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# Selective Speciation of Cr(III) and Cr(VI) by Micro-emulsion Using UV-Vis. Spectrophotometry

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Abstract

A novel UV-Vis. spectrophotometric detection system is introduced for speciation of Cr(III) and Cr(VI) via interaction with a new micro-emulsion generated between a sweet crude oil as nonpolar phase, H_2O as polar phase and C_2F_4 (R22) gas as disperser. This micro-emulsion is selective for Cr detection and determination via observation of absorption peak at 578 nm wavelength. Determination of Cr is achieved under optimized conditions such as 3.0 mL of sweet crude oil/R22/water with mole fractions of 0.2, 0.2 and 0.6, respectively at 25°C and pH ~7.0. For Cr speciation, Cr(III) is detected via directly interaction with the synthesized micro-emulsion. Whereas Cr(VI) is detected via difference between total Cr and Cr(III) during reduction using 0.055 g of $S_2O_3^{2-}$ as reducing agent. Relative standard deviation for at least 5 replicate analyses is 1.73%. Reliability of the method has also been evaluated via determination of Cr in some wastewater samples.
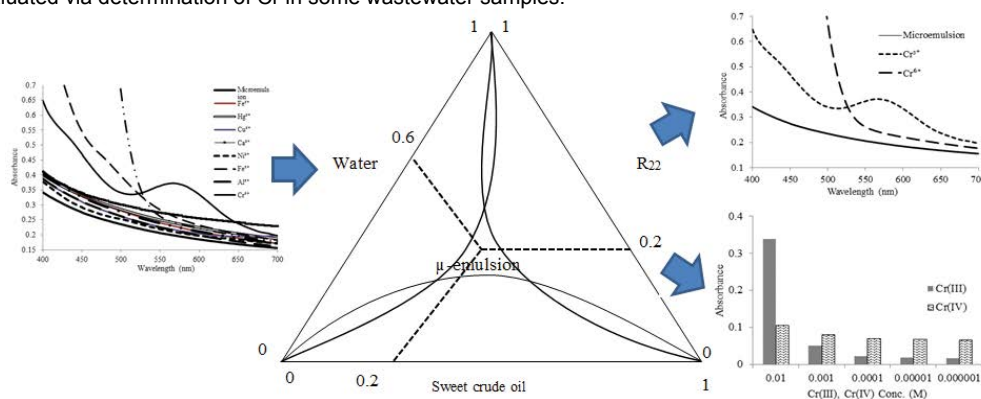
Keywords: Micro-emulsion; Cr determination; Spectrophotometry; Speciation

Introduction

In a continuous nonpolar organic phase, reverse micelle solution is defined as water in oil micro-emulsion [1]. Micro-emulsion is a transparent, isotropic and thermodynamically stable mixture of oil, water and surfactant in which water has been dispersed in oil phase and a disperser such as a surfactant is located between the oil/water phases [2]. In the micro-emulsion, the dispersing molecules usually contain a polar head and a nonpolar tail which is able to interact with oil and aqueous phases [3]. The disperser includes various molecules such as spherical, cylindrical or ellipsoidal micelles and so on [3].

Micro-emulsions are suitable systems for using in many processes due to their ease of formation and stability [4]. There is an extremely huge capacity in the micro-emulsions for utilizing in chemical and industrial processes because of their exclusive properties such as low interfacial tension, high interfacial area and their ability to dissolve immiscible liquids [2]. Over the last decade, many practical employments have adopted micro-emulsions for various purposes such as in the chemical reactors, in the drug delivery vehicles [5] and for promotion of the oil recovery during the analysis purposes [6]. However among these applications, determination aspect of the micro-emulsion is more important. For instance, micro-emulsion seems to be applicable during identification of various species such as chromium (Cr) in a real sample [7]. Effluents of many industrial processes also introduce Cr into the surrounding [7]. Cr as toxic species is important due to its state of oxidation and its carcinogenic agent [8]. Consequently it is important to specify and control this element everywhere which it's possible to present.

Up to now several analytical techniques have been used for Cr determination such as spectroscopy [9], chromatography [10], and electrochemistry [11]. For example, Dominguez et al. [12] used adsorptive stripping voltammetry for determination of Cr(III) and Cr(VI). Eiras et al. [13] focused on various solvents for determining Cr(III). Daulton et al. [14] determined Cr(III) and Cr(VI) based on the electron energy loss. Xiang et al. [15] employed fluorimetric method to determine Cr(III) species [15]. Beni et al. [16] detected Cr(VI) by liquid-liquid extraction technique [16]. Domínguez-Renedo et al. [17] used metal nanoparticles such as gold and silver for detection of Cr(VI) [17]. Elci et al. [18] analyzed total Cr using CO_3^{2-} leaching. Hashemi et

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al. [19] adopted cloud point extraction to determine Cr(III) and Cr(VI) in the aqueous real samples [19]. Kachoosangi et al. [20] utilized voltammetry for determination of Cr (VI) by using modified carbon composite electrode [20] and finally Fridaus et al. determined Cr by calorimetric methods in 2014 [21].

In these analytical techniques in spite of their great advantages such as high sensitivity, sometimes suffer from challenges such as low selectivity, impossibility to speciation of Cr species, and /or high response time [18-21]. It seems that micro-emulsions due to possessing significant characteristics like presence of plenty of functional groups as active cites on their surface, having nanometric sphere as template, stability and homogeneity [4-7] are considered as good candidate for selective determination purpose using rapid analytical techniques such as UV-Vis. spectrophotometry. For this purpose hereby in this study a new, rapid, and low cost method is introduced for speciation of Cr(III) and Cr(VI) via formation of micro-emulsion between a sweet crude oil as nonpolar phase, H_2O as polar phase and a C_2F_4 (R_{22}) gas as disperser.

Experimental

Reagents and solutions

All the chemical reagents were from their analytical grades and were used as received without any further purification. For Cr speciation, 50.0 mL of each Cr(III) and Cr(VI) stock solution (0.01 M) was prepared via dissolving 0.1144 g of chromium acetate, $Cr(CH_3COO)_3$, and 0.1470 g of potassium dichromate, $K_2Cr_2O_7$ in two distinct volumetric flasks followed by dilution to the marks using triply-distilled water. In addition, 50.0 mL of $S_2O_3^{2-}$(as reducing agent during reduction of Cr(VI) to Cr(III)) was prepared via dissolving 0.0950 g of $Na_2S_2O_3$ in a volumetric flask using the triply-distilled water. In this study, NaOH (Flucka) and citric acid (60%, Flucka) were adopted to adjust the pH of the solution. NaCl (Merck) was selected as a soluble salt to evaluate the effect of ionic strength on the sensitivity of the detection system. Soluble aqueous solutions including different cations and anions such as Al^{3+}, Cu^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cl^-, SO_3^{2-}, NO_3^-, etc. were individually selected as foreign species to study the interfering effects. All these reagents were from Merck Company. To prepare the micro-emulsion, sweet crude oil [22] with low viscosity (Company: Mexican state oil, average molecular weight: ~500 g mol^{-1}) was selected as organic phase. Triply-distilled water was also adopted as the polar phase during using R_{22} gas (Linde, 99% purity, molecular weight: 100 g mol^{-1}) as suitable disperser. some wastewater samples were selected as the real sample during evaluation of the reliability of the recommended procedure and method.

Apparatus

To prepare the micro-emulsion, an autoclave (model: SM-Yamato Scientific America, Inc.) was adopted. A pH meter (Model: Metrohm 827) was utilized to control the pH of the prepared solution. During the synthesis of the micro-emulsion, a mechanical shaker (model: MS-400) as well as a sonicator bath (model: PH350EL, frequency: 80 kHz) were used. Temperature of the solution was controlled using a heating mantle (model: Ringwood) and set using Hg thermometer (model: FAQs HP). UV-Vis. Spectrophotometer (model: ultrospec 4000) was also selected using a 1.0-cm quartz cell. Atomic absorption spectrometry (AAS, model: Varian) was adopted to evaluate the reliability of the quantity of Cr in the wastewater samples. To control the optimum mole fraction of each oil, R_{22} and water, a turbidimeter (model: 965 Digital Turbidimeter, Orbeco-Hellige) was used as the controlling system.

Synthesis of micro-emulsion

To synthesize the micro-emulsion, a new procedure was introduced. For this purpose, ~50.0 mL of the sweet crude oil (mode fraction: 0.2) was heated to ~70°C using a mantle inside a 200-mL beaker located in a beaker containing paraffin (LLC TRADING COMPANY ALMAZ), along with controlling the temperature by the thermometer and rotation with the rate of ~2000 rpm using a mechanical stirrer (model: Silnik laboratoryjnego mieszadła mechanicznego). Then ~100.0 g of the R_{22} gas (mode fraction: 0.2) was gravimetrically weighted and added to the medium with the rate of ~1.0 mL per min. This process was then achieved using virial coefficient [23]. Then in order to have homogenous mixture of oil/R_{22}, the temperature of the mixture was increased to ~110°C for ~1 h, followed by cooling to the room temperature with the rate of ~-2°C min^{-1}. This heating/cooling process was repeated for at least 5 times to get partially homogeneous and transparent reagent. To complete the homogeneity of the reagent, it was transferred into an autoclave and heated to ~70°C at 10.0 bar pressure for 2 h. All these processes led to have completely homogenous oil (color: brown). Then ~10.0 mL of triply-distilled water (mode fraction: 0.6) was slowly added to the reagent with the rate of ~2.0 mL min^{-1}, along with vigorously shaking using the shaker to get a yellow color. Formation of the micro-emulsion was finalized by the sonication of the prepared reagent using the sonicator (frequency: 500 kHz) for ~30 min. The prepared micro-emulsion was then adopted for selective speciation of Cr(III) and Cr (VI).

Procedure

For Cr speciation, the pH of the solution was adjusted to ~7.0 using citric buffer solution (0.01 M). Then, ~2.0 mL of the prepared micro-emulsion was diluted 500 times using triply-distilled water and mixed with ~10.0 mL of the aqueous solution containing Cr(III) ion, along with vigorously shaking for ~1.0 min. The temperature of the solution was adjusted to the room temperature. Then ~3.0 mL of the reagent was transferred into the quartz cell and the absorbance was measured at 578 nm wavelength.

To determine the total Cr species including Cr(III) and Cr(VI), ~10.0 mL of solution containing 0.01 M $S_2O_3^{2-}$ as reducing agent was added to the micro-emulsion to reduce Cr(VI) to Cr(III), followed by speciation of Cr-containing aqueous solution according to the procedure reported in the previous paragraph. Speciation of Cr(VI) was then achieved via difference between total Cr and Cr(III).

Real sample

To validate the proposed analytical approach, an analytical test was performed. Standard addition method was selected to analyze the Cr contained in some wastewater samples, followed by comparison to the result analyzed by AAS method.

Results and Discussion

Micro-emulsions due to having special characteristics such as high flexibility, compatibility between nonpolar/polar phases, low cost as well as their template behavior have been considered as one of the most important media during synthesis of nanostructures, extractions, as well as determination purposes [1-4]. All these characteristics point to the importance of the introduction of various synthetic methods during enlarging the analytical applications of micro-emulsion. This requirement is the basic of this research during the fabrication of an new kind of micro-emulsion using oil, R_{22} and water, followed by investigation on its selective properties during speciation of Cr(III)

and Cr(VI). In this analysis parameters having influence during speciation of Cr include: mole fraction of oil/R_{22}/water, volume as well as the ratio of micro-emulsion and the Cr-containing real or standard sample solution, and finally effects of some effective parameters such as pH and the temperature of the synthesized micro-emulsion during interaction with Cr species.

In this study, the synthesized micro-emulsion was used for speciation of Cr(III) and Cr(VI) species (1.0 mM) using UV-Vis. spectrophotometry at 578 nm wavelength. For this purpose, absorbance intensity was selected as the detection system. Effect of different mole radios of each oil, R_{22} and water during the generation of micro-emulsion has been schematically shown in Figure 1. To further optimize the mole fractions of each of the sweet crude oil, R_{22} and water, turbidity was selected as detection system. For this purpose, different mole fractions of these reagents ranging between 0.0-1.0 were tested. Based on the results, minimum turbidity was evaluated at mole fractions the same as 0.2, 0.2 and 0.6 for each of sweet crude oil, R_{22} and water. The results are shown in Figure 2. As the lower the turbidity, the more transparent medium was evaluated for the generated micro-
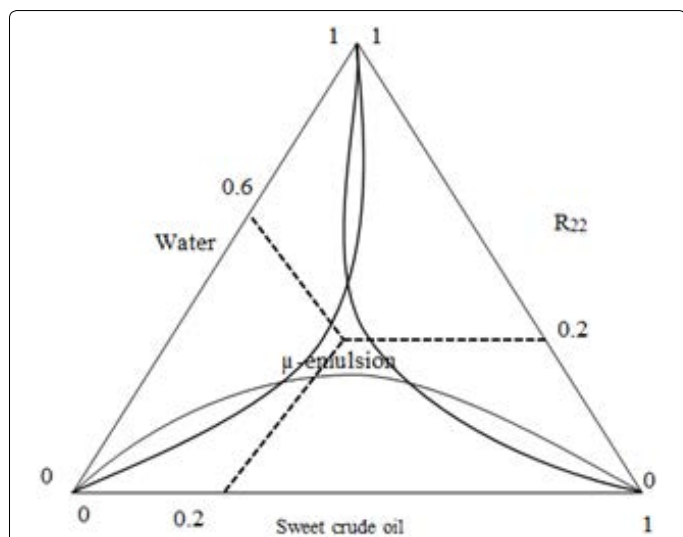

Figure 1: Diagram showing the effect of mole fraction of oil, water and R_{22} on the absorbance intensity of 1.0 mM Cr(III) at 578 nm wavelength.
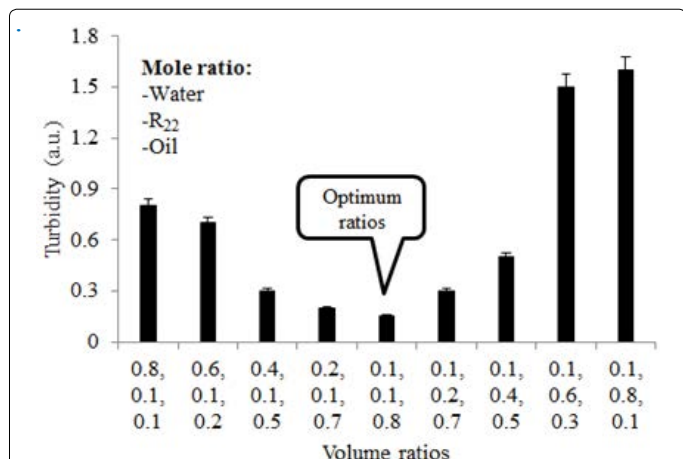

Figure 2: Histogram representing the effect of mole fraction of oil, water and R_{22} on the turbidity.

emulsion. Therefore these values were selected as optimum mole fractions during the generation of the micro-emulsion for the quantity purposes.

The volume ratio of each micro-emulsion to the aqueous solution containing the analyte is considered as another important factor during the analysis of the analyte. In this study different ratios of each micro-emulsion and aqueous solution such as 1:1, 1:5, 5:2, and 5:1 was tested at 578 nm wavelength. The results are shown in Figure 3. Based on the results (Figure 3) at some ratios such as 1:1, the synthesized micro-emulsion was not so homogeny. In addition the white color of the fluid was so high that large baseline was observed in the background of the system. In addition, maximum absorbance was observed during analysis of solution 1.0 mM Cr(III) at volume ratios between 1:5, 5:2 and 5:1. Therefore volume ratio of 5:2 was selected as optimum value. This volume ratio simply led to have sensitive response during analysis of trace amounts of Cr species.

No significant absorbance peak was observed in the sensitivity of the system during analysis of Cr(III) at different buffer acidic and basic conditions that were provided using NaOH and citric acid. Selection of citric acid was based on the organic structure of the citric acid, which was in more compatible with the oil phase in comparison with other inorganic weak acids. Therefore for simplicity, neutral condition (pH ~7.0) was selected using the buffer solution generated using solution of 1.0 mM citric acid. In addition, due to the insensitivity of temperature ranging between 0-60°C on the absorbance intensity during analysis of Cr species, room temperature (25 ± 1°C) was selected as optimum temperature.

To optimize the influence of ionic strength on the sensitivity of this technique for Cr determination and speciation, NaCl was selected as suitable probe. For this purpose, different concentrations of NaCl ranging between 1.0×10^{-2}-1.0×10^{-4} M containing a fixed concentration (1.0 mM) of Cr(III) were provided and the absorbance intensity was evaluated at maximum wavelength (i.e. 578 nm). Based on the result (Figure 4), the least quantity of NaCl, the maximum sensitivity was detected during Cr determination. This process is probably related to the salting-out effect of the water reagent presented in the matrix of the micro-emulsion. It seems that presence of citric acid as buffer solution provided enough ionic strength that there was no need to increase the ionic strength further during addition of a soluble salt such as NaCl. Therefore in this study it is recommended to measure the absorbance at minimum ionic strength without addition of any soluble salt to the micro-emulsion matrix.

As the synthesized micro-emulsion has no interaction with Cr(VI), therefore for speciation of each Cr(III) and Cr(VI) species two independent analyses are needed, one for Cr(III) analysis and the other for the Cr(VI) speciation in the presence of a suitable reducing agent. Therefore speciation of Cr(VI) is simply possible via difference between total Cr and Cr(III). This phenomenon is related to the specific interaction between Cr(III) and the synthesized micro-emulsion in comparison between other foreign species even Cr(VI).

Based on the literature, $S_2O_3^{2-}$ has been considered as suitable reducing agent during reduction of Cr(VI) to Cr(III) [24-28]. In this study, effect of $S_2O_3^{2-}$ as suitable reducing agent was therefore evaluated in detail. To optimize the quantity of $S_2O_3^{2-}$ during reduction of Cr(VI) to Cr(III) factors such as sensitivity was also evaluated. As $S_2O_3^{2-}$ solution has a partial absorbance at 578 nm wavelength therefore to have rapid reduction of Cr(VI) to Cr(III) maximum concentration of $S_2O_3^{2-}$ without providing any significant background was evaluated in
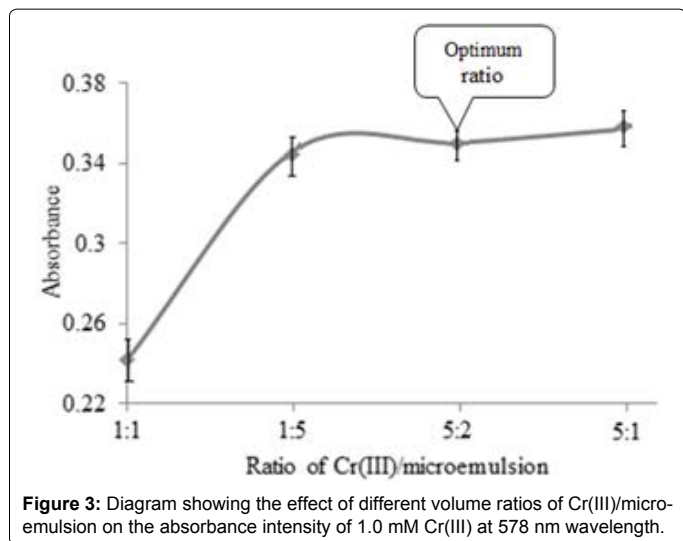
Figure 3: Diagram showing the effect of different volume ratios of Cr(III)/micro-emulsion on the absorbance intensity of 1.0 mM Cr(III) at 578 nm wavelength.
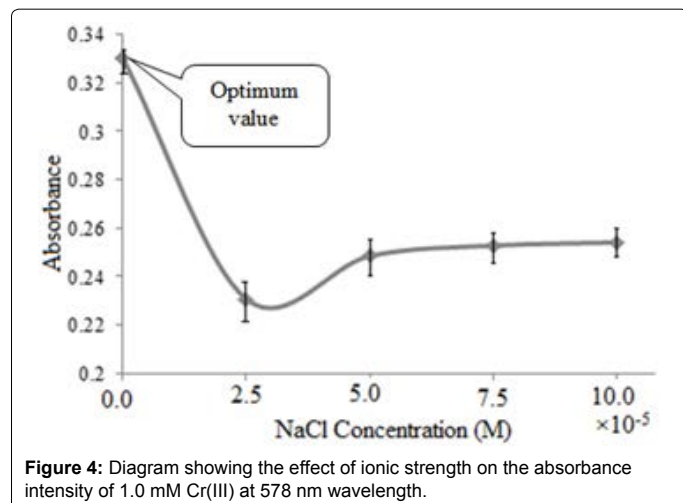

Figure 4: Diagram showing the effect of ionic strength on the absorbance intensity of 1.0 mM Cr(III) at 578 nm wavelength.

detail. For this purpose, the effect of various concentrations of $S_2O_3^{2-}$ solution between 0.2-2.0 mM was evaluated during reduction of Cr(VI) solution with 1.0 mM molar concentration [29,30]. The results are shown in Figure 5. As clearly shown, the higher the concentration of $S_2O_3^{2-}$, the more was the intensity of the Cr(VI) solution. However in spite of the positive effect of higher concentrations of $S_2O_3^{2-}$ during promotion of the sensitivity, but high concentrations of $S_2O_3^{2-}$ resulted to have colloidal suspension. This phenomenon then led to have noisy signal with low single-to-noise ratio. Therefore higher concentrations of $S_2O_3^{2-}$ from one side promoted the sensitivity and from the other side reduced the reproducibility of the system during analysis of trace amount of Cr species. Therefore minimum concentration of $S_2O_3^{2-}$ (i.e. 0.2 mM) was selected as optimum ratio during reduction of Cr(VI) to Cr(III).

Analytical figures of merit

The UV-Vis. spectra of Cr(III) and Cr(VI) are shown in Figure 6. As shown, maximum intensity was observed at 578 nm wavelength that was selected for speciation of Cr species. The calibration curves for both Cr(III) and Cr(VI) are illustrated in Figure 7A and 7B. As shown, the introduced micro-emulsion was suitable for Cr(III) and Cr(VI) detection and determination yielding linear dynamic range between

0.0001–0.05 M for Cr(III) and between 0.0001- 0.01 M for Cr(VI), respectively. The detection limit was defined as the triple values of the standard deviation of the blank divided by the calibration sensitivity (slope of the calibration curves, Figure 7). Based on this definition, the limit of detection was found as ~0.1 μM for Cr(III) and ~1.0 μM for Cr(VI) species, respectively. This difference was related to the small absorbance intensity of $S_2O_3^{2-}$ at 578 nm wavelength.

The sensitivity of this method was evaluated according to the slope (calibration sensitivity) of the calibration curves (Figure 7). These values were evaluated to 28.91 (a.u.) M^{-1} for Cr(III) and 2.73 (a.u.) M^{-1} for Cr(VI) species. Significant difference between the calibration sensitivities was attributed to the reducing step during the reduction of Cr(VI) to Cr(III). These values had also been comprised with each other via following the histogram during analyses of each Cr(III) and Cr(VI) with different molar concentrations (Figure 8). High sensitivity of this method is strongly attributed to the intrinsic behavior of the synthesized micro-emulsion. Reproducible results were also obtained during several analyses of a constant concentration of Cr(III) with 1.0 mM concentration. According to the results, relative standard deviation (RSD) was 1.73% for total Cr species.

To evaluate the selectivity of the micro-emulsion during the quantitation process, the UV-Vis. spectra of the micro-emulsion during analyses of at least 0.01 M solution of foreign species such as Fe^{2+}, Fe^{3+},
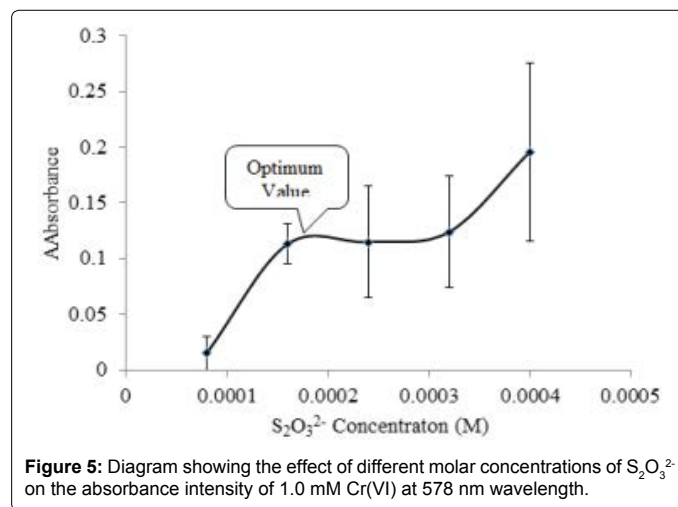

Figure 5: Diagram showing the effect of different molar concentrations of $S_2O_3^{2-}$ on the absorbance intensity of 1.0 mM Cr(VI) at 578 nm wavelength.
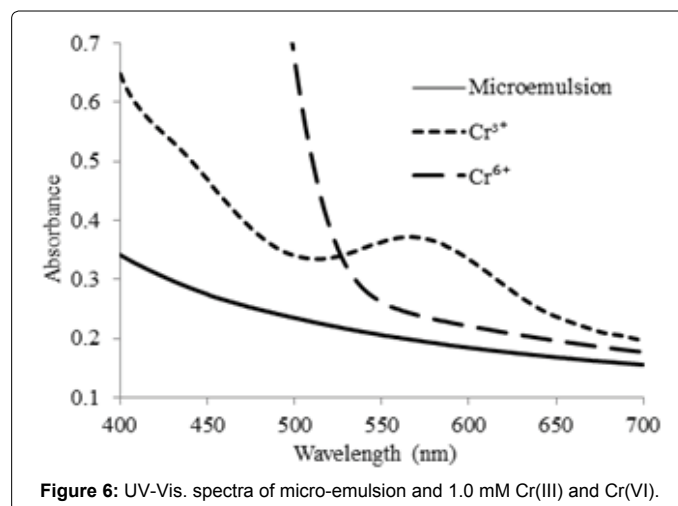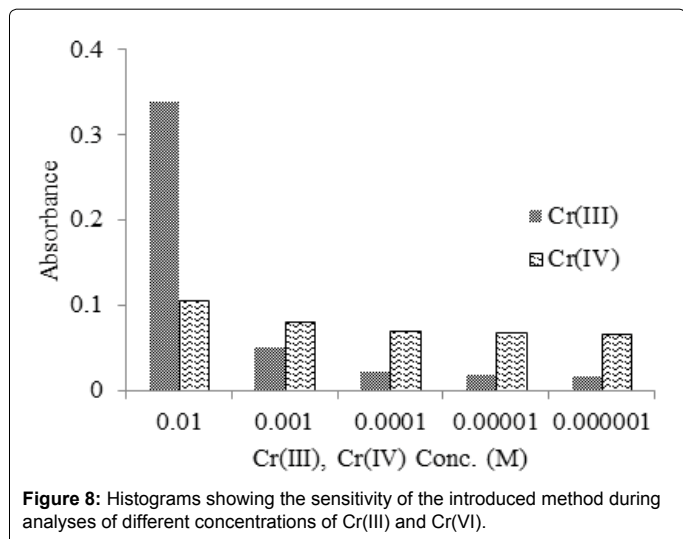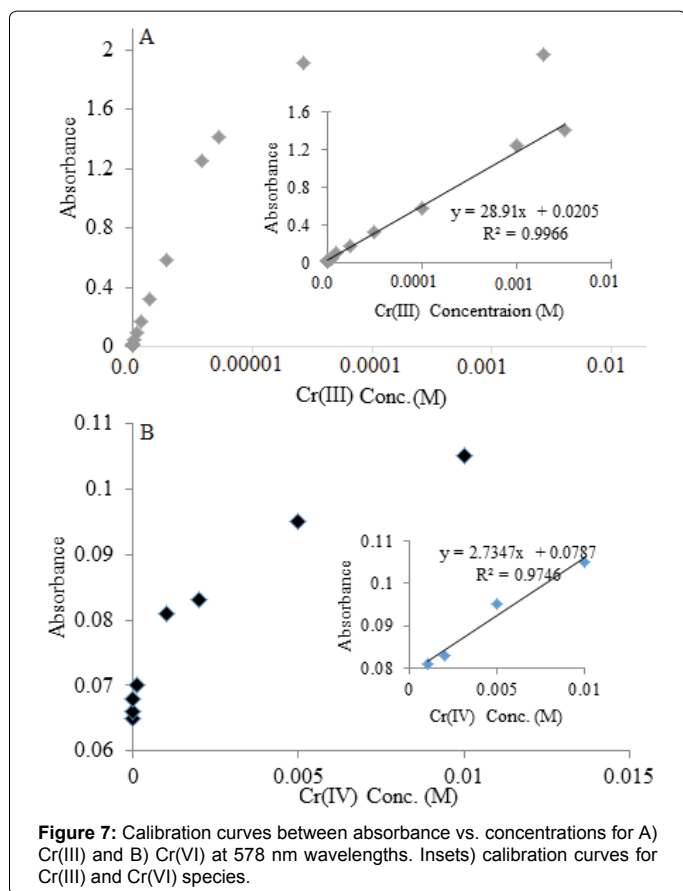

Figure 6: UV-Vis. spectra of micro-emulsion and 1.0 mM Cr(III) and Cr(VI).

Figure 7: Calibration curves between absorbance vs. concentrations for A) Cr(III) and B) Cr(VI) at 578 nm wavelengths. Insets) calibration curves for Cr(III) and Cr(VI) species.

Figure 8: Histograms showing the sensitivity of the introduced method during analyses of different concentrations of Cr(III) and Cr(VI).

Pb^{2+}, Cu^{2+}, Al^{3+}, Ca^{2+}, Ni^{2+}, SO_4^{2-}, NO_3^-, etc. were evaluated in detail. The results are shown in Figure 9. Based on the results the synthesized micro-emulsion was selected only to Cr(III) during observing of absorbance peak at 578 nm. Also, compared to the spectrum of Cr(VI), absorbance peak at this wavelength clearly pointed to the capability of this micro-emulsion for selective detection of Cr(III) even in the presence of Cr(VI). Therefore, in spite of the high sensitivity of the introduced method, no interfering effect was observed for each of cations and anions such as Fe^{2+}, Cu^{2+}, Al^{3+}, Ca^{2+}, SO_4^{2-}, NO_3^-, etc. during the Cr speciation.

Real sample analysis

The validation of the method was evaluated by an analysis test via comparison between this method with AAS as reference and accepted analytical method, followed by evolution of the relative error percentage. The results are shown in Table 1. Good agreement was evaluated during comparing the results of this method with that evaluated using AAS, revealing the reliability and acceptance of this method for Cr speciation and detection.

Conclusions

In this work, a sensitive and reproducible Cr speciation technique is introduced based on the great advantages of a new micro-emulsion, synthesized using sweet crude oil/R_{22}/water with mole radio of 0.2, 0.2 and 0.6, respectively. In Table 2, this method has been comprised with the previously reported articles from aspects such as detection limit and
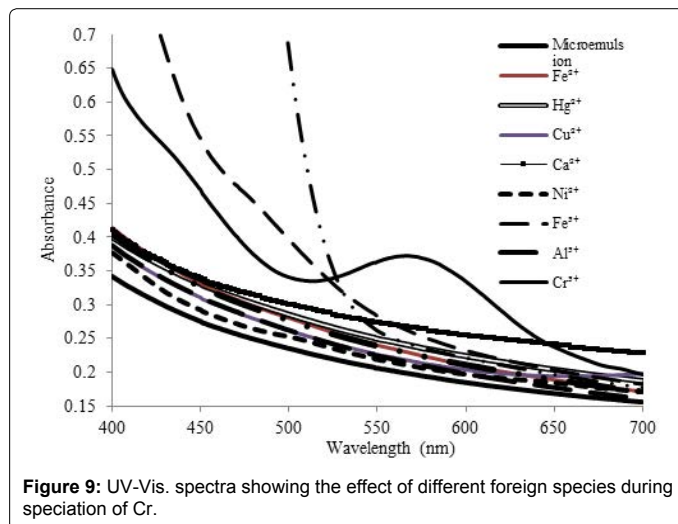
Samples	Species	Cr analysis (M)× 10⁻⁴		Relative Standard deviation (%)³
		¹Poposed method	AAS² (Total Cr)	
Wastewater 1	Cr(III)	1.291 ± 0.002	1.625 ± 0.006	+1.78
	Cr(VI)	0.363 ± 0.003		
Wastewater 2	Cr(III)	5.824 ± 0.003	8.487 ± 0.005	-1.85
	Cr(VI)	2.506 ± 0.004		
Wastewater 3	Cr(III)	8.511 ± 0.005	24.105 ± 0.008	+1.44
	Cr(VI)	15.247 ± 0.003		

Note: ¹The data of the average of at least 3 independent analyses; ²Atomic absorption spectrometry; ³AAS is considered as reference analytical method.

Table 1: Determination of Cr species in some wastewater samples.

Researchers	Figures of merit	
	Detection limit	RSD%
Duarte et al. [22]	70 µg kg⁻¹	10
Dittert et al. [25]	1 µg kg⁻¹	4-20
Myöhänen et al. [26]	6.2 µg L⁻¹	<5
Wenling Hu et al. [27]	7.4 µg L⁻¹	3.9
Shujuan Chen et al. [28]	3.76 µg L⁻¹	1.66
Najafi et al. [29]	3.05 µg L⁻¹	2-4
Fariñas et al. [30]	0.13 µg L⁻¹	<10
Present study	<0.1 µM	1.7

Table 2: Comparison between present study and previously reported methods for Cr detection.

Figure 9: UV-Vis. spectra showing the effect of different foreign species during speciation of Cr.

RSD%. Compared to the previously reported methods, this technique has some beneficial aspects such as more simplicity, high selectivity, fast response time and more improved detection limit.

Acknowledgements

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