (18.2 Ω cm) was obtained in the laboratory with the aid of PURELAB Classic, (ELGA Labware, UK), fitted to ELGA MICRMEGS (MC: DS) filter system (Veola Water System Ltd, UK) and equipped with UV dual-wavelength system; 254 nm and 185 nm for destruction of microorganisms and reduction of organics respectively. Water for HPLC was filtered through a 0.22 μm pore size, 47 mm diameter MS MCE Membrane filter, (Membrane Solutions, USA). The certified reference material, SLRS-4, was purchased from the NCR, Canada (Fig. 1).

2.2. Instrumentation

Chromatographic separation was achieved with Shimadzu LC-20AT pump equipped with a DGU-20ASR Degassing unit, SIL-20A HT auto-sampler, CTO-10AS VP oven and SPD-M20A detector. The stationary phase was Zorbax Eclipse Plus C18 (150 mm × 4.6 mm, 5 μm), analytical column and Zorbax Eclipse Plus C18, analytical guard column (12.5 mm × 4.6 mm, 5 μm) were obtained from Agilent Technologies (USA). The pH meter was Metler-Toledo (FiveEasy F20, Switzerland). Total chromium was determined with the ZEEnit 650 P GF-AAS (Analytik Jena Germany). The vacuum pump was the BUCHI V-700 model (BUCHI Labortechnik AG, Switzerland). The chromatographic and GF-AAS conditions are presented in Table 1

3. Sampling and sample treatment

The procedure for sampling the water samples followed the USEPA method 7199 and 3060A suitable for sampling waters and sediments for the purpose of Cr(VI) analysis. Fig. 2 depict the sampling areas. HDPE plastic containers 1 L or 2 L capacity were used for sample storage. Drinking water (DW) and tap water (TW) were collected from commercial dispensers and residences in Petaling Jaya Section 17. Within the confines of the University of Malaya, Kuala Lumpur, (UMKL) river water (RW) and pond water (PW) was sampled from the tributary of Sungai Pantai and UMKL pond respectively. Wastewater samples were obtained from the ninth residential college of the UMKL and a central residential wastewater unit opposite UMKL international house, Petaling Jaya, Selangor.

The grab sampling method was employed in this study. The samples for total Cr analysis were preserved with concentrated nitric acid at pH 2.0 whereas; those collected for the purpose of Cr speciation analysis were adjusted to pH 8–8.5 with ammonia-ammonium sulfate buffer [37,38]. The samples were kept in a freezer prior to analysis. Before further preparation, the preserved samples were vacuum filtered through the MN 615, Ø 110 mm filter paper, (Macherey-Nagel GmbH, Germany). Sample preparation for speciation analysis was carried out within 48 h of sampling. Composite samples of multiple samples from within the same points were used for the analysis.

3.1. Sample preparation for Cr speciation analysis

A 3 mL of acetate buffer, pH 4.5 was dispensed in a 50 mL centrifuge tube and 1 mL (or desired volume to give a desired amount of analyte) of 5 mg L^{-1} Cr(III) or Cr(VI) aqueous solution or both were dispensed into the tube and the mixture was made up to 20 mL with DI water. The pH of the mixture was adjusted to pH 4.5 with 0.1 M HNO_3 and 0.1 M NaOH. 1.5 mL of 2% (w/v) APDC solution was added to the mixture and the pH was adjusted to pH 4.5. The mixture was transferred into the hot CGT, (O.D × L, 13 mm × 110 mm, and 1.5 mm wall) or (O.D × L, 13 mm × 110 mm, and 2.0 mm wall) that was being kept at equilibrium at 110 °C on a hot plate or heat gun, DeWalt D26414, (DeWalt Germany). The CGT and content were placed in a homemade insulating system with a pair of forceps and then allowed to stand for 10 min. The mixture was transferred to the 50 mL centrifuge tube and the glass tube was rinsed with 5 mL ethyl acetate and added to the sample. It was then vortexed at 2400 rpm for 5–10 s to mix and centrifuged at 5000 rpm for 3 min with KUBOKU 4200 centrifuge, (Kuboku, Japan). A 4 mL portion of the ethyl acetate (upper) layer was withdrawn with a pipette into a 140 mm × 18 mm (L × O.D) test tube and evaporated under vacuum on a water bath at 60 °C. The residue was taken up in 1.5 mL acetonitrile, vortexed at 2400 rpm for about 5–10 s before filtering with 0.45 μm PTFE syringe filter into a 2 mL screw cap vial for HPLC analysis.

The real sample was clean-up with Al_2O_3 (WN-6. Neutral activity grade, Super I, Sigma – Aldrich, USA). A 500 mg Al_2O_3 adsorbent was sandwiched between glass fritz at both ends in a 3 mL Bond Elut