

Speciation of Cr (III) and Cr (VI) Ions via Fabric Phase Sorptive Extraction for their Quantification via HPLC with UV Detection

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Abstract

Simultaneous extraction of the morpholino dithiocarbamate (MDTC) chelates of Cr(III) and Cr(VI) ion from aqueous samples was accomplished by applying fabric phase sorptive extraction (FPSE) using a cellulose fabric modified with a sol-gel/polytetrahydrofuran composite. Following extraction, the chelates were separated by HPLC on a reverse phase C18 column with acetonitrile:water (65:35; v/v) as the mobile phase and UV detection at 320 nm. A single peak is found for the Cr(MDTC)₃ but two peaks are caused by Cr(VI) due to the formation of the complexes Cr(MDTC)₂(OMDTC) and Cr(MDTC)₃ (where OMDTC stands for oxy-MDTC). The limits of detection for the Cr(III) and Cr(VI) complexes are 0.001 and 0.003 ng·mL⁻¹, respectively. The method can be used for the determination of chromium species in aqueous samples and displays high precision, sensitivity and reliability.

Keywords: Chromium; Speciation; HPLC; Morpholino dithiocarbamate; MDTC; Fabric phase sorptive extraction; FPSE

Introduction

Metal ions exist in variable oxidation states and have different impacts on health and environment. For an accurate assessment of their impact, it is essential to quantify the individual oxidation states of these metal ions within a sample rather than the total metallic concentration. Chromium is the heavy metal ions that exist in two different oxidation states i.e., trivalent chromium; Cr(III) and hexavalent chromium; Cr(VI) [1]. Cr(III) ion is an essential nutrient that maintains a glucose tolerance factor in human body [2], and involved in mechanism of action of pancreatic insulin [3]. Cr(VI) ion is toxic and does not occur naturally. It is introduced to the environment by various kinds of manufacturing units such as plastics, dyes, ink, metal casting and paint industries [4]. Unlike Cr(III), Cr(VI) ion may cross the cellular membranes by non-specific ion carriers and exert its noxious influence in the cell [5]. It affects the air quality through coal burning which eventually lead to water and soil contamination. After inhalation or oral exposure it effects on liver, kidney, immune system and even ulceration of skin [6]. Due to varied impact of different oxidation states, metal speciation has become an important research direction in past decade to obtain their respective toxicological assessment [7]. Therefore, interest and demand is continuously increasing for chromium speciation in biological and environmental samples.

Different methods used for the preconcentration of chromium complexes are liquid-liquid extraction [8], cloud point extraction [9], solid phase microextraction [10] and solid phase extraction [11]. For the analysis of chromium ions, various techniques are used frequently but high performance liquid chromatography (HPLC) meets most of the analytical requirements of metal determination. HPLC provides several advantages over other methods for separation and quantitation of Cr ions down to the trace level concentration [12]. A number of HPLC methods have been evaluated [13,14] and a selective determination of both species can be achieved successfully by using HPLC coupled to inductively coupled plasma mass spectrometry [15] ion chromatography-ICP-MS [16], flame atomic absorption spectrophotometry [17] and capillary electrophoresis [18].

Dithiocarbamate constitute the most exhaustively studied group of ligands used in the chromatographic speciation of Cr ions

[19], diethyldithiocarbamate [20] and ammonium pyrrolidine dithiocarbamate [21] are the reported complexing reagents for HPLC-UV determination. But being highly hydrophilic, morpholino dithiocarbamate (MDTC) is used as a preferred chelating agent in the developed method.

Fabric phase sorptive extraction has already established itself as a viable alternative to the other conventional preconcentration techniques [22]. Fabric phase sorptive extraction used for the preconcentration of chromium metal ions followed by HPLC-UV detection. It ensures the faster preconcentration of target analytes, while at the same time minimizes the number of laborious and cumbersome sample preparation steps.

FPSE incorporates most of the advantageous features of other microextraction techniques such as SPME by utilizing flexible fabric surface as the substrate platform for sol-gel derived high-efficiency sorbent coating resulting into an efficient microextraction device [23]. High sample capacity of sol-gel fabric sorbent and the inherently porous formation of cellulose substrate synergistically facilitate the achievement of high preconcentration factors for the target analytes in a relatively short period of time from an original and unmodified sample matrix. The flexibility of FPSE media allows direct insertion into the sampling container holding the sample. FPSE media can face the harsh chemical environment (pH 1-12) for prolonged period of time without compromising the extraction performance. The strong chemical bonding between the extraction sorbent and the substrate allows exposing the FPSE media to any organic solvent of choice for elution process.

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The aim of this study is to evaluate the speciation of Cr(III) and Cr (IV) ions by chelating it with MDTC followed by preconcentration with FPSE media and HPLC-UV determination.

Experimental

Instrumentation

The Dionex HPLC unit consists of a P680 solvent delivery pump, a UVD 170 detector capable of detecting four wavelengths was interfaced to a computer loaded with Chromeleon software (version 6.70). A Supelco Ascentis Express reversed phase column of size 10 cm × 4.6 mm filled with C₁₈ material (2.7 μm) was used for separation. The IR spectra were recorded on FTIR (PerkinElmer). Elico SL-164 double beam UV-visible spectrophotometer loaded with Spectra Treatz software was used to record the spectra with quartz cuvettes. A digital pH meter-101 (Delux, India) was used to adjust the pH of solutions. Gaussian 03 software was used for the optimization of the structure of metal complexes.

A digital vortex mixer (Fisher Scientific, USA) was employed for thoroughly mixing of sol solutions. An ultrasonic cleaner-2510 (Branson Inc., USA) was used to make sol solution free of trapped gas or bubbles. Centrifugation of sol solution, to obtain particle free solution, was carried out in an Eppendorf centrifuge model 5415 R. A Barnstead Nano Pure Diamond (Model D11911) deionized water system was used to obtain ultra-pure deionized water (18.2 MΩ cm) for sol-gel synthesis.

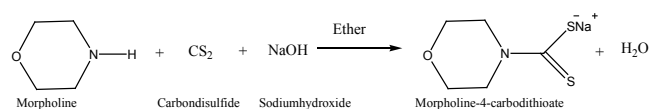
Materials chemicals and reagents

Cellulose substrates used to create FPSE media were purchased from Jo-Ann Fabric (Miami, FL, USA). Polytetrahydrofuran, acetone, dichloromethane, methyltrimethoxysilane (MTMS), trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich (<https://www.sigmaaldrich.com>) (St. Louis, MO, USA). Sodium hydroxide and hydrochloric acid were purchased from Thermo Fisher Scientific (<http://www.thermofisher.com>) (Milwaukee, WI, USA). All the solvents used were of HPLC-grade and purchased from J.T. Baker Chemicals (Phillipsburg, NJ), and filtered by using Nylon-6,6 membrane filters (Rankem, India) in a filtration assembly (Perfit, India). Cr(III) nitrate nonahydrate, potassium dichromate, sodium acetate trihydrate, glacial acetic acid, and sodium hydroxide were obtained from Merck (<http://www.merck.com/index.html>). Prior to injection, all samples were

filtered through 0.22 μm syringe filters (Rankem, India).

Synthesis of MDTC

MDTC was used as a chelating agent and prepared by method reported by Macrotrigiano [24].



In brief, morpholine with dry ether was taken into round bottom flask. To this, stoichiometric amount of CS₂ was added with constant stirring with magnetic bead and then reaction mixture was cooled. To this solution a stoichiometric quantity of NaOH was added with constant stirring for 3-4 h. Then the product formed was filtered, washed with ether and re-crystallized from alcohol. White needle shaped crystals were obtained with melting point 170°-174°C. In IR spectra, the presence of characteristic C=S stretching bands at 1083 cm⁻¹ and two bands at 1437 and 1164 cm⁻¹ due to C-N and C-O stretching, respectively confirmed the formation of MDTC (Figure 1).

A 10% w/v solution of sodium morpholine-4-carbodithioate was prepared in distilled water and it was standardized titrimetrically using mercuric acetate as titrant and diphenylcarbazone as an internal indicator [25]. The sol solution for creating the sol-gel poly-THF coating was prepared by using a modified version of a previously described method [26].

Complexation procedure

10 mL solution containing Cr(III) and Cr(VI) ions (2 milli-moles and 7 milli-moles respectively) was transferred to a well stoppered bottle. To this, 1 mL (0.4 moles) of MDTC solution (10% w/v) was added. The total volume of solution was made up to 25 mL with water and acetate buffer solution (0.1 M) such that the pH of the resulting solution was 4.0. The prepared solution was heated on water bath at 55°C temperature. The complex obtained was then dissolved in 10 mL acetonitrile solvent to obtain the stock solution. The stock solution was then diluted further as per requirement.

Spectrometric analysis of chromium complexes

The different kinds of interaction of both chromium ions towards

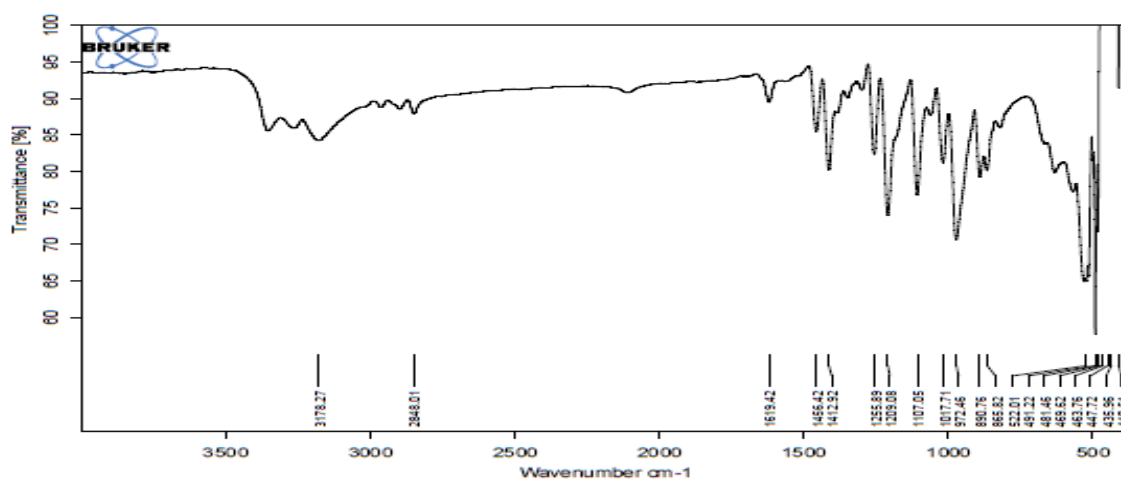


Figure 1: IR spectrum of the morpholine-4-carbodithioate.

dithiocarbamates make their determination easier. The IR spectra of 1:3 adduct of tris(morpholinedithiocarbamate)Cr(III) was recorded using KBr pellets. The shift of C-S band from 1083 cm^{-1} to 1050 cm^{-1} after complexation indicates that the ligand binds with metal through sulfur atoms. A band at 870 cm^{-1} may be attributed to S-O stretching vibration which confirmed the formation of oxy complex. The oxy complex formation of $\text{Cr}(\text{MDTC})_2(\text{OMDTC})$ was due to reduction of Cr (VI) with the reagent where Cr-O-S bond is formed in the complex [27]. The formation of complexes was also confirmed by thin layer chromatography. With solvent system methanol : ether : toluene (5:70:25), one spot for Cr(III) complex with Rf value 0.154 and two spots for Cr(VI) complex with Rf values 0.154 and 0.67 were obtained. Single absorption maximum ($\lambda_{\text{max}}=298\text{ nm}$) for Cr(III)-MDTC complex and two absorption maxima ($\lambda_{\text{max}}=298, 350\text{ nm}$) for Cr(VI)-MDTC complex were obtained in their respective UV-Vis spectra. It clearly indicates that Cr(III) ion form single product as $\text{Cr}(\text{MDTC})_3$ and Cr(VI) ion form two distinct products as $\text{Cr}(\text{MDTC})_2(\text{OMDTC})$ and $\text{Cr}(\text{MDTC})_3$. The complete optimization and frequency calculations for the complexes were carried out using Hartree Fock (HF) level of theory in combination with the STO-3G basis set via the Gaussian 03 software package. The energy minimization studies of chromium complexes interpreted that both complexes are energetically stable (Figure 2a and 2b).

Sample preparation

Ground water was obtained from the bore well located within Punjabi university campus, Patiala, India. The bore well water is pumped out at the depth of around 400 feet from ground level. Drinking water was obtained from water purification appliances installed in Punjabi university Patiala. The bore well water is fed to the appliance as raw water. Water is allowed to pass through an ultra-violet radiation treatment system and a set of activated carbon cartridges (particle size 1 and 5 μm) and is made ready for drinking. Industrial waste water was obtained from the effluent stream coming out of industrial area located in vicinity of Chandigarh city, India. Since industrial waste water contains high concentrations of particulate matter and suspended impurities, samples were first filtered with Whatman filter paper (grade no. 1) and then with 0.45 μm pore size Nylon-6, 6 membrane filters in a filtration assembly. Prior to the FPSE process, all water samples were degassed with ultrasonic bath.

Results and Discussion

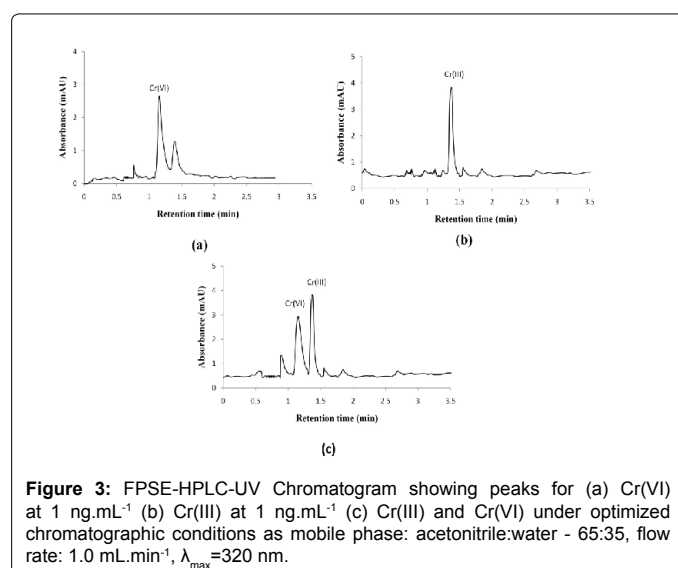
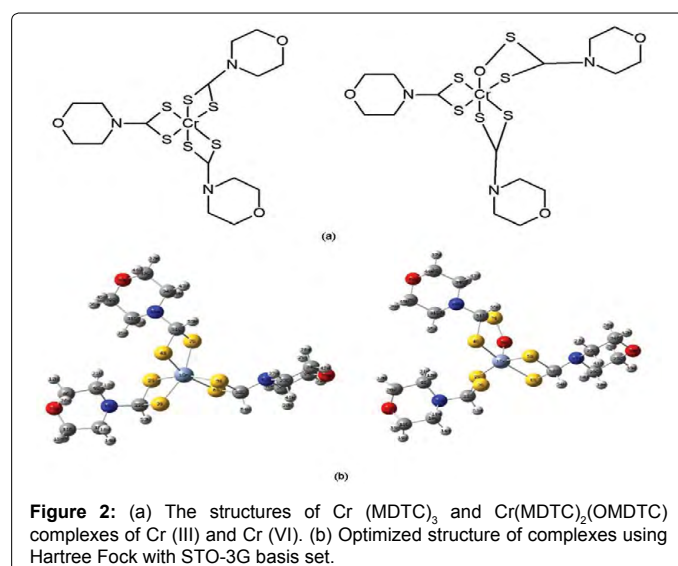
Chemistry of sol-gel coated FPSE media

Sol-gel technology for creating microextraction sorbents was developed by Malik et al. [22] and based on this technology hundreds of sol-gel based sorbents with unique selectivity, extraction sensitivity and applications have emerged. It was prepared by dissolving 10 mL of sol-gel precursor methyltrimethoxysilane (MTMS), 10 g THF polymer, 20 mL methylene chloride: acetone (50:50 v/v) as the organic solvent, 4 mL 5% trifluoroacetic acid as sol-gel catalyst. The sol mixture was vortexed, centrifuged and sonicated for 2-3 minutes and finally clear supernatant sol solution part was transferred to a clear amber glass bottle. Due to its capability to extract both polar and non-polar analytes, polytetrahydrofuran, a medium polarity polymer containing tetramethylene oxide repeating units and terminal hydroxyl groups, was selected as the organic polymer. In addition to the organic polymer, methyltrimethoxysilane (MTMS), trifluoroacetic acid (containing 5% water v/v), and methylene chloride/acetone (50/50 v/v) were used as the inorganic precursor, sol-gel catalyst and solvent system, respectively.

During the condensation, the growing sol-gel poly-THF network reacts with available surface hydroxyl groups of cellulose microfibrils, resulting in a covalently bonded sol-gel poly-THF ultra-thin film uniformly distributed throughout the substrate with characteristic high solvent and chemical stability as well as highly accessible active sites for efficient and fast analyte extraction. The characterization of sol-gel coated poly-THF fabric media was performed with scanning electron microscopy and spectroscopic techniques in our previous paper [22].

FPSE procedure

To extract and preconcentrate the Cr-MDTC complex using FPSE, 10 mL aqueous solution containing the analytes (1 ng.mL^{-1}) was transferred to the glass vial. A clean Teflon coated magnetic stirring bar was inserted into it along with FPSE media. The solution was stirred for optimized duration of time. After this, the FPSE media was taken out of the solution, wiped gently to remove residual water and transferred into the vial containing 500 μL acetonitrile for desorption of analytes. The eluent was injected into injection loop of HPLC for chromatographic separation (Figure 3). The schematic representation of FPSE procedure is described in Figure 4.



HPLC analysis

Chromatographic system was conditioned by passing the mobile phase through the column until a stable signal was obtained. The selection of mobile phase depends upon resolution of peak as well as signal response. Efficient separation of the chromium complex was achieved with acetonitrile and water. The optimized ratio of solvents in mobile phase was acetonitrile: water (65:35 v/v). The flow rate of mobile phase was maintained at 1 mL.min⁻¹ with UV detection at 320 nm. The peaks were obtained at retention time of 1.2 and 1.4 min for Cr(MDTC)₂(OMDTC) and Cr(MDTC)₃ complexes, respectively.

Optimization of FPSE conditions

Different parameters affecting the performance of FPSE procedure towards extracting the metal complexes were optimized. Aqueous sample (10 mL) was taken for subsequent experimentations. Optimized conditions were used for validation and application to the environmental samples. The following parameters were optimized:

Optimization of sample extraction time: Equilibrium extraction time is one of the most important FPSE parameters. Once the extraction equilibrium is reached, FPSE media cannot extract the target analyte any further under the given conditions. The porous sol-gel sorbent network, high primary contact surface area and the permeable cellulose substrate synergistically reduces the extraction equilibrium time. The sample containing analytes (1 ng.mL⁻¹) was examined to study the effect of extraction time. Extraction times from 5 to 25 min were taken for observation. As the extraction time increases, extraction of target analytes onto the FPSE fiber increases and becomes almost constant at 15 min. So the extraction time of 15 min was optimized for further experimentation shown in Figure 5.

Effect of eluting/ back-extraction solvent: Once the target analytes are extracted into the FPSE media, a quantitative desorption into a suitable organic solvent is needed. The solvent breaks the analyte-sorbent interaction and dissolves the analyte into it. Different solvent mixtures were tried for the back-extraction of target analytes. Acetonitrile was the best elution/back-extraction solvent shown in Figure 6.

Effect of elution/back-extraction time: Elution/back-extraction time was optimized by performing the experimentation with back-extraction time ranging from 2 to 10 min. An elution/back-extraction time as 6 min was selected while keeping the other optimized parameters to their fixed values (Figure 7).

In addition to all these factors carry over effect was also studied for FPSE sorbent. A thorough clean up step was required in order to remove the matrix effect. Fiber was washed thoroughly with acetonitrile before the subsequent experimentation. The carry over effect was checked by injecting the eluent 3-4 times before analyzing the next sample. The matrix effect can also be minimized by using the new fiber for each extraction process, as it is inexpensive.

Method validation

The optimized FPSE-HPLC-UV conditions were used to prepare the calibration curves in the range 1-100 ng.mL⁻¹ for all kinds of samples. Over the range, a linear response with the regression coefficient 0.997 and 0.995 was obtained for Cr(III) and Cr(VI) complexes, respectively. In the unknown samples, the concentrations of Cr(VI) can be determined by measuring the peak areas obtained due to Cr(MDTC)₂(OMDTC) using the calibration curve. Proposed method is suitable for speciation of both Cr(III) and Cr(VI) in a sample

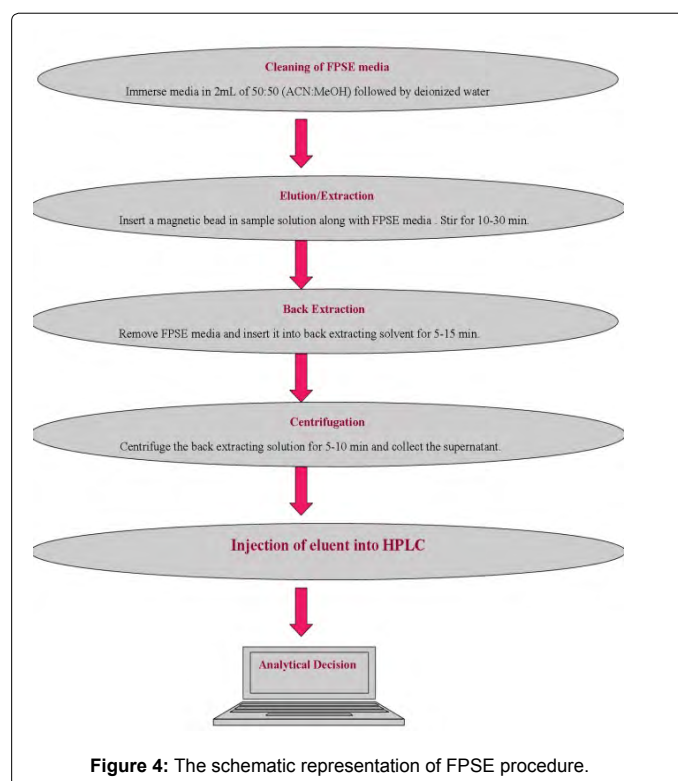


Figure 4: The schematic representation of FPSE procedure.

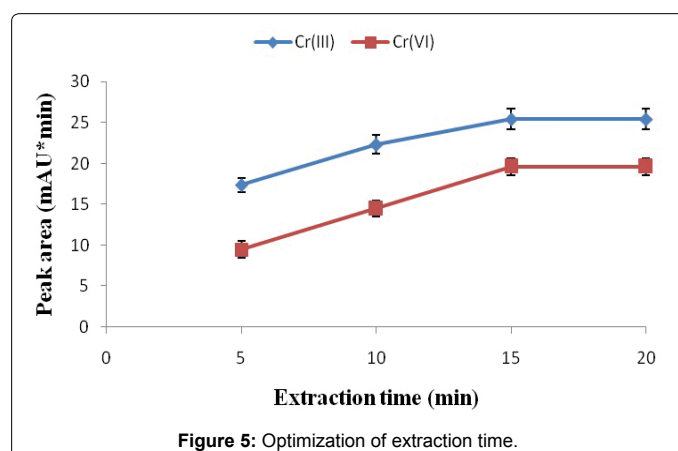


Figure 5: Optimization of extraction time.

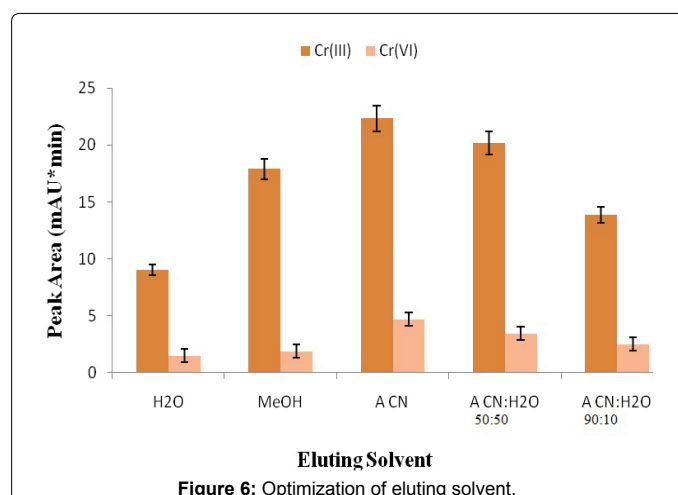


Figure 6: Optimization of eluting solvent.

using quantitative calculations based on the ratio of respective peak areas of absolute Cr(III)-MDTC complex and absolute Cr(VI)-MDTC complex. The concentration of Cr(III) can be calculated by subtracting the value corresponding to Cr(MDTC)₃ obtained from Cr(VI).

Comparison of method

The results obtained from the developed method were compared with the same from other techniques such as FAAS [27], ICP-MS [28] etc. and LOD values obtained were lower than the earlier published reports (Table 1). The values of accuracy and precision were comparable with other methods for the analysis of Cr(III) and Cr(VI) complex. The use of Ascentis Express column has reduced the analysis time to greater extent compared to earlier studies. In earlier reports, the chromatographic run time was from 5 to 6 min [8] but in the developed method 3 min was sufficient to carry out the analysis. The developed method is more rapid and robust.

Interference of other ions

The interference of various metal ions such as Co(II), Ni(II), Pd(II), Zn(II), Sn(II), Ag(I), Cu(II), Mo(VI), V(V) was studied. Different amount of these diverse metal ions were added individually to aliquots containing Cr(III) and Cr(VI) ions. At room temperature Co(II), Ni(II) and Pd(II) ions form complexes with morpholinedithiocarbamate (MDTC) and can be removed by pre-extraction in chloroform. As Cr ions do not form complex at room temperature with MDTC so these could be left in aqueous sample and be analyzed by the developed procedure. Vanadium and molybdenum ions require highly acidic conditions (pH<4) for complexation, so no interference was observed. Cr(III) or Cr(VI) ions have shown different tolerable concentration limits for different metal ions during complexation phenomenon. The tolerable concentration ratio added to 100 ng.mL⁻¹ Cr(III) or Cr(VI) ions was 1000 times for Na⁺ and K⁺, 100 times for Zn²⁺, Hg²⁺, Cd²⁺ and 10 times for Cu²⁺, Mn²⁺, Pb²⁺, Co²⁺ and Fe³⁺ ions. Effect of the additions of anions such as sulfate, chloride, bromide, iodide, nitrite, acetate, oxalate, nitrate ions etc. was also examined. Anions did not interfere much up-to 50-60 mg.L⁻¹ concentration. This demonstrates that the common potentially interfering ions do not have a significant effect on the speciation of Cr (III) and Cr (VI) ions.

Analytical applications

The effectiveness of the developed method was verified by the determination of Cr (III) and Cr (VI) complex in various kinds of aqueous samples. The environmental aqueous samples were analysed under optimized extraction conditions to demonstrate the performance and practical applicability of the developed method. A good agreement was obtained between the added and recovered analytes concentration by the developed FPSE-HPLC-UV method (Table 2). The results obtained were satisfactory with recovery more than 95% for a broad concentration range. This proves that the developed procedure is suitable for genuine environmental and consuming water applications. During their determination no major interfering peaks were present at the retention time of these analytes. FPSE-HPLC-UV chromatogram of spiked ground water, drinking water and industrial waste water at 1 ng.mL⁻¹ concentration are presented in Figure 8a-8c. The welldefined peaks of the analytes demonstrated that FPSE-HPLC-UV was an adequate extraction and clean up procedure for the analysis of chromium ions in aqueous environmental samples. The results of the determination are shown in Table 3.

Conclusion

Compared to other sorbent-based sorptive microextraction

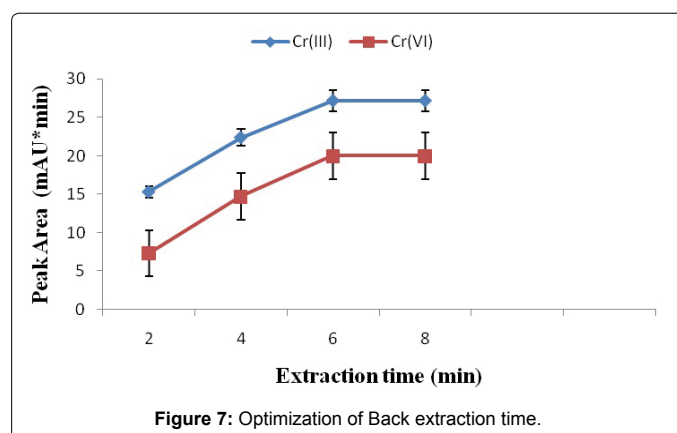


Figure 7: Optimization of Back extraction time.

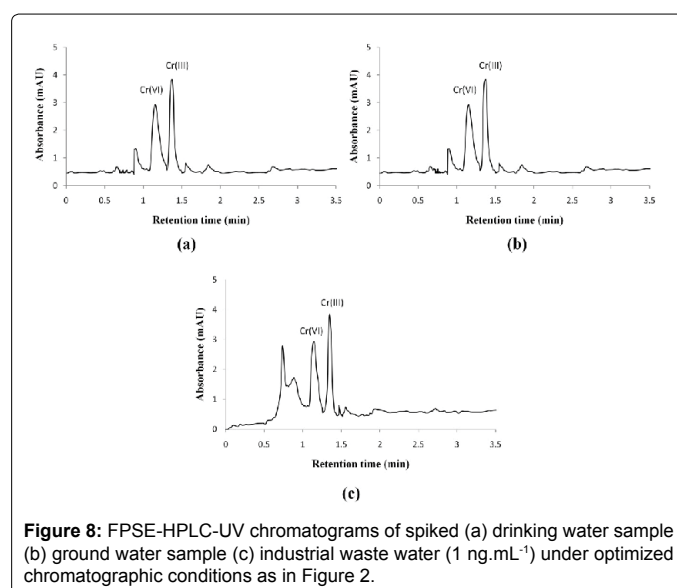


Figure 8: FPSE-HPLC-UV chromatograms of spiked (a) drinking water sample (b) ground water sample (c) industrial waste water (1 ng.mL⁻¹) under optimized chromatographic conditions as in Figure 2.

S No	Analytical technique	LOD [Cr(III)] (ng.mL ⁻¹)	LOD [Cr(VI)] (ng.mL ⁻¹)
1	*CPE-HPLC	3.4	5.2
2	IC-ICP-MS	>0.2	>0.2
3	HPLC-UV	0.005	0.007
4	*IC	0.02	0.02
5	HPLC-UV	400	1000
6	HPLC-ICP-MS	0.13	0.13
7	*LLE-GFAAS	N/A	0.2
8	FPSE-HPLC-UV	0.001	0.003

*CPE: Cloud Point Extraction; *IC: Ion Chromatography; *LLE: Liquid Liquid Extraction

Table 1: Comparison of detection limits of developed method with the previously reported methods.

Parameters	Sample preparation using FPSE	
	Cr(MDTC) ₃ in Cr(III)	Cr(MDTC) ₂ OMDTC in Cr(VI)
Wavelength (nm)	320	320
Correlation coefficient (R ²)	0.997	0.995
Retention time (min)	1.4	1.2
Regression equation	0.50x+4.8	0.275x+1.85
LOD (ng.mL ⁻¹)	0.001	0.003
LOQ (ng.mL ⁻¹)	0.003	0.009
RSD (%)	2.1-2.4	1.9-2.1

Table 2: Analytical characteristics of developed FPSE-HPC-UV method.

Analyte	Spiked Conc. (ppb)	Industrial Water		Bore well Water		Drinking Water	
		Obtained Conc. (RSD)	Recovery (%)	Obtained Conc. (RSD)	Recovery (%)	Obtained Conc. (RSD)	Recovery (%)
Cr(III) complex	1	0.89 (2.7)	89.60	0.98 (2.1)	98.70	0.97 (2.3)	97.60
	5	4.50 (2.5)	90.00	4.88 (2.0)	97.60	4.78 (2.3)	95.60
	10	9.16 (2.0)	91.60	9.75 (1.9)	97.59	9.65 (2.2)	96.70
Cr(VI) complex	1	0.87 (2.9)	87.00	0.97 (2.3)	97.50	0.98 (2.1)	98.50
	5	4.56 (2.6)	91.20	4.82 (2.2)	96.50	4.90 (2.0)	98.00
	10	9.13 (2.5)	91.30	9.86 (2.1)	98.60	9.68 (1.9)	96.80

Table 3: Recoveries of Cr (III) and Cr (VI) using FPSE-HPLC-UV.

techniques, FPSE possessed many advantages and has been proved to be a simple, economic, high extraction efficiency, faster extraction equilibrium and efficient sample preparation technique for the detection of chromium species using HPLC-UV. Trace level determination of Cr species is accomplished by using FPSE. Real samples were analysed after spiking with chromium complexes in order to confirm the validity of the developed method. This method shows potential as a rapid screening method to determine chromium species quantitatively in three kinds of water samples.

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