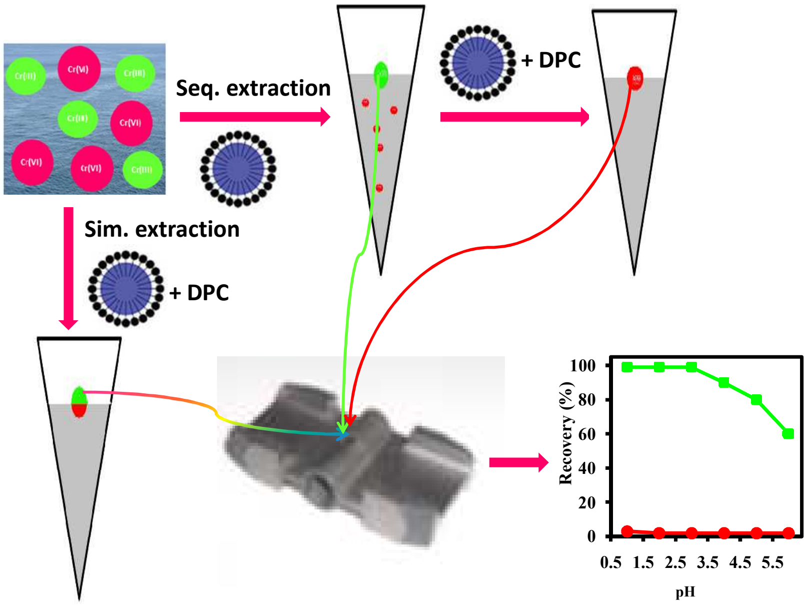
A novel non-chromatographic strategy for sequential/simultaneous extraction and analysis of chromium species by electrothermal atomic absorption spectrometry in effluents and different water sources

Journal:	*Journal of Analytical Atomic Spectrometry*
Manuscript ID:	JA-ART-06-2014-000206.R2
Article Type:	Paper
Date Submitted by the Author:	25-Aug-2014
Complete List of Authors:	Meeravali, Noorbasha; CCCM, R., Manjusha; CCCM, Kumar, Sunil; CCCM,

Graphical abstract



A novel non-chromatographic strategy for sequential/simultaneous extraction and analysis of chromium species by electrothermal atomic absorption spectrometry in effluents and different water sources

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A novel surfactant assisted dispersive liquid–liquid microextraction based on solidification of floating organic drop procedure is developed for sequential and simultaneous pre-concentration of Cr(III) and Cr(VI) from tap, river, ground and wastewaters. The sequential extraction is based on the selective formation of extractable complexes of Cr(III) with reactive head group solubilising sites of dispersing dodecyl benzene sulfonate surfactant, in presence of Cr(VI). The extracting, 1-undecanol pre-concentrates the formed extractable Cr(III) from bulk aqueous solution and solidifies it on lowering the temperature. The Cr(VI) present in the aqueous solution is subjected to a similar extraction procedure after addition of diphenylcarbazide. In the simultaneous extraction, both the species are extracted by adapting a similar extraction procedure after addition of diphenylcarbazide and surfactant to fresh aliquots, to determine total chromium. The chromium concentrations in 1-undecanol phases are determined using continuum source ETAAS (Electrothermal Atomic Absorption Spectrometry). The parameters affecting the process are optimized. Under the optimized conditions, the pre-concentration factors and limits of detections for Cr(III) and Cr(VI) in sequential and total Cr in simultaneous extractions are 25, 50 and 40; and 3, 1 and 4 pg mL^{-1}, respectively. The recoveries are in the range of 94-99% at 50-400 pg mL^{-1} for Cr(III) and Cr(VI). The accuracy of the procedure is validated by comparing the sum of the concentrations of each individual species obtained from sequential extraction with total chromium obtained in the simultaneous extraction procedure applied to certified reference materials such as BCR 713 effluent, BCR 714 influent and NIST 1643c water and water samples.

Introduction

Ensuring safe drinking water for human beings worldwide is a top priority for all agencies concerned because its quality causes direct impact on human health.[1] Data from the recent past shows that chromium, especially Cr(VI) needs regular monitoring in drinking water.[2] It is mainly due to its high carcinogenicity, mobility and bioavailability.[3] Hence, recently the Office of Environmental Health Hazard Assessment (OEHHA) of California EPA given a public health goal of 0.02 ng mL^{-1} for Cr(VI) in drinking water at a risk level of one-in-one-million.[4,5] However, due to extensive use of Cr(VI) in industrial processes large quantities are discharged mostly to natural water bodies. Hence, it is essential to monitor individual species along with total Cr at these levels for providing safe drinking water.

Nowadays, dispersive liquid–liquid microextraction, DLLME and solidified floating organic drop microextraction, SFODME are the two most frequently used miniaturized non-chromatographic procedures used for pre-concentration of organic pollutants and inorganic metal chelates.[6,7] Furthermore, the parameters affecting these extractions and their advantages and limitations are well documented.[7-10] One of the greatest limitations of these extractions is the longer extraction times and lower extraction efficiencies of hydrophilic inorganic species and polar organic compounds.[11,12] To overcome the former limitation, in recent past, dispersive liquid–liquid microextraction based on solidification of floating organic drop, DLLME-SFO concept has been introduced, which exhibits synergism compared to the methods mentioned previously.[13-15] In this concept, an organic dispersive solvent is introduced into SFODME procedure, which increases the contact surface area between the aqueous sample and extraction solvent as a result organic toxicants and metal chelates are extracted faster.[15-18] However, it is unable to overcome the latter limitation due to lack of any reactive solubilizing sites in both dispersive and extracting organic solvents. This can be overcome by using reactive surfactants as a dispersive or extracting solvent. Surfactants are environmental friendly, non-toxic, non-volatile and amphiphilic, which when used as solvents can act as better dispersers than the commonly used organic solvents. Recently, sodium dodecyl sulfate as a dispersive and decanoic acid as a extracting solvents are used respectively, in DLLME and DLLME-SFO for the extraction of Cr(VI).[19,20] The concept of utilizing the surfactant as a dispersive solvent in DLLME-SFO has scarcely been studied.

Until now, all the reported DLLME, SFOME and DLLME-SFO procedures have used a common concept of differential speciation approach to determine either Cr(III) or Cr(VI), using selective chelating agents followed by total chromium after oxidation of Cr(III) or reduction of Cr(VI).[19-25] Only one microextraction procedure has reported a sequential extraction approach using chelating agent for the determination of chromium species.[26]

In this work, for the first time, we describe a new strategy for sequential and simultaneous extraction of Cr(III) and Cr(VI) from various water samples using surfactant assisted dispersive liquid–liquid microextraction based on solidification of floating organic drop, DLLME-SFO procedure prior to the determination by continuum source ETAAS. The diphenylcarbazide, DPC forms a cationic Cr(III)-diphenylcarbazone selectively with Cr(VI), in presence of Cr(III). The addition of sodium dodecyl benzene sulfonate, SDBS an anionic surfactant reacts simultaneously with both cationic species (Cr(III) and Cr(III)-diphenylcarbazone) and pre-concentrate into a small volume of 1-undecanol, without using any oxidation/reduction steps, which gives total chromium. In the sequential extraction, a fresh aliquot is subjected to similar extraction procedure with SDBS alone (without DPC), which reacts selectively with cationic Cr(III) and leaves the anionic Cr(VI) in the aqueous solution. This aqueous solution is subjected to a similar extraction procedure with DPC, which pre-concentrates the Cr(VI) after forming cationic Cr(III)-diphenylcarbazone. The accuracy of the procedure is validated by comparing the sum of the concentrations of each individual species obtained from sequential extraction and total chromium obtained in the simultaneous extraction procedure with the certified values of BCR-713 effluent, BCR-714 influent and NIST 1643c water certified reference materials.

Experimental

Instrumentation

Chromium concentrations in the organic phases were determined by using continuum source ETAAS (Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube, MPE 60 auto sampler and xenon short arc lamp in hot-spot mode operated at 300W as a continuum radiation source were used. A high resolution double monochromator consisting of a prism and an echelle grating monochromator, providing a spectral bandwidth per pixel of ca. 2 pm at 200 nm were used. A linear charge coupled device (CCD) array detector total 588 pixels, out of which 200 pixels were used for the determination of dispersed radiation. An analytical line at 357.6687 nm was used to measure the integrated absorbance of chromium. The absorbance was measured using the central pixel (CP) ± 1 pixels. Argon with a purity of 99.99% was used as the purge gas. The optimized temperature programme used for determination of chromium is given in Table 1. Magnetic stirrer (Tarson, Chennai, India) was used for mixing the solutions.

Reagents and standard solutions

Ultra pure water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Sub-boiled HCl and HNO_3 (Merck, Darmstadt, Germany) were prepared in our laboratory using quartz stills kept inside the clean bench. Stock standard solutions (0.1 mg mL^{-1}) of Cr(III) and Cr(VI) were prepared using 1 mg mL^{-1} Cr(III) and Cr(VI) solutions (Sigma-Aldrich, Steinheim, Germany). Working standards were prepared daily by subsequent dilution. The solutions of 10% m/v sodium dodecyl benzene sulfonate, SDBS, sodium dodecyl sulfate, SDS, Triton X-114, cetyl trimethyl ammonium bromide, CTAB procured from Sigma-Aldrich, Steinheim, Germany were prepared in water except SDBS prepared in methanol. 1-Undecanol (Sigma Aldrich, Steinheim, Germany) was used directly without any further purification. The solution of 0.05% m/v diphenylcarbazide, DPC (Merck, Darmstadt, Germany) was prepared in 5% v/v H_2SO_4 and methanol. Interference study was carried out by using 1 mg mL^{-1} of Ca^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} solutions. Influents and effluents of waste water treatment plant located in Hyderabad city were collected in cleaned plastic containers and were initially rinsed three times with the same water. Tap, samples were also collected in the same manner. The river water was collected from river Ganges from the city of Allahabad during Kumbha Mela in April 2013. These were filtered through a 0.45 µm membrane and kept in a refrigerator at 4^oC until use.

Surfactant assisted DLLME-SFO procedure

Sequential extraction of chromium species

Extraction of Cr(III)

Aliquots of 1-5 mL certified reference materials and water samples were taken in pre-cleaned sample vials containing a PTFE coated stirrer bar and the pH was adjusted to 1. Then, 1 mL of 10% m/v sodium dodecyl benzene sulfonate, 0.4 mL of 30% m/v NaCl and 0.3 mL v/v 1-

undecanol were added. These solutions were made up to 10 mL using the Milli-Q water. A cloudy solution was formed by the uniform dispersion of 1-undecanol in the aqueous phase in presence of dispersive surfactant. The magnetic stirrer was turned on and the solution was mixed for 2 min at 500 rpm to enhance the rate of the reaction between Cr(III) and reactive head group solubilising sites of anionic surfactant. After stirring, the fine droplets of the 1-undecanol were floating at the top of the sample vial. Then, the sample vial was transferred into a beaker containing mixture of ice and salt for cooling. After 2 min, the 1-undeconal phase was solidified and the same was transferred into a conical ETAAS auto-sampler vial, where it melted immediately at room temperature and the volume was found to be 0.2 mL, which was made up to 0.4 mL by adding 0.2 mL methanol. An aliquot of 10 μL was injected into the graphite tube for quantification of Cr(III). Procedural blank was also prepared in the same manner.

Extraction of Cr(VI)

The anionic Cr(VI) present in the above aqueous phase is subjected to a similar extraction procedure after addition of 0.4 mL of 0.05% m/v diphenylcarbazide, 0.2 mL of 10% m/v sodium dodecyl benzene sulfonate, 0.4 mL of 30% m/v NaCl and 0.1 mL v/v 1-undecanol. The solidified 1-undecanol phase in the conical ETAAS auto-sampler vial was made up to 0.2 mL by adding 0.1 mL methanol. An aliquot of 10 μL was injected into the graphite tube for quantification of Cr(VI). Procedural blank was also prepared in the same manner.

Simultaneous extraction of chromium species

Fresh aliquots of 1-5 mL certified reference materials and water samples were taken into a pre-cleaned sample vial containing a PTFE coated stirrer bar and the pH was adjusted to 1. These solutions were subjected to similar extraction procedure after addition of 0.4 mL of 0.05% m/v diphenylcarbazide, 0.6 mL of 10% m/v sodium dodecyl benzene sulfonate, 0.4 mL of 30% m/v NaCl and 0.2 mL v/v 1-undecanol. The 0.15 mL solidified 1-undecanol phase in the conical ETAAS auto-sampler vial was made up to 0.25 mL by adding 0.1 mL methanol. An aliquot of

10 μL was injected into the graphite tube for quantification of total Cr. Procedural blank was also prepared in the same manner.

Results and discussion

Optimization of surfactant assisted DLLME-SFO parameters

The parameters affecting the sequential/simultaneous non-chromatographic separation and pre-concentration of kinetically inert hydrophilic cationic $Cr(H_2O)_6^{3+}$ and labile anionic $HCrO_4^-$ species by the reactive solubilising sites of anionic SDBS surfactant were studied separately using 100 pg mL^{-1} each of Cr(III) and Cr(VI) spiked tap, ground and wastewaters.

Effect of type and concentration of dispersive surfactant

Surfactants are amphiphilic molecules and form micelles aggregate consisting of various reactive hydrophobic and hydrophilic solubilising sites. It disperses quickly in aqueous samples than the organic dispersive solvents and interacts effectively with targeted species using its reactive solubilising sites, and avoids the addition of an external chelating agent. Therefore, the effects of non-ionic Triton X-114, cationic CTAB and anionic SDS and SDBS surfactants at 0.5% v/v concentration on the relative absorbance signal of Cr(VI) and Cr(III), respectively were studied in presence and absence of DPC for selecting the appropriate surfactant in sequential and simultaneous DLLME-SFO extraction of chromium species. The results of sequential DLLME-SFO are given in Fig. 1. These results indicated that the relative absorbance signal of 5, 8, 20 and 100% for Cr(III) and 10, 5, 40 and 100% for Cr(VI) were obtained, respectively for Triton X-114, CTAB, SDS, and SDBS. The low relative absorbance signals of Triton X-114 and CTAB is mainly due to the absence of any reactive hydrophilic solubilising sites in the Triton X-114 and strong repulsion between positive head group solubilising sites of CTAB with cationic Cr(III) and Cr(VI) with DPC. In the case of anionic SDS, separation of 1-undecanol droplet after solidification was found to be difficult. Similar behaviour of chromium species were observed in the case of the simultaneous extraction of both the species in presence of DPC. Hence, a SDBS anionic surfactant was selected for further optimizations of sequential and simultaneous extraction of chromium species.

However, the concentration of SDBS decides the shapes of aggregates formed and their selective reaction and transfer of analyte species into extracting solvents. The critical micelles concentration (CMC) of SDBS is 0.035%. Hence, the effect of SDBS concentration in the range of 0-1.4% m/v on the sequential and simultaneous recovery of Cr(III) and Cr(VI) from tap/drinking and ground water samples were studied. The results are shown in Fig. 2 (a, b & c). As can be seen in Fig. 2 (a), in the concentration range of 1-1.4% SDBS, the recovery of Cr(III) was 94-98% for both tap/drinking and ground water samples, whereas only 4-7% recovery of Cr(VI) was observed in the whole studied concentration range of SDBS. Thus, a 1% m/v SDBS concentration was selected for selective sequential extraction of Cr(III), in the presence of Cr(VI). As can be seen in the Fig. 2(b), the anionic Cr(VI) present in the aqueous phase after separation of Cr(III) in the above procedure is converted into cationic Cr(III)-diphenylcarbazone[15] by the addition of 0.002% m/v DPC, which showed a the recovery between 94-96% above 0.2% SDBS concentration. Thus, a 0.2% m/v SDBS concentration was selected for sequential extraction of Cr(VI) in presence of DPC. As can be seen in the Fig. 2(c), simultaneous extraction of both Cr(III) and Cr(VI) were carried out by taking fresh aliquot of sample in presence of 0.002% m/v DPC. These results indicates that the above 0.6% SDBS both Cr(III) and Cr(VI) showed quantitative recovery between 93-96% in both tap and ground water samples. Thus, a 0.6% m/v SDBS concentration was selected in simultaneous extraction.

Effect of volume of extraction solvent

For quantitative extraction of Cr(III) and Cr(VI) in both sequential and simultaneous surfactant assisted DLLME-SFO procedure, optimizing the extracting 1-undecanol volume is important to improve the pre-concentration factor. Therefore, the volume of 1-undecanol was studied in the range of 0.01-0.5 mL by keeping the other parameters constant. The results are shown in Fig. 3, which indicates that when the volume of 1-undecanol is less than 0.005 mL, there was no proper phase separation, but when 0.05 mL was used a clear phase separation was seen. However, using sequential extraction, when the volume was around 0.1 mL near quantitative extraction (96%) of Cr(VI) was obtained, but it was only 50% for Cr (III). In order to improve the extraction of Cr(III) the volume of 1-undecanol needs to be increases and maximum recovery of 98% at 0.25 mL volume was obtained and it remained constant up to the studied volume of 0.5 mL. In case of simultaneous extraction of both the species, a maximum recovery of 97% was obtained with volume of 0.15 mL or more of 1-undecanol. The different behaviour of Cr(III) and Cr(VI) in sequential and simultaneous extraction with 1-undecanol may be due to the difference in the hydrophobicity of the extracted species and its formed ion-associates with anionic surfactant at room temperature. Hence, based on the above results, 0.3, 0.1 and 0.2 mL of 1-undecanols were selected for sequential and simultaneous extraction of Cr(III) and Cr(VI), respectively.

Effect of solution pH

Chromium exists in various forms and the relative concentration of each species depends up on the pH of the aqueous solution. For selective formation of an extractable hydrophobic ion-associate of Cr(III) and Cr(VI) with anionic SDBS surfactant, in the absence and presence of DPC depends on the pH of the aqueous solution. Hence, the effect of pH on the recovery of Cr(III) and Cr(VI) in tap water samples were studied in the absence and presence of DPC in the pH range of 1-6 in both sequential and simultaneous extraction procedures. The results are shown in Fig. 4 (a, b & c). In the absence of DPC, 98-99% recovery of Cr(III) was achieved in sequential extraction between the pH 1-3 at room temperature (25°C), and by further increase in the pH of the solution to 6, it was decreased to 60%, the results are shown in Fig. 4(a). This observation is mainly due to the existence of Cr(III) in cationic form $Cr(H_2O)_6^{3+}$ in the pH range between 1 to 3. It was also observed that in the 1-6 pH range, only 2-3% recovery of Cr(VI) was obtained due to repulsions between anionic Cr(VI) species and anionic SDBS aggregates. Thus, pH 1 was used for selective sequential separation and pre-concentration of Cr(III) in presence of Cr(VI), at room temperature (25^{o}C). In the presence of DPC, 95-98% recovery of Cr(VI) was achieved in sequential extraction between pH 1 and 3, and then decreased to 40% at pH 6, the results are shown in Fig. 4(b). This behaviour of Cr(VI) is mainly due to the formation of cationic species with DPC in the pH range between 1 to 3 and anionic species at pH >3. Thus, pH 1 was used for selective pre-concentration of Cr(VI) in the sequential extraction.

The addition of DPC to a fresh aliquot of sample showed 97-98% and 94-96% recoveries for Cr(III) and Cr(VI), respectively in the pH range 1-3 and results are presented in Fig. 4(c). It is mainly due to simultaneous existence of cationic forms of Cr(III) and Cr(VI) in presence of DPC, which react simultaneously with anionic head group solubilising sites of SDBS micelles aggregates. Therefore, pH 1 was selected for simultaneous extraction of Cr(III) and Cr(VI).

Effect of ionic strength

The presence of electrolytes often improves the extraction efficiencies of analytes in conventional microextraction due to the salting-out effect. Hence, the effect of the concentration of NaCl, a common electrolyte, on the sequential and simultaneous recovery of chromium species spiked to tap water samples were studied in the range of 0-4% m/v by keeping other parameters constant. These results indicated that without NaCl, the recoveries of Cr(III) and Cr(VI) were 45 and 72 % in sequential and 80 % in simultaneous extraction process. These recoveries were found to increase by increase in the concentration of NaCl to 0.5%, 1.2% and 1% NaCl, respectively for simultaneous extraction of total chromium (Cr(III)+Cr(VI)) and sequential extraction of Cr(III) and Cr(VI). Further increase in the concentration of NaCl up the studied concentration does not change the recoveries of chromium spices in both sequential and simultaneous extraction process. Therefore, an optimum value of 1.2% m/v NaCl was selected for both sequential and simultaneous extractions.

Stirring rate and extraction time

The rate of formation of ion-associates and their mass transfer into extracting solvents enhanced with increasing the stirring rate of the sample solution. Hence, the effect of stirring rates (0, 100, 200, 400, 800 and 1000 rpm) using a magnetic stirrer on the sequential extraction efficiency of Cr(III) and Cr(VI) were studied by keeping constant the extraction time of 2 min. These results indicates that the extraction efficiencies were found to increase with the rate of stirring to 400 rpm and then it remained constant for both Cr(III) and Cr(VI). Hence, a stirring rate of 500 rpm was selected for further studies.

The effect of extraction time on the extraction efficiency was studied in the range of 0-5 min by keeping other parameters constant. The results showed that there was no significant difference between the different extraction times above 2 min. It is mainly due to fast dispersion of fine droplets of the extraction solvent, 1-undecanol in presence of surfactant dispersant, SDBS. It increases the surface area of extraction solvent compared to aqueous sample solutions and there is a fast mass transfer of hydrophobic ion-associates of chromium species, hence the extraction was carried out for a period of 2 min.

Extraction temperature

The effect of incubation temperature on the sequential and simultaneous recovery of Cr(III) and Cr(VI) in spiked wastewater samples were studied in the range of 25-70^{o}C by keeping other parameters constant. These results indicated that at the incubation temperature of 25^{o}C, the sequential recovery of Cr(III) and Cr(VI) were in between 94-96%. These recoveries remain constant by further increase in the incubation temperature to 70^{o}C. Therefore, an optimum incubation temperature of 25^{o}C (room temperature) was selected for the sequential extraction. The simultaneous recovery of chromium species is also found to be quantitative at room temperature indicating the suitability of the procedure for the determination of total chromium without using any heat treatment.

The amount of disperser, extractant and incubation temperature and time decides the pre-concentration factor (PCF). The PCF is the ratio of the analyte concentration in the solidified 1-undecanol phase to that of the initial aqueous phase. Under the optimized conditions, the PCF was found to be 25 and 50 for sequential extraction of Cr(III) and Cr(VI) and 40 for the simultaneous extraction of both the chromium species. The species extracted in to 1-undecanol phase has provided stable signal for more than a week, which indicates the strong complexing ability of the anionic surfactant used in this procedure.

Analytical recovery

The recovery studies of Cr(III) and Cr(VI) in both sequential and simultaneous DLLME-SFO were performed by spiking these species in tap water ground and wastewater samples. The results obtained after spiking the 10 mL water samples with 100–20,000 pg mL^{-1} Cr(III) and Cr(VI) are given in Table 2. The recoveries were between 92–98%, which indicated that the studied concentration range of the Cr species have no significant effect on the recoveries of individual chromium species in the proposed procedure. The relative standard deviations were in between 1-4%.

Interference

In order to evaluate the performance of this procedure to different types of water bodies, the highest tolerability of various common interfering ions were studied. Interferences may occur due to the competition of other metal ions to form ion-associates with dispersing agent SDBS. The tolerability limits of various foreign ions on the sequential extraction of Cr(III) and Cr(VI) were 400 mg L^{-1} of Ca^{2+} and Mg^{2+}, 40 mg L^{-1} of Al^{3+}, Ni^{2+} and Cd^{2+}, 10 mg L^{-1} of Zn^{2+} and Cu^{2+} ; and 600 mg L^{-1} of Ca^{2+} and Mg^{2+}, 60 mg L^{-1} of Al^{3+}, Ni^{2+} and Cd^{2+}, 25 mg L^{-1} of Zn^{2+} and Cu^{2+}, respectively. Approximately same tolerability of these foreign ions was obtained for simultaneous extraction of both the chromium spices. These results demonstrated the high selectivity of the proposed procedure for sequential and simultaneous extraction of chromium species. Therefore, the reported procedure can be applied to most of the water samples.

Analytical figures of merit

Under the optimized experimental conditions, the calibration curves were obtained by pre-concentrating the successively spiked standards of Cr(III) and Cr(VI) in the range of 40–1000 pg mL$^{-1.}$ The correlation coefficients were between 0.9985-0.9994. Quantifications have been performed by external calibration using aqueous standards prepared in 0.2% HNO_3. The limit of detection (LOD) calculated based on three times the standard deviation of ten measurements of procedural blanks were 3 and 1 pg mL^{-1} for sequential and 4 pg mL^{-1} for simultaneous extraction of Cr(III) and Cr(VI). A comparison of the proposed procedure with the recently published microextraction procedures for the speciation analysis of chromium is given in Table 3, which indicates that the present procedure shows better LOD compared to reported procedures and meet the EPA recent requirements.[4,5]

Validation of the procedure and analysis of real samples

The accuracy of the proposed procedure developed for sequential and simultaneous extraction and analysis of chromium was verified by analyzing certified reference materials such as NIST 1643c water, BCR 713 effluent and BCR 714 influents. The results are given in Table 4. The results showed that the sum of the concentrations of individual chromium species obtained by sequential extraction procedure were found to be in good agreement with the values obtained from micelle and mixed micelle cloud point extraction[27] and also agreed with the certified concentration for total chromium as well as values obtained by simultaneous extraction procedure. It indicated the accuracy of the both sequential and simultaneous extraction procedures. This procedure has also been applied to the determination of individual Cr(III) and Cr(VI) species and total chromium in real samples such as tap water, river water and influent and effluents of wastewater treatment plant. These samples were analyzed directly without any sample pre-treatment. The sum of the values obtained for Cr(III) and Cr(VI) determined individually in the sequential extraction were in good agreement with total chromium determined in the simultaneous extraction procedure. These results indicated that the value of Cr(VI) found in tap, river samples were higher than the values specified by EPA, but total chromium is with-in the limits. In the case of effluent samples, Cr(VI) and total chromium were more than the specified levels, which indicating the necessity of further treatment of these wastes before discharged into the environmental water bodies. It is interesting to note that, in this study, total Cr in samples obtained from river Ganges was 1 ng mL^{-1}, which is within the specified limits, but most of it is in the form of Cr(VI) which is more alarming and much higher than the present EPA limit for drinking water.[4,5]

Conclusions

A novel sequential and simultaneous non-chromatographic speciation procedure has been reported for the determination of Cr(III) and Cr(VI) and total Cr in various water samples. The reactive solubilizing sites of anionic surfactant have been used for selective extraction of Cr(III) and Cr (VI). This procedure avoids the commonly used oxidation/reduction steps and facilitates the room temperature extraction and stability of the extracted chromium species in the sediment phase. This procedure is useful to handle the samples at sampling sites and transporting the small volume containing individual and total chromium species to environmental laboratories for further quantification.

Acknowledgement

The authors are thankful to Dr. B. N. Jagatap, Director, Chemistry group, NCCCM/BARC, for his keen interest and consistent encouragement during this work.

References

1. U.S. Environmental Protection Agency Polluted Runoff (Nonpoint Source Pollution). Available from http://www.epa.gov/OWOW/NPS/facts/point1.htm.
2. Z. Sun and P. Liang, *Microchim. Acta,* 2008, **162,** 121-125.
3. F. L. Petrilli and D. DeFlora, Appl. *Environ. Microbiol.,* 1977, **33(4),** 805-809.
4. http://www.oehha.org/water/phg/072911Cr6PHG.html.
5. http://www.oehha.org/water/phg/pdf/cr6phg072911.pdf
6. S. Dadfarnia and A. M. H. Shabani, *Anal. Chim. Acta,* 2008, **658,** 107-119.
7. F. Pena-Pereira, I. Lavilla and C. Bendicho, *Spectrochim. Acta, Part B,* 2009, **64,** 1-15.
8. V. Andruch, I. S. Balogh, L. Kocúrová and J. Šandrejová, *J. Anal. At. Spectrom.,* 2013, **28,** 19-32.
9. P. Viñas, N. Campillo, I. L. García, M. H. Córdoba, *Anal. Bioanal. Chem.*, 2014, **406(8),** 2067-2099.
10. A. Vasil, I. S. Balogh, L. Kocúrová and J. Šandrejová, *Applied Spectrosco. Rev.,* 2013, **48,** 161-259.
11. M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji and A. Saleh, *J. Hazard. Mater.,* 2010, **78,** 766-770.
12. M. R. K. Zanjani, Y. Yamini, S. Shariati and J. Å. Jönsson, *Anal. Chim. Acta,* 2007, **595** 286-293.
13. M. I. Leong and S.D. Huang, *J. Chromatogr. A,* 2008, **1211,** 8-12.
14. M. M. Sanagi, H. H. Abbas, W. A. W. Ibrahim and H. Y. A. Enien, *Food Chem.,* 2012, **133,** 557-562.
15. M. Mirzaei, M. Behzadi, N. M. Abadi and A. Beizaei, *J. Hazard. Mater.,* 2011, **186,** 1739-1743.
16. H. Xu, Z. Ding, L. Lv, D. Song and Y. Q. Feng, *Anal. Chim. Acta,* 2009, **636,** 28-33.

17. M. I. Leong and S.D. Huang, *J. Chromatogr. A*, 2009, **1216,** 7645-7650.

18. M. Rezaee, Y. Yamini, A. Khanchi, M. Faraji and A. Saleh, *J. Hazard. Mater.,* 2010, **178,** 766-770.

19. S. M. Yousefi and F. Shemirani, *J. Hazard. Mater.,* 2013, **254-255,** 134-140.

20. M. D. M. Abadi, M. Chamsaz, M. H. A. Zavar, F. Shemirani, Anal. Methods 5 (2013) 2971-2977.

21. P. Hemmatkhah, A. Bidari, S. Jafarvand, M.R.M. Hosseini and Y. Assadi, *Microchim. Acta,* 2009, **166,** 69-75.

22. I. Lopez-García, M. Briceño, Y. Vicente-Martínez and M. Hernandez-Córdoba, *Talanta,* 2013, **115,** 166-171.

23. H. Chen, P. Du, J. Chen, S. Hu, S. Li and H. Liu, *Talanta,* 2010, **81,** 176-179.

24. M. R. Moghadam, S. Dadfarnia and A. M. H. Shabani, *J. Hazard. Mater.,* 2011, **186,** 169-174.

25. I. Lopez- García, Y. Vicente-Martínez and M. Hernandez-Córdoba, *J. Anal. At. Spectrom.*, 2012, **27**, 874-880.

26. S. Sadeghi and A. Z. Moghaddam, *Talanta,* 2012, **99,** 758-766.

27. N. N. Meeravali, K. Madhavi and S. J. Kumar, *J. Anal. At. Spectrom.*, 2011, **26**, 214-219.

Table 1 Optimized temperature program used for determination of chromium in extraction solvent of surfactant assisted DLLME-SFO using continuum source ETAAS

Step	Temperature/^{o}C	Ramp/^{o}C s^{-1}	Hold/s	Ar flow/ mL min^{-1}
Drying-1	80	6	20	250
Drying-2	110	5	10	250
Pyrolysis	1200	300	10	250
Gas adaption	1200	0	5	250
Atomization	2300	500	4	0 (read)
Cleaning	2350	500	3	250

Table 2 Sequential and simultaneous recovery of Cr(III) and Cr(VI) in various water samples (n=4)[a]

Matrices	Spiked/pg mL^{-1}		Recovery (%)		
			Sequential extraction		Simultaneous extraction
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III + VI)
Tap water	0	0	300 ± 8[b]	50 ± 9[b]	355 ± 6 [b]
	100	0	94 ± 2	-	96 ± 2
	0	100	-	98 ± 3	97 ± 2
	100	10000	96 ± 3	94 ± 2	97 ± 4
	100	20000	95 ± 3	93 ± 3	95 ± 3
	10000	100	94 ± 4	95 ± 4	98 ± 4
	20000	100	92 ± 5	97 ± 5	97 ±
Ground water	0	0	270 ± 10[b]	185 ± 10 [b]	460 ± 8 [b]
	100	0	93 ± 2	-	94 ± 2
	0	100	-	96 ± 4	95 ± 3
	100	150	92 ± 4	95 ± 2	94 ± 3
Wastewater (effluent)	0	0	2.2 ± 0.4[c]	0.8 ± 0. [c]	3.1 ± 0.9[c]
	400	0	93 ± 3	-	98 ± 3
	0	300	-	98 ± 3	99 ± 4
	400	300	92 ± 2	96 ± 1	97 ± 3

[a] Values are mean of four measurements ± standard deviation. [b] Values are in pg mL^{-1}. [c] Values are in ng mL

Table 3 Comparison of advantages of proposed procedure with other reported micro extraction procedures for the speciation of chromium in natural waters

Extraction scheme and instrument	Speciation approach	Chelating agent	Extraction temp.(^{o}C)/ time (min)	Dispersant/ Extractant	LOD/pg mL^{-1}			Ref.
					Cr^{3+}	Cr^{6+}	Cr^{T}	
DLLME [a]-FAAS	Cr(VI) & Cr(T), D[b]	APDC [c]	40/15 80/15	Ethanol/CCl_4	-	70	80	21
SFODME [d]-ETAAS	Cr(III) & Cr(T), D[b]	TTA [e]	RT/35	No/ 1-Undecanol	6	-	-	24
IL-DLLME [f]-ETAAS	Cr(VI) & Cr(T), D[b]	APDC	-	Ionic liquid/ No	-	2	-	25
TCME [g]-ETAAS	Cr(VI) & Cr(III), S[h]	APDC	45/5 45/25	Triton X-114/ (HMIM)(PF6)[i]	5.4	2.45	-	26
DLLME-SFO-CS-ETAAS	Cr(III) & Cr(VI), S[h] & Cr(T), S[j]	No & DPC & DPC	RT/5	SDBS/ 1-Undecanol	3	1	4	This work

[a] Dispersive liquid-liquid microextraction. [b] Cr(VI) and total chromium using differential speciation approach. [c] Ammonium pyrrolidine dithiocarbamate. [d] Solidified floating organic drop microextraction. [e] 2-thenoyltrifluoroacetone (TTA). [f] Ionic liquid dispersive liquid–liquid microextraction. [g] Temperature-controlled microextraction. [h] Cr(VI) and Cr(III) were extracted sequentially. [i] 1-hexyl-3 methylimidazolium hexa flourophosphate. [j] Simultaneous extraction of Cr(III) and Cr(VI).

Table 4 The determined values of Cr(III), Cr(VI) and total Cr in certified and real water samples using the procedure described in this work

Matrices	Measured value [a] (ng mL^{-1})				
	SA-DLLME-SFO			Cloud point extraction [b]	
	Sequential extraction		Simu. extraction	Sequential extraction	
	Cr(III)	Cr(VI)	Cr(III+VI)	Cr(III)	Cr(VI)
NIST 1643c water	17.2 ± 0.8	1.4 ± 0.4	18.8 ± 0.9 (19.0 ± 0.6) [c]	18.8 ± 1.4	2.8 ± 1.2
BCR-713 effluent	16.3 ± 1.0	5.2 ± 1.4	21.6 ± 1.5 (21.9 ± 2.4) [c]	16.6 ± 1.2	5.6 ± 1.9
BCR-714 influent	78.6 ± 5.5	49.5 ± 6.2	130.5 ± 8.5 (123 ±10) [c]	76.8 ± 6.5	48.6 ± 6.5
Analysis of real samples					
Tap water	0.312±0.016	0.055±0.013	0.365 ± 0.018	0.326±0.015	0.060±0.015
Ganges river water	0.100 ± 0.035	0.950 ±0.0 55	1.000 ± 0.158	0.120± 0.025	0.915±0.035
Influent	17.8 ± 1.7	7.5 ± 1.3	25.6 ± 3.7	17.6 ± 2.2	6.8 ± 2.4
Effluent	2.6 ± 0.3	0.6 ± 0.2	3.3 ± 1.5	2.3 ± 0.8	0.4 ± 0.2

[a] Mean of four determinations ± standard deviation. [b] Values are obtained using micelle and mixed micelle cloud point extraction ref.27. [c] Certified values.

Figure capitations:

Fig. 1 Effect of type of dispersive solvents such as Triton X-114, CTAB, SDS and SDBS on the relative absorbance signal of Cr(III) and Cr(VI) extracted sequentially using DLLME-SFO at pH 1 in presence of 0.5% v/v surfactants, 2 % m/v NaCl and 0.5 mL of 1-undecanol.

Fig. 2 Effect of SDBS concentration on the recovery of Cr(III) and Cr(VI) using surfactant assisted DLLME-SFO extraction at pH 1, in presence of 1.2% m/v NaCl and 0.5 mL of 1-undecanol. Sequential extraction: (a) without DPC (extraction of Cr(III)) and (b) with DPC (extraction of Cr(VI)). Simultaneous extraction: (c) with DPC (extraction of Cr(III) and Cr(VI)).

Fig. 3 Effect of 1-undecanol concentration on the recovery of Cr(III) and Cr(VI) in sequential and simultaneous DLLME-SFO procedure at room temperature (n=3).

Fig. 4 Effect of pH on the recovery of Cr(III) and Cr(VI). Sequential extraction: (a) extraction of Cr(III) (1% m/v SDBS, 1.2% m/v NaCl and 0.3 mL of 1-undecanol) and (b) extraction of Cr(VI) (0.2% m/v SDBS, 1.2% m/v NaCl, 0.002% m/v DPC and 0.1 mL of 1-undecanol) and simultaneous extraction: (c) extraction of Cr(III) and Cr(VI) (0.6% m/v SDBS, 1.2% m/v NaCl, 0.002% m/v DPC and 0.2 mL of 1-undecanol).

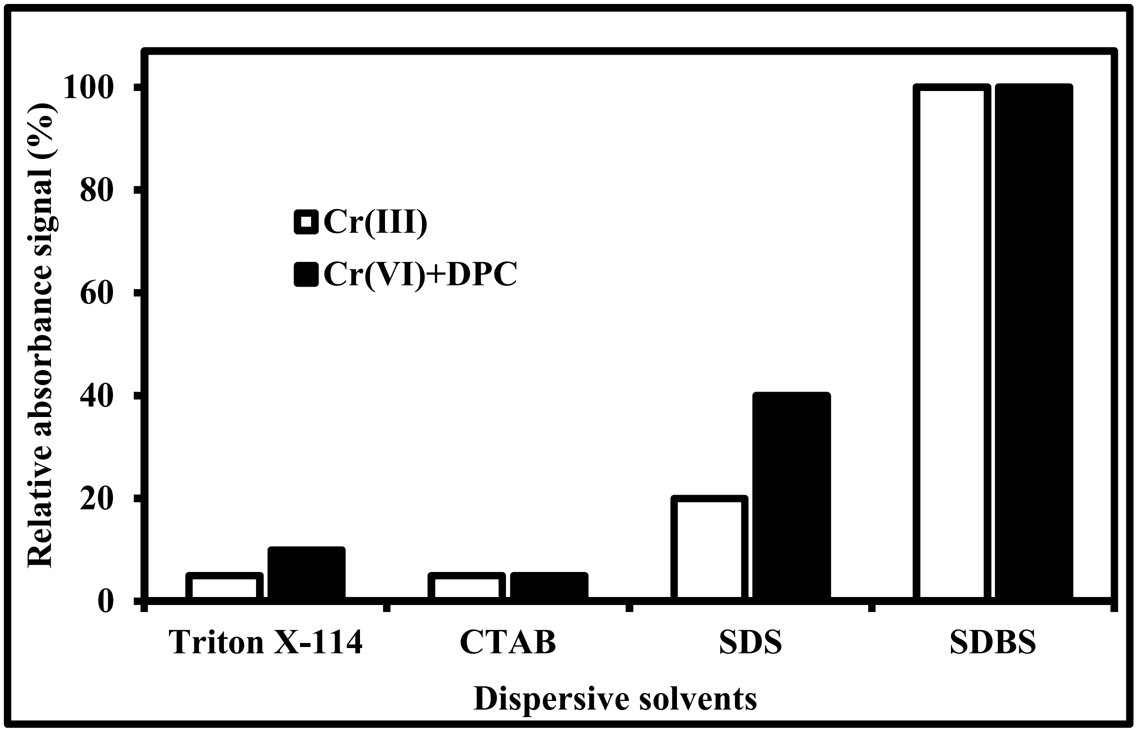
Relative absorbance signal (%)
100
80
60
40
20
0
☐ Cr(III)
■ Cr(VI)+DPC
Triton X-114
CTAB
SDS
SDBS
Dispersive solvents

Fig. 1

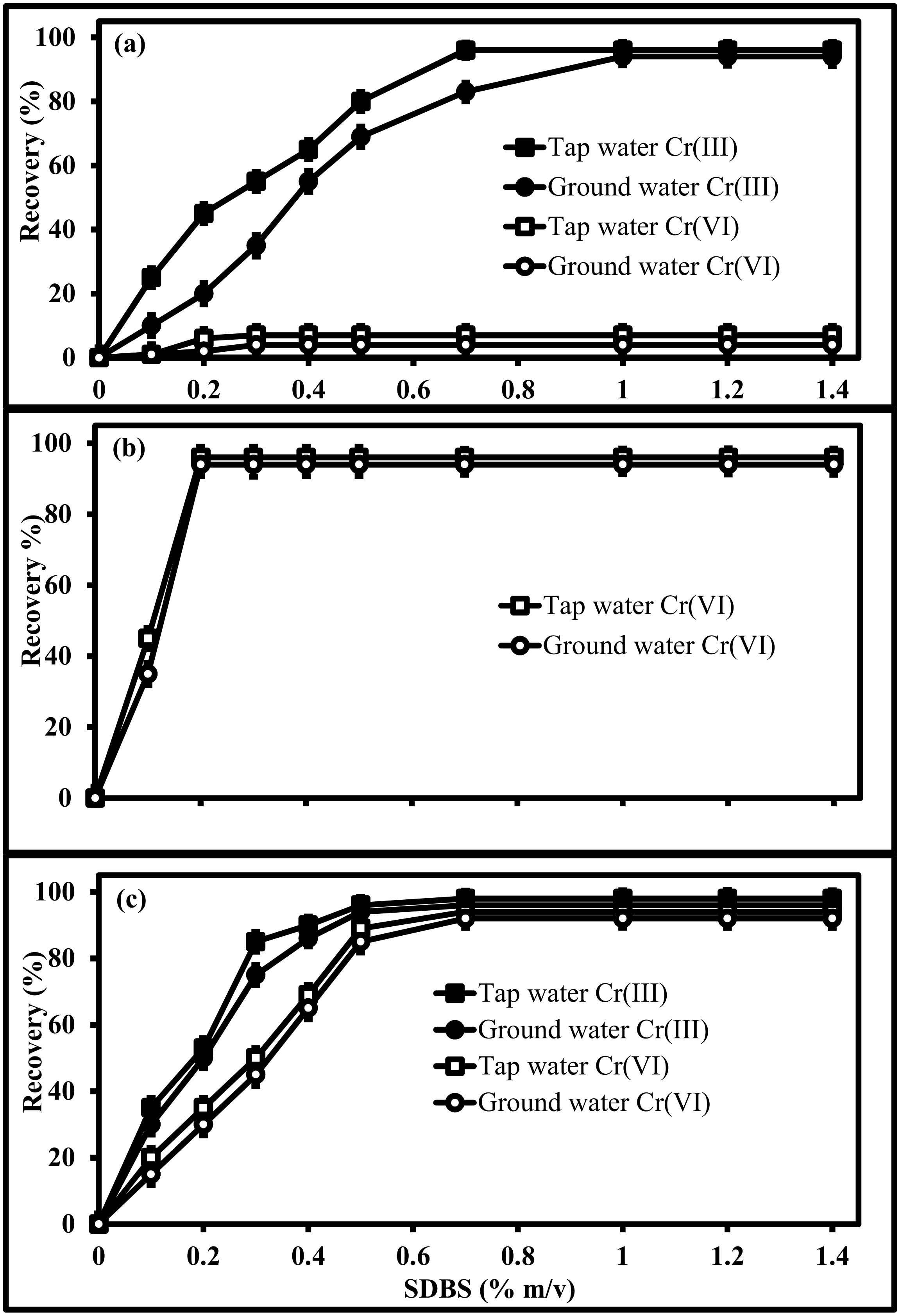
(a)
Recovery (%)
0
20
40
60
80
100
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Tap water Cr(III)
Ground water Cr(III)
Tap water Cr(VI)
Ground water Cr(VI)
(b)
Recovery %)
Tap water Cr(VI)
Ground water Cr(VI)
(c)
Recovery (%)
Tap water Cr(III)
Ground water Cr(III)
Tap water Cr(VI)
Ground water Cr(VI)
SDBS (% m/v)

Fig. 2

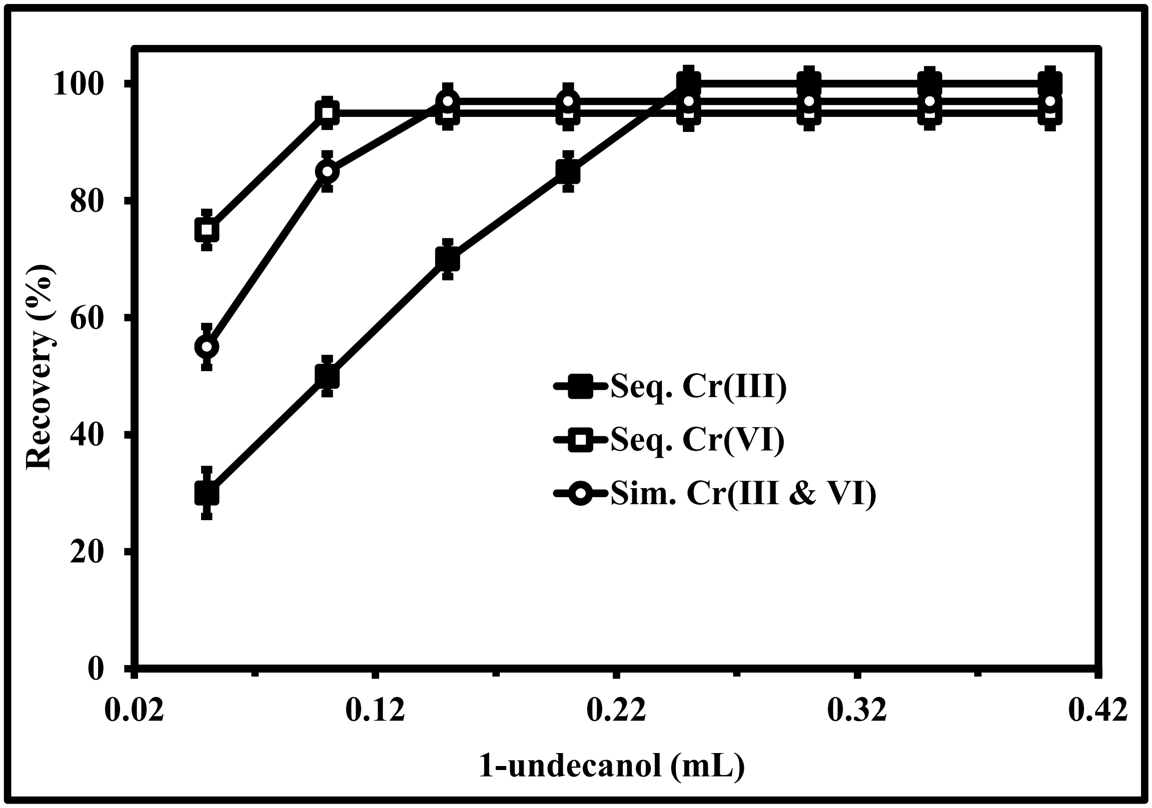
100
80
60
40
20
0
Recovery (%)
0.02
0.12
0.22
0.32
0.42
1-undecanol (mL)
Seq. Cr(III)
Seq. Cr(VI)
Sim. Cr(III & VI)

Fig. 3

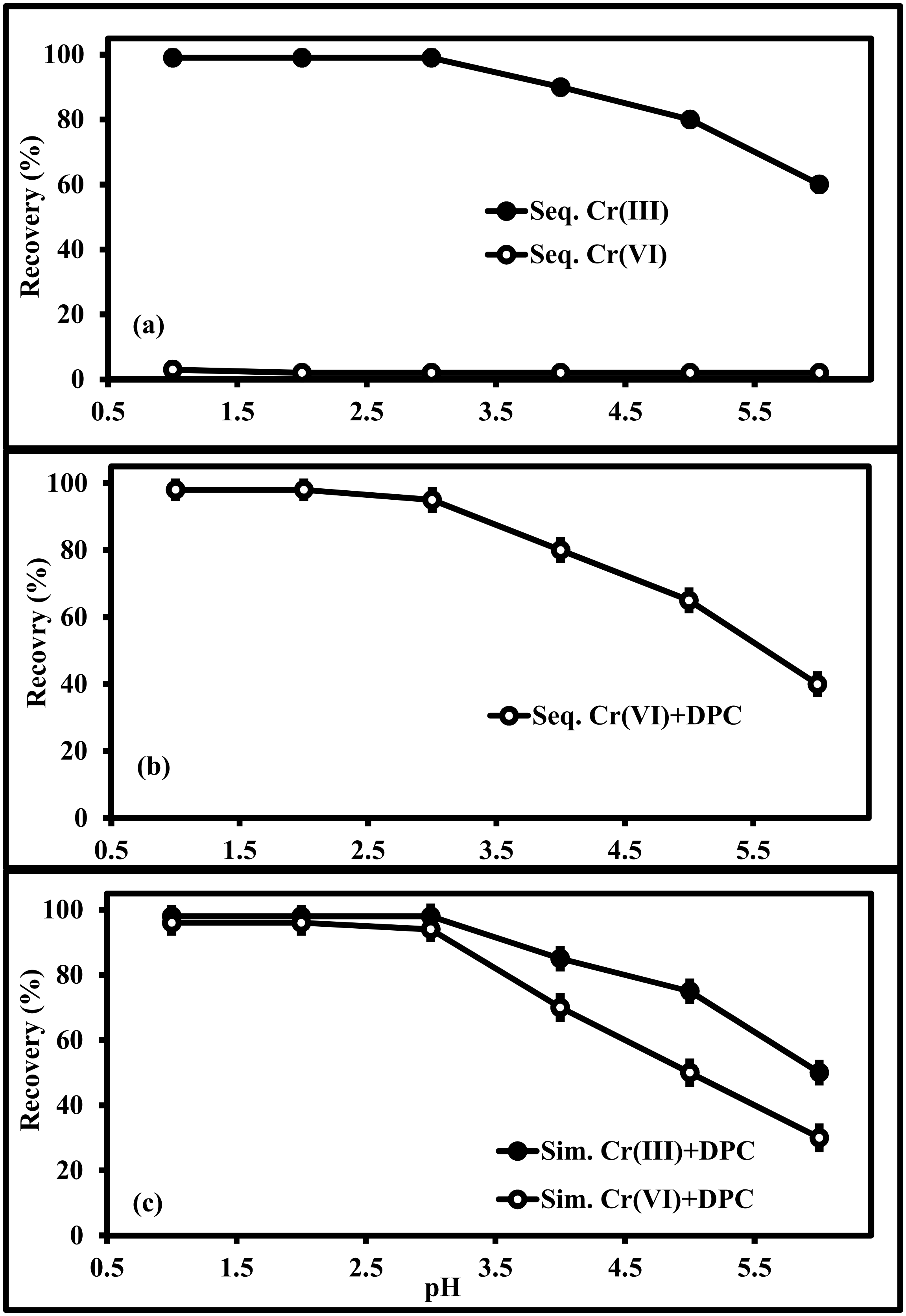
(a)
Recovery (%)
100
80
60
40
20
0
0.5
1.5
2.5
3.5
4.5
5.5
Seq. Cr(III)
Seq. Cr(VI)
(b)
Recovry (%)
Seq. Cr(VI)+DPC
(c)
Recovery (%)
Sim. Cr(III)+DPC
Sim. Cr(VI)+DPC
pH

Fig. 4