Talanta 181 (2018) 401–409

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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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ARTICLE INFO

Keywords:
Speciation analysis
Chromium
Customized glass tube
HPLC-PDA

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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https://doi.org/10.1016/j.talanta.2018.01.041
Received 11 September 2017; Received in revised form 12 January 2018; Accepted 15 January 2018

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

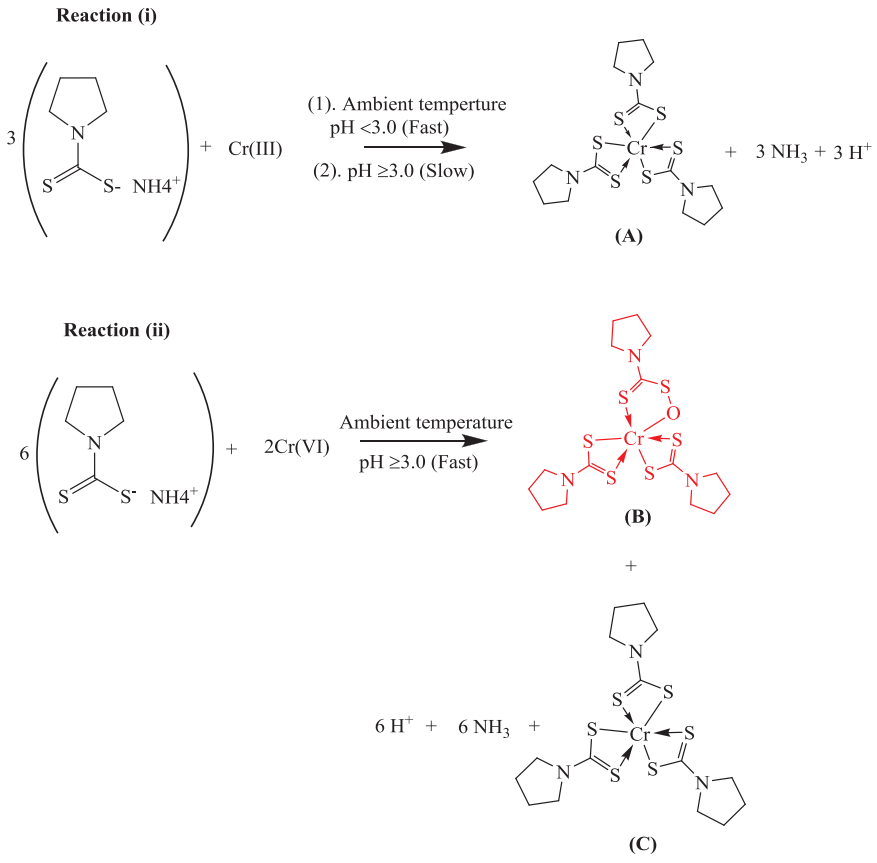

Fig. 1. The demonstration of the reaction of Cr(III) and Cr(VI) with APDC. The only product of Cr(III) –APDC reaction (A), major product of Cr(VI)-APDC reaction (B), and the by-product of Cr (VI)-APDC reaction (C).

Table 1
Chromatographic and GF-AAS conditions for Cr speciation analysis and total Cr determination, respectively.

Parameter	Setting
	HPLC-PDA
HPLC pump system	Shimadzu LC-20AT Pump fitted with a DGU-20ASR Degassing unit, SIL-20A HT Autosampler, CTO-10AS VP Oven and SPD-M20A
Column	Zorbax Eclipse Plus C18 (150 mm × 4.6 mm, 5 μm)
Oven Temperature	33 °C
Eluent	Acetonitrile-Water (70–30)%(v/v)
Inj. Volume.	20 μl
PDA wavelength	190–300 nm
	GF-AAS
Wavelength	357.90 nm
Platform	Liquid
Calibration / mode	Standards / dilution
Drying temperature/time	80–110 °C/ 50 s
Pyrolysis temperature/ time	350–1300 °C / 30 s
Atomization temperature /time	2300 °C/5 s
Clean temperature /time	2450 °C/4 s
Statistic parameter	95% confidence level, 3 replicates

Reservoir, (Agilent Technologies, USA). The BUCHI V-700, Switzerland served as the vacuum pump. After activating the cartridge with deionized water, the filtered sample was vacuum pumped through the Masterflex precision pump tubes, (Cole-Parmer, USA). into the adsorbent for cleanup.

A 100 mL water sample, previously clean-up with Al_2O_3 adsorbent was treated as earlier described but with three pre-heated CGTs. The combined sample after treatment was extracted with 15 mL ethyl acetate in a 250 mL separatory funnel. The lower layer was discarded. The wall of the funnel was rinsed with 5 mL ethyl acetate and the rinsate combined with the extract and treated as earlier described, before analysis.

3.2. Total chromium in water samples

The USEPA method 3005A was used for the determination of total chromium in water samples. The digestion process involved the use of concentrated HCl and HNO_3, (Merck, Germany) and Thermo-Line hot plate, (MS400, Bante Instr, China). The analysis was carried out with a GF-AAS (ZEEnit 650P, Analytic Jena, Germany). Triplicate determinations were made and the results of the analysis are presented in Table 7.

4. Results and discussion

4.1. Method development

Preliminary studies included the manipulation of the separation conditions of HPLC-PDA with Cr standards. The C_{18} reversed phase column was the stationary phase while a water/ acetonitrile mixture was the mobile phase. The mobile phase composition, flow rate, column temperature and sample injection volume were manipulated to achieve optimum separation conditions as shown in Table 1. The second step was the manipulation of the reaction conditions to obtain optimum conditions for the procedure.

4.2. Water samples clean-up

Table 2 and Figs. S1 and S2 (Supplementary) showed the result of the clean-up process with two adsorbents, the LC-C18, and Al_2O_3 adsorbents. The recovery obtained from spiked samples were better with Al_2O_3 adsorbents (117% and 118% for Cr(III)-PDC and Cr(VI)-PDC respectively. The chromatograms of wastewater samples before and after the clean-up process showed the effect of the clean-up process with the Al_2O_3 adsorbent.

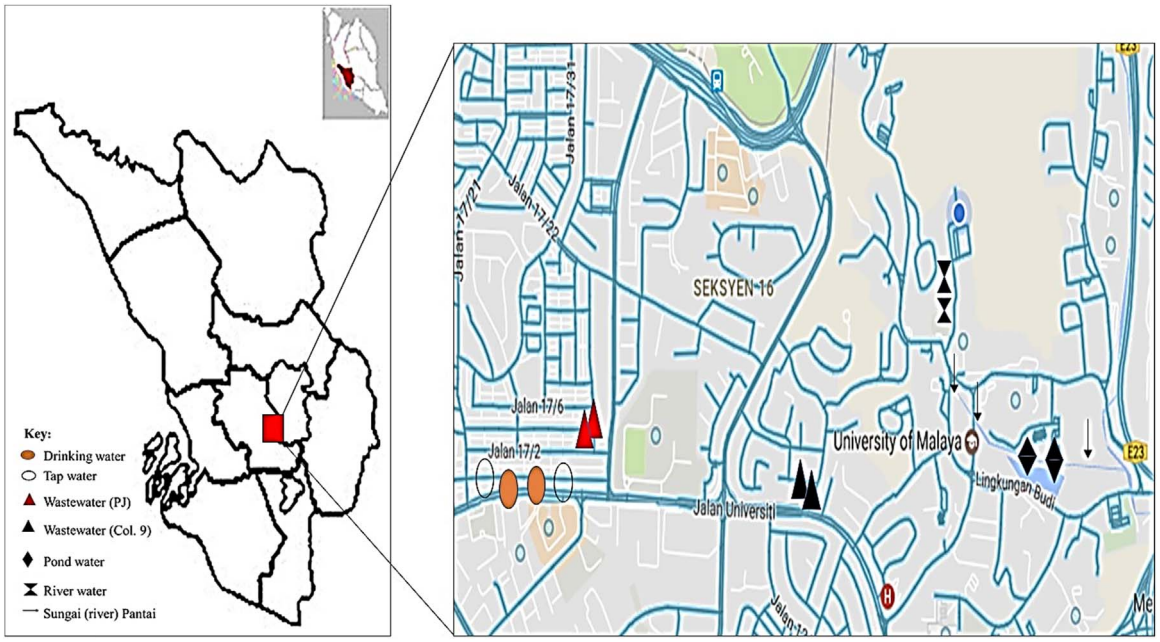

Fig. 2. A schematic map of the sampling areas.

4.3. Method optimization

4.3.1. Reaction time

The time taken for the reaction to complete was determined. The procedure followed the earlier described. However, the CGT was heated on a hot plate or with a heat gun at about 90 °C for 8 min. The reaction mixture was adjusted to pH 4.0 and was allowed to stand in the homemade insulator at various duration ranging from 5 min to 35 min. From Fig. S3 (supplementary), the optimum reaction time was 10 min.

4.3.2. Temperature optimization

A study of the reaction temperature was done by monitoring the temperature at which the CGTs, are heated. The steps earlier described were followed and the acetate buffer was prepared at pH 4.0. The CGT was heated on a hot plate or heat gun at a temperature ranging from 35 °C to 130 °C for 5 min. The mixture was placed in the homemade insulating system for the optimum time of 10 min. The optimum temperature of the reaction (Fig. S4 supplementary) at the optimum reaction time was found to be 110 °C.

4.3.3. The CGT preheating time

The Thermo-Line, MS400, (Bante Instr, China), or heat gun, D26414, (DeWalt Germany) was set at an optimal temperature, 110 °C and the CGT was heated for periods ranging from 0.5 to 7.0 min. The spiked blank samples containing 0.25 mg L^{-1} each of Cr(III) and Cr (VI)) standard solutions at pH 4.0, were transferred into the tubes and placed in the homemade insulating system for 10 min optimum time, before treatment as earlier described. The optimal heating time was 3 min (Fig. S5 supplementary).

4.3.4. Effect of pH on the method

The effect of pH on the method was studied within pH 2.5 and pH 8.0. The blank samples spiked with 0.25 mg L^{-1} analytes were treated as in the procedure at different pH values. The CGT was heated at 110 °C and the reaction mixture contained in the CGT was allowed to stand in the homemade insulating system for 10 min. Fig. 2 indicates pH 4.5 as suitable for the simultaneous speciation analysis of the Cr(III) and Cr(VI) APDC complexes. Above pH 4.5, Cr(III)-PDC complexation drastically reduces as triaquohydroxide ($[Cr(H_2O)_3(OH)_3]$)(s) complex of Cr(III) is formed which is stable and difficult to be replaced by the ligand. At lower pH values, however, Cr(VI) may be reduced to Cr(III) thus decreasing the concentration of the former [2].

4.3.5. Effect of metals and sulfide

The interference study of metals and sulfide on the method was monitored at the optimum conditions using a combination ICP multi-element standard XVI, (Merck, Germany), Ge and Na_2S. The ions, S^{2-}, Mn, Fe, As, Co, Ni, Cu, Zn, and Ge. are known to interfere with the stability of the chromium species in either soil, water or air. Standard solutions containing Cr(III) and Cr(VI) were spiked with 0.05 mg L^{-1} to 0.25 mg L^{-1} of the combined interferences solution and treated as in the procedure. In Fig. S6 (supplementary), the effect of the metals and sodium sulfide on the stability of Cr(VI) in aqueous medium was observed as the increasing concentration of these interferences tend to enhance the signal response of $[Cr(III)(PDC)_3]$ complex. This can be attributed to redox reaction which converts the Cr(VI) to Cr(III) [2].

4.4. Method validation

Parameters of interest were studied in order to prove the cogency of

Table 2
The LC-C18 and Al_2O_3 adsorbents clean-up results.

Analyte	Sample/adsorbent	Spiked (mg L^{-1})	Mean Recovered (mgL^{-1}) (n = 3)	Mean recovery (%) (n = 3)	STDev (s) (n = 3)	RSD%
Cr(III)-PDC	WW / Al_2O_3	0.20	0.234	117	0.003	1.15
	WW / LC-18	0.20	0.196	98	0.003	1.65
Cr(VI)-PDC	WW / Al_2O_3	0.45	0.529	118	0.007	1.24
	WW / LC-18	0.45	0.518	115	0.008	1.52

Key: WW = wastewater.

the method. Tri and hexavalent chromium were determined as [Cr(III)$(PDC)_3$] and [Cr(III)$(PDC)_2$(OPDC)] respectively. The calibration (external), procedure studied the direct response of the detector with changes in the analyte concentration. This was done by analyzing blank samples containing various amounts of Cr standards ranging from 0.20 mgL^{-1} to 1.0 mg L^{-1} previously passed through sample preparation as earlier described. The calibration parameters are depicted in Table 5.

The dynamic and working ranges were studied with analytes concentration ranging from 0.001 mg L^{-1} to 4.0 mg L^{-1} Cr(III) or Cr(VI) in blank samples. The instrument showed a dynamic response to changes in analyte concentration within the range of concentration used. Nevertheless, the working ranges that is, the response of the instrument with accept uncertainty to changes in analyte concentration, were 0.05 mg L^{-1} to 3.0 mgL^{-1} and 0.006 mg L^{-1} to 3.0 mg L^{-1} for Cr(III) and Cr(VI) respectively, Fig. S7 (a) and (b) (supplementary).

The specificity study is to ensure that the peaks recorded are those of the analytes. This was monitored by comparing peaks from reagent water or real sample spiked with known Cr(III) and Cr(VI) standards with the peaks from unspiked samples as shown in Fig. 3. The LabSolutions software of the Shimadzu HPLC calculated the selectivity of the analytes and it ranged from 1.067 to 1.145 Cr(III) and 1.065–1.113 Cr (VI) complexes. The theoretical plates were between 3477 to 7327 and 1518–5128 for Cr(III) and Cr(VI) complexes respectively.

The accuracy of the method was investigated following the method described by Al-Rimawi [39], Narola, Singh, Mitra, Santhakumar and Chandrashekhar [40]. Nine determinations from triplicate analysis of three concentration levels, (0.25 mg L^{-1}, 0.625 mg L^{-1} and 0.875 mg L^{-1} Cr(III) and Cr(VI)) were performed. The percentage recovery and percentage relative standard deviation of each level were computed (Table 3) and compared with the literature [40]. Similarly, the mass balance study was done with the same amount of analytes which were acid digested, made up to 20 mL and analyzed with GF-AAS. (Fig. 4)

The agreement of a set of measurements with each other was investigated by determining the instrument and method precisions. Spiked blank or real samples were previously passed through sample preparation before analysis. The instrument precision was established by injecting seven replicates of a spiked blank water sample containing 0.2 mg L^{-1} standards of Cr(III) and Cr(VI). But the method precision was evaluated by obtaining seven replicates from single injections of seven portions of the river water sample previously spiked to 0.2 mg L^{-1} of each analyte [39,40]. The RSD (%) of the response and retention time (Table 4), were compared with the acceptable values of ≤5% and ≤10% for instrument and method precisions respectively [40]

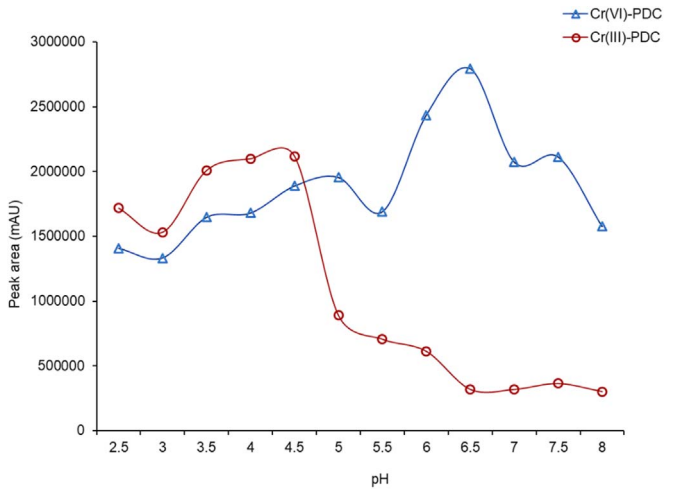

Fig. 3. Effect of pH on the reaction of Cr(III) and Cr(VI) with APDC using 0.25 mg L^{-1} of the standard solutions.

The robustness of a method signifies its capability to withstand slight changes in some conditions of analysis. Robustness was studied by deliberate alteration of the eluent composition, flow rate and column temperature of the analysis. The percentage recovery and RSD (%) were calculated and compared with the acceptable values (Fig. 5): recovery (80% to 120%) and RSD ≤5%. [39,40]. The recovery of Cr(III)-PDC ranged from 90% to 97%, while RSD (%) was 0.04–0.25%. On the other hand, 112–121% and 0.09–4.05% are the recovery (%) and RSD(%) respectively for Cr(VI)-PDC.

The limit of detection (LOD) of an analyte represents a detectable but not necessarily reliably quantifiable concentration of the analytes. While the limit of quantitation (LOQ), denotes the smallest but reliably quantifiable amount of the analytes. The signal to noise ratio (S/N) method is widely employed for LOD and LOQ determination in chromatography where peak signal measurement is important and in cases where the noise signal of the instrument is stable [39,41]. A noise stability test of the Shimadzu PDA detector performed by replicate determinations of a blank sample and computed by the American Society for Testing and Materials (ASTM) method of the LabSolutions software gave the RSD(%) of 57.392% indicating instability, Fig. S8 (a) (Supplementary). Similarly, the extent to which the analysis parameters are affected by the fluctuating noise of the detector was examined by replicates chromatographed of a spiked sample. The calculated RSD(%) of the retention time, peak area, peak height, and recovery (%) was < 5% each, while that of the noise signal was between 15% and 40%. Nevertheless, the analytes recovery was > 84% and > 95% for Cr (III) and Cr(VI) respectively (Fig. S8 (b) Supplementary), indicating no significant effect on the overall analytical result by the noise. Thus a procedure though cumbersome but described as metrologically better for chromatography determination of LOD and LOQ was employed [41,42]. Briefly, ten blank samples spiked with 0.04 mg L^{-1} Cr(III) or Cr(VI) standard solution previously passed through sample preparation were chromatographed to give ten replicate analyses. The residual standard deviation, (σ°) of the peak area was calculated. The standard deviation, (σ^{*}) to be used for LOD and LOQ was computed as in Eq. (1). While the LOD and LOQ were determined using Eqs. (2) and (3) respectively [42] before validation.

$$\sigma^{*} = \frac{\sigma^{\circ}}{\sqrt{n}} \quad (1)$$

$$LOD = \frac{3\sigma^{*}}{m} \quad (2)$$

$$LOQ = \frac{10\sigma^{*}}{m} \quad (3)$$

Were, m = slope of the calibration, σ° = residual SD, σ^{*} = SD for limits calculation.

The calculated limits and limits validation RSD% are presented in Table 5 where the LODs and LOQs are 0.0029 mg L^{-1} and 0.0098 mg L^{-1} and 0.0014 mg L^{-1} and 0.0047 mg L^{-1} Cr(III) and Cr (VI) respectively.

To validate the limits, it was important to bear in mind that, the RSD (%) > 5% for replicates measurements from a single sample indicates non-precision of the measurement. This phenomenon arises when the concentration of the analyte cannot be quantified with certainty. The validation analysis, gave the RSD(%) of the LOD and LOQ of Cr(VI) are 10.7% and 3.7% respectively, indicating that 0.0014 mg L^{-1} Cr(VI) (which is the LOD), is detectable but not accurately quantifiable. Similarly, the LOD and LOQ of Cr(III) validation gave the RSD(%) 15.1% and 2.2% respectively from the replicates analysis thus, confirming both limits. A comparison of LOD of this method with others is shown in Table 6.

5. Matrix effect

The matrix effect (ME), was studied by the signal-based approach

Table 3
Accuracy and mass balance study of the method with reagent water spiked to 0.25 mg L^{-1}, 0.625 mg L^{-1} and 0.875 mg L^{-1} Cr(III) and Cr(VI) standards.

Accuracy								Mass balance analysis			
Spiked (mg/L^{-1})		Mean found (mg/L^{-1})		Recovery (%)		STDev (s)		Total Spiked	Mean found (mg/L^{-1})		
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III) / Cr(VI)	HPLC-PDA	GF-AAS	STDev (s)
0.25	0.25	0.244	0.275	97.68	110.00	0.0002	0.0012	0.5	0.519	0.581	0.111
0.625	0.625	0.507	0.665	81.13	106.44	0.0003	0.0051	1.25	1.172	1.198	2.044
0.875	0.875	0.890	0.979	101.67	111.91	0.0005	0.0001	1.75	1.869	1.630	0.722

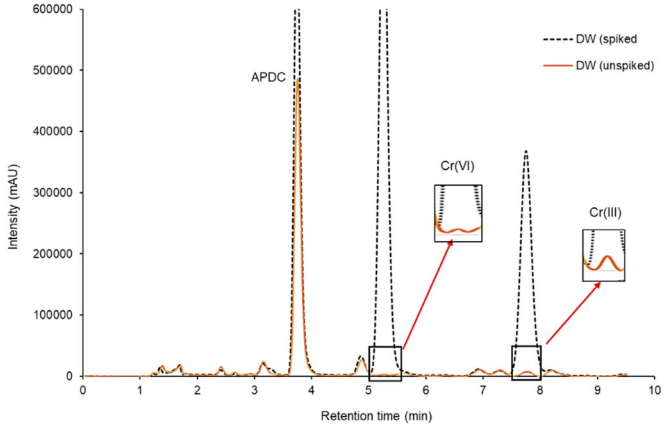

Fig. 4. Specificity of the method with a chromatogram of spiked and unspiked drinking water (DW) sample.

Table 4
Instrument and method precision.

Analyte	Parameter	RSD (%) (n = 7)	
		Method	Instrument
Cr(III)	Retention time (min)	0.35	0.07
	Peak area (mAU)	3.34	0.41
Cr(VI)	Retention time (min)	0.15	0.03
	Peak area (mAU)	3.51	1.29

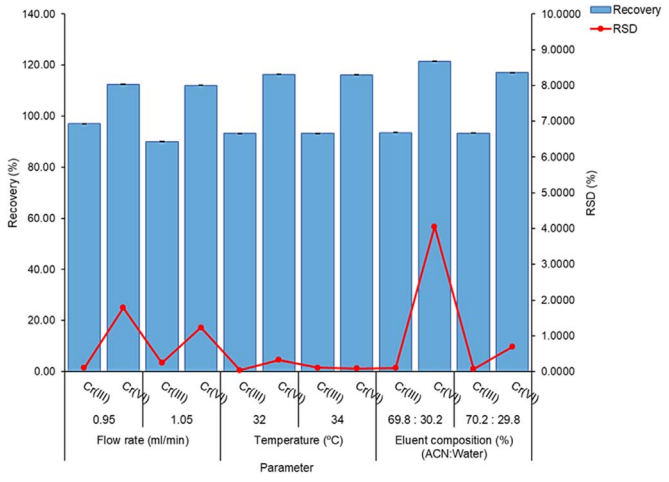

Fig. 5. Robustness of the method using blank sample spiked to for 0.25 mg L^{-1} Cr(III) and Cr(VI) standards.

[46] and reported as a percentage relative matrix effect (RME(%)), due to non-availability of Cr-APDC commercial complexes [47]. To obtain the results in Table 4, known amounts of Cr standard were spiked in DI water and real matrices and were subjected to sample preparation.

Table 5
Parameters of the tri-and hexavalent Cr-APDC complexes, [Cr(III)$(PDC)_3$] and [Cr(III)$(PDC)_2$(OPDC)] denoted as Cr(III) and Cr(VI) respectively.

Parameter	Analytes	
	Cr(III)	Cr(VI)
Working range (mg L^{-1})	0.05–3.0	0.006–3.0
Cal. linearity (mg L^{-1})	0.2–1.0	0.2–1.0
R^2	0.9996	0.9980
LOD (mg L^{-1})	0.0029	0.0014
LOQ (mg L^{-1})	0.0098	0.0047
Validation of limits (n = 6)		
LOD precision (RSD(%))		
Retention time	0.2128	0.35
Peak area	15.1931[a]	10.689[a]
Peak height	7.9016[a]	13.359[a]
LOQ precision (RSD(%))		
Retention time	0.435	0.032
Peak area	2.183	3.74
Peak height	2.227	2.567

[a] RSD(%) > 5% for replicates from a single sample indicates non-precision.

Similar amounts of the synthesized complexes were spiked in ACN of the same volume as the matrices. The signals of the analytes were obtained and the RME(%) was thus determined as in Eq. (4). From literature, signals suppression, (RME(%) < 100%) and enhancement, (RME(%) > 100%) are indication of matrix effect. While RME(%) = 100% is an indication that no matrix effect was observed [47–49]. Most signal enhancements were observed when comparing between spiked blank and spiked real samples signals, and signal suppression was prominent when comparing signals from the synthesized complex in ACN with that from the spiked real sample. The latter observation is expected as the synthesized complexes were from a purer source of chromium species. Recovery was calculated by Eq. (5) gave 83–92%, Cr (III) and 97–111% Cr(VI), is an indication that the matrix effect on the analyte signals is not detrimental to the overall analytical result. This is true for the reason that the recovery from the analysis agreed with the acceptable recovery range of 80–120% [39,40]. The relative recovery (RR(%), was computed AOAC [50] method represented in Eq. (6). and was between 62–71% in Cr(III) and 84–101% Cr(VI) which fell with the expected range. This further showed that ME is not detrimental to the overall analytical result.

$$\text{RME}(\%) = \frac{\text{ANALYTE SIGNAL (post-extracted spiked matrix)}}{\text{ANALYTE SIGNAL (solvent or post extracted spiked blank)}} \text{x } 100 \quad (4)$$

$$\text{Recovery}(\%) = \frac{C_f}{C_A} \text{x } 100 \quad (5)$$

$$\text{RR}(\%) = \frac{(C_f - C_u)}{C_A} \text{x } 100 \quad (6)$$

C_f = concentration in a fortified sample,
C_u = concentration in unfortified sample,
C_A = concentration analyte added to sample.

Table 6
Comparison of LODs obtained from the speciation analysis of chromium by this method with the literature.

Matrix	Sample preparation	Technique	LODs	References
River, tap, waste, and drinking waters	Preheated glass tube, derivatization with APDC, incubate in homemade incubator, extracted with ethyl acetate	HPLC-PDA	0.0029 mg L^{-1} Cr(III) and 0.0014 mg L^{-1} Cr(VI)	This method
Waste water	Incubation and centrifugation; derivatized with APDC and preconcentrate with $[C_4MIM][PF_6]$	HPLC-DAD	0.0019 mg L^{-1} Cr(III) and 0.0010 mg L^{-1} Cr(VI)	[32]
Sediment	End-over-end shaking with DI water and filtration. CPE with TAN and 1.25% (v/v) Triton X-114, pH 5.5 1-(2-thiazolylazo)-2-naphthol (TAN)	HPLC-UV–Vis	0.0075 mg L^{-1} Cr(III) 0.0035 mg L^{-1} Cr(VI)	[43]
Tap, river and mineral water	Dual electro membrane extraction (DEME) and derivatized with APDC	HPLC-UV–Vis	0.0051 mg L^{-1} Cr(III) 0.0028 mg L^{-1} Cr(IV)	[1]
Drinking water	Filtration; derivatization with EDTA	HPLC –ICP-MS	0.00009 mg L^{-1} Cr(III); 0.0010 mg L^{-1} Cr(VI)	[10]
Work place air	Ultrasonic extraction at pH 4.0, dilute with mobile phase and filter; derivatization with EDTA	HPLC –ICP-MS	0.0004 mg L^{-1} Cr(III) to 0.0006 mg L^{-1} Cr(VI)	[44]
Chromate workers' urine	Pre-treatment with TEA containing EDTA/ incubation or allow mixture to stand at room temp; filtration; derivatization with EDTA	HPLC-ICP-MS	0.00003 mg L^{-1}	[45]

Table 7
Relative matrix effect (RME(%)) by the signal-based method, recovery (%), and relative recovery (RR(%) by the AOAC method.

Sample	Cr(III) RME(%)		Cr(VI) RME(%)		Recovery(%)		RR(%)	
	A	B	A	B	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
DW	102.67	88.19	99.72	100.45	89.19	108.25	65.85	101.58
PW	107.14	92.03	103.15	103.90	91.25	111.76	71.25	98.42
RW	105.72	90.81	103.20	103.95	85.91	103.46	62.58	93.46
TW	97.83	84.03	94.98	95.67	87.65	106.34	64.32	99.67
WW1	100.40	86.24	97.84	98.55	83.16	97.38	63.16	87.38
WW2	88.84	80.54	88.97	89.61	92.22	111.71	62.22	101.71
MIN	**88.84**	**80.54**	**88.97**	**89.61**	**83.16**	**97.38**	**62.22**	**87.38**
MAX	**107.14**	**92.03**	**103.20**	**103.95**	**92.22**	**111.76**	**71.25**	**101.71**

Key: A = RME(%) compare to spiked blank; B = RME(%) compare to synthesized Cr-PDC complexes dissolved in acetonitrile; RR(%) = relative recovery.

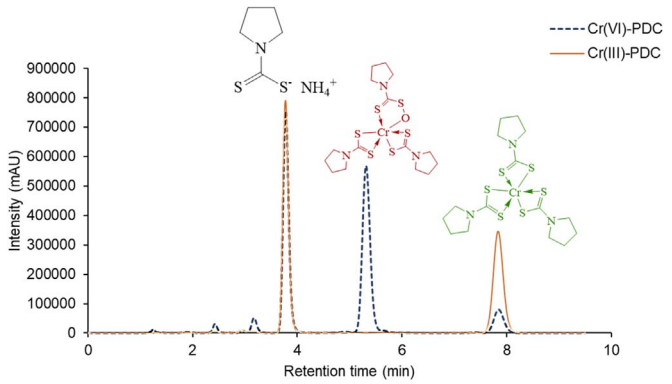

Fig. 6. Chromatogram of 0.25 mg L^{-1} chromium spiked in blank water sample under optimal conditions.

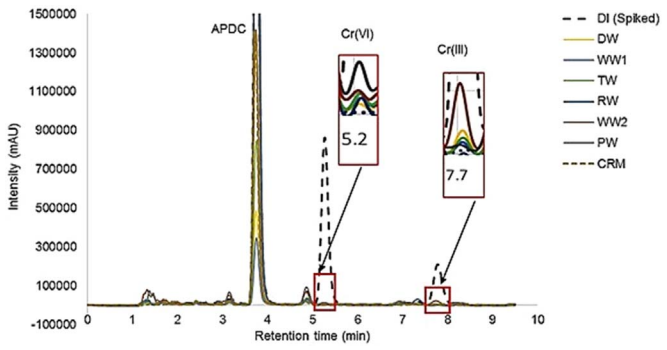

Fig. 7. Chromatogram of real samples compared to spiked deionized (DI) water, Drinking water (DW), wastewater (WW), tap water (TW), river water (RW), pond water (PW) and certified reference material (CRM) SLRS-4 samples.

6. Application to water samples

In Table 7, the analysis characteristics and concentration of the analytes from HPLC-PDA and GF-AAS analysis are presented. The specificity of separation is depicted in Figs. 6 and 7. Chromium species were elucidated and detected as $[Cr(PDC)_3]$ and $[Cr(PDC)_2(OPDC)]$ representing Cr(III) and Cr(VI) respectively with the HPLC-PDA analysis. Quantitation was based on external calibration and peak area signals of the analytes. Samples including wastewater, tap water, drinking water, pond water and river water were analyzed by the method. The concentration of Cr(III) ranged from 0.06 mg L^{-1} to 0.09 mg L^{-1} and that of Cr(VI) was between 0.02 mg L^{-1} to 0.04 mg L^{-1} (Table 8).

The CRM contains only Cr(III) with a certified concentration of 0.33 μg L^{-1} (0.00033 mg L^{-1}) which is below the detection limit of the CGT method. This was evident by the absence of analyte signals at the retention time of Cr(III) and Cr(VI) of the unspiked CRM sample. Elsewhere, Ying, et al., found 0.0176 mg L^{-1} and 0.0465 mg L^{-1} in wastewater samples [32], while 0.0111 mg L^{-1} Cr(VI) in mineral water reported by Safari, Nojavan, Davarani and Morteza-Najarian [1]. Recovery from spiked water samples containing various amounts of Cr(III) and Cr(VI) standards ranged from 87% to 110% and 92–117% respectively. Spiked recovery from CRM was 92% and 115% of Cr(III) and Cr (VI) respectively. The STDs of the results were less 5.0 mg L^{-1} and the RSD% were less than 10% in both the speciation and total chromium analysis.

The total Cr concentration in the water samples as determined by GF-AAS ranged from 0.038 mg L^{-1} to 0.043 mg L^{-1}. Spike recovery fell between 90% and > 119%. The contribution of waste and river water to the spiked samples seems to enhance analyte recovery. The recovery

Table 8
Mean values (n = 3), from the speciation analysis of Cr(III) and Cr(VI) APDC complexes by HPLC-PDA and total Cr analysis by GF-AAS of spiked, unspiked water samples and certified reference material SLRS-4.

Sample	HPLC-PDA analysis						STDev (s)		RSD (%)		GF-AAS analysis			STDev(s)	RSD (%)
	Spiked (mg L^{-1})		Found (mg L^{-1})		Recovery (%)						Spiked (mg L^{-1})	Found (mg L^{-1})	Recovery (%)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)					
DW	0.60	1.00	0.58	1.06	96	106	0.016	0.012	2.816	1.098	0.050	0.049	98	0.210	0.40
PW	0.15	0.30	0.15	0.28	99	92	0.001	0.001	0.454	0.338	0.050	0.060	120	0.285	0.40
RW	0.40	1.00	0.36	1.13	88	113	0.000	0.001	0.090	0.106	0.050	0.047	95	0.272	0.30
TW	1.60	0.80	1.39	0.94	87	117	0.001	0.003	0.044	0.333	0.050	0.052	103	0.233	0.40
WW1	0.45	0.80	0.49	0.93	110	116	0.015	0.017	3.062	1.813	0.050	0.060	119	0.206	0.30
WW2	0.15	0.20	0.13	0.19	89	94	0.000	0.000	0.212	0.171	0.050	0.059	117	0.206	0.30
CRM	0.40	0.50	0.37	0.58	92	115	0.001	0.008	0.316	1.441	0.050	0.049	99	0.457	0.90
DW	–	–	0.07	0.02	–	–	0.000	0.001	0.086	5.133	–	0.040	–	0.056	0.10
PW	–	–	0.06	0.04	–	–	0.000	0.000	0.505	0.524	–	0.038	–	0.257	0.60
RW	–	–	0.07	0.03	–	–	0.000	0.001	0.662	2.058	–	0.042	–	0.046	0.10
TW	–	–	0.07	0.02	–	–	0.000	0.000	0.290	0.352	–	0.039	–	0.217	0.50
WW1	–	–	0.06	0.03	–	–	0.000	0.000	0.043	0.540	–	0.039	–	0.174	0.40
WW2	–	–	0.09	0.03	–	–	0.001	0.000	0.567	0.478	–	0.041	–	0.174	0.40
CRM	–	–	ND	–	–	–	–	–	–	–	–	0.005	–	0.021	0.40

Key: DW = Drinking water, RW = River water, WW = Waste water, TW = Tap water, and PW = Pond water.

from CRM was 88% and the total amount of Cr was 0.005 mg L^{-1}. The World Health Organization (WHO), and the National Water Quality Service (NWQS), Malaysia recommends 0.05 mg L^{-1} as the total concentration of Cr in drinking water [51].

7. Conclusion

The simplicity of the CGT method lies in the use of inexpensive tools for sample preparation and the insulation system made from scraps. The separation and detection of the analytes are equally simple and used readily available solvents. It is also not pH dependent or needs expensive detectors like the inductively coupled plasma mass spectroscopy (ICP-MS). The CGT sample preparation is fast and completes within 10 min compared to others that take a longer time at about 50 °C to 60 °C. The method also proved to be efficient due to good recovery from spiked samples and CRM SLSR-4. Its sensitivity is comparable to other methods as detection limits (LODs) were similar and in some cases lower when compared to literature. Due to the use of on-hand apparatus, reagents and detector system, the CGT sample preparation and speciation analysis are inexpensive.

Acknowledgement

***Funding and support*:** The Institut Pengurusan dan Perkhidmatan Penyelidikan (IPPP) of The University of Malaya funded this research through grant No. PG057 2013B. The Federal University of Technology, Minna, Nigeria, and The Tertiary Education Trust Fund (TETFund) Abuja, Nigeria granted study fellowship to The University of Malaya, Kuala Lumpur.

Gratitude: Dr. M. A. Ashraf formerly of Geology Department, University Malaya, Kuala

Lumpur, contributed in the preliminary stage of the research.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2018.01.041.

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