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CHROMIUM (VI) ANALYSIS IN EFFLUENTS USING LIQUID-LIQUID EXTRACTION COUPLED WITH FLAME ATOMIC ABSORPTION SPECTROMETRY

(Analisis Kromium (VI) dalam Efluen Menggunakan Pengekstrakan Cecair-Cecair Bersama Spektrometri Serapan Nyalaan Atom)

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Abstract

Simple sample preparation was investigated and developed to selectively determine Cr(VI) in wastewater samples or effluents based on the liquid-liquid extraction principle using tetrabutylammonium hydrogensulfate (TBAHS) as the ion-pair reagent in an acidic medium. TBAHS was prepared in an organic solvent to improve the extraction efficiency. The extracted Cr(VI) in the organic phase endured the acid digestion, and its atomic absorption was measured at 357.9 nm. The influences of several working parameters, namely, organic solvents (methyl isobutyl ketone-MIBK, dichloromethane-DCM, and chloroform), pH values (lower than 1.0, 1.0, 2.0, and 3.0) in the aqueous phase, TBAHS concentrations in the organic solvent (0.02, 0.04, 0.05, and 0.06 mol L^{-1}), extraction duration (from 3 to 30 minutes), number of extraction cycles (single or repeated extraction), sample preservation duration at ambient temperature, and co-existence of Cr(III) in the sample matrices, were investigated to discover the optimized working parameters. The results showed that dichloromethane (DCM) was the most effective extraction solvent. The most favorable conditions for complex formation were determined as follows: a pH of around 1.0 to 3.0; 0.05 mol L^{-1} TBAHS prepared in DCM, triple extraction, and a shaking duration of 15 minutes for each extraction cycle. The calibration curve was linear in the range of 0.05, 0.10, 0.20, 0.40, 0.60, 0.90, 1.2, 1.5 and 2.0 mg L^{-1}, and the regression equation was $y = 0.1068x + 0.0012$ with $R^2 = 0.9994$, exhibiting goodness of linearity. The method detection and quantification limit values were estimated to be 0.012 mg L^{-1} and 0.04 mg L^{-1}, respectively. The repeatability ($RSD_r = 0.71\%$) and reproducibility ($RSD_R = 1.1\%$) were favorable according to the requirements presented in Appendix F of AOAC (2016) for analytical method validation. The proposed method was applied to real wastewater samples and spiked samples, showing very low Cr(VI) concentrations for most samples and proper recoveries (91.1-109%).

Keywords: Cr(VI), Cr(III), liquid-liquid extraction, TBAHS, dichloromethane, DCM, ion-pair reagent

Abstrak

Penyediaan sampel yang mudah telah dikaji dan dibangunkan bagi penentuan terpilih Cr(VI) di dalam air sisa atau efluen berdasarkan prinsip pengekstrakan cecair-cecair menggunakan tetrabutylammonium hidrogensulfat (TBAHS) sebagai reagen pasangan ion di dalam medium berasid. TBAHS telah disediakan dalam pelarut organik bagi tujuan meningkatkan keberkesanan pengekstrakan. Cr(VI) yang telah diekstrak di dalam fasa organik melalui penghadaman asid, dan serapan atom telah diukur pada 357.9 nm. Pengaruh parameter seperti pelarut organik (metil isobutil keton-MIBK, diklorometana-DCM, dan klorofom), nilai pH (dibawah 1.0, 1.0, 2.0 dan 3.0) di dalam fasa akues, kepekatan TBAHS di dalam pelarut organik (0.02, 0.04, 0.05, dan 0.06 mol L^{-1}), tempoh pengekstrakan (dari 3 hingga 30 minutes), bilangan kitaran pengekstrakan (pengekstrakan tunggal atau ulangan), tempoh pengawetan sampel pada suhu sekitar, dan kehadiran bersama Cr(III) dalam matrik sampel turut dikaji untuk penentuan parameter kerja yang optimum. Hasil kajian menunjukkan diklorometana (DCM) paling efektif sebagai pelarut pengekstrakan. Keadaan paling baik untuk penghasilan kompleks ditentukan seperti berikut: pH antara 1.0 hingga 3.0; 0.05 mol L^{-1} TBAHS disediakan dalam DCM, tiga kali pengekstrakan, dan masa goncangan ialah 15 minit bagi setiap kitaran pengekstrakan. Lengkung kalibrasi adalah linear pada julat 0.05 hingga 2.0 mg L^{-1}, dan persamaan regresi ialah $y = 0.1068x + 0.0012$ dan $R^2 = 0.9994$. Had pengesanan dan kuantifikasi telah dihitung masing-masing pada 0.012 mg L^{-1} and 0.04 mg L^{-1}. Kebolehulangan ($RSD_r = 0.71\%$) dan kebolehhasilan semula ($RSD_R = 1.1\%$) adalah baik berdasarkan keperluan yang dinyatakan dalam Appendix F of AOAC (2016) bagi validasi kaedah analisis. Kaedah yang dicadang ini telah digunapakai bagi analisis sampel air sisa sebenar dan sampel yang dipaku, ia menunjukkan kepekatan Cr(VI) yang rendah dan perolehan semula yang baik (91.1-109%).

Kata kunci: Cr(VI), Cr(III), pengekstrakan cecair-cecair, diklorometana, reagen pasangan ion

Introduction

Chromium (Cr) has been known as the non-essential and toxic element for human beings and animals despite existing in trace quantities [1, 2]. The emission of Cr into the environment is mainly derived from metallurgical, electroplating, pigments, etc. The two most common species of chromium are Cr(III) and Cr(VI), whereby Cr(VI) exhibits remarkably high toxicity due to its higher solubility and flexibility than Cr(III) [3, 4], 100 times more toxic than Cr(III). Many studies have indicated death risks from lung cancers during working and direct exposure to Cr(VI). Moreover, Cr(III) is considered an essential micro-nutrient and is responsible for blood glucose control and lipid metabolism in mammals. Because of their toxicity differences, the determination of total Cr concentrations did not provide enough reliable and accurate information to evaluate the toxicity potentials toward the environment. Additionally, the selective determination of Cr species has helped the scientists to recognize their origins and behaviors to find adequate solutions to remove these exposed pollutants from the environment. Modern instrumental methods using ICP-OES or ICP-MS coupled with liquid chromatography have met the requirements for direct analysis of Cr species in various sample matrix due to their selectivity and sensitivity [5, 6]. However, such methods are costly and not easily equipped in many laboratories. Therefore, another cheap, convenient, simple, and effective analytical method by using selective solvent or liquid-liquid extraction techniques (LLE) and measured on the Flame-Atomic Absorption Spectrometry (F-AAS) analysis, a common instrument for metal(loid)s quantification in various environmental laboratories, should be developed for Cr(VI) detection in complicated sample matrices such as wastewater.

For trace analysis of metal ions, solvent extraction has become a popular technique to serve the analyte enrichment and/or matrix removal purposes. Moreover, such techniques allow to easy control of the volumes of the aqueous and organic phases, which makes them possible to be coupled with any potentially suitable analytical methods for determining various metal ions. Typically, the volume of organic solvent used in the extraction is smaller than that of the sample volumes, resulting in higher enrichment factors and lower method limits of detection and quantification. At the industrial scale, solvent extraction has been utilized in chemical industries for the purification of chemical elements and/or for the separation and concentration of metals of interest [7, 8]. However, for the analytical method development, the single application of organic solvents is usually faced with a lack of selectivity. Therefore, in order to enhance the selectivity of the LLE, complexing agents in organic solvents could be used. The separation of Cr(III) and Cr(VI) using ion-exchange and/or complex reagents in organic solvent have gained considerable interests among the scientists since the last few decades, e.g., zephyramine [9], bis(2-ethyl hexyl phosphoric acid) in benzene [10], diphenyl carbazide with isoamyl alcohol [11], and 4-methyl-3-pentene-2-one [12]. In 2009, Kalidhasan and Rajesh published the determination of Cr(VI) based on the LLE using tetrabutylammonium iodide (TBAI) as an ion-pair reagent in methyl isobutyl ketone (MIBK) used as the extraction solvent [8]. The ion-pair complex was back-extracted using ascorbic acid to convert Cr(VI) into free Cr(III) before spectrophotometric measurement for quantification purposes. The extraction of Cr(VI) using TBAB as the ion-pair reagent in dichloromethane was performed with 95% recovery [13].

As an emerging country with rapid development in industrialization and urbanization, Vietnam has been facing the risk of serious water pollution, as the heavy metals discharged from industrial activities have identified as a threat to public health and the safety of the ecosystem. Notably, the wastewater from the mechanical, electronic, dyeing, and tanning industries, etc., potentially has high concentrations of heavy metals, e.g., Cr, and in many cases, may exceed the permitted levels. In the present study, we employed the liquid-liquid extraction (LLE) using tetrabutylammonium sulfate (TBAHS) as the ion-pair reagent prepared in the extraction solvent of dichloromethane to separate Cr(VI) from the effluents into the organic phase before measuring the quantity using Flame Atomic Absorption Spectrometry (F-AAS). The preparation of TBAHS in the organic solvent instead of in water aimed to assist the chemical reaction between the analyte and the complexing agent, then to increase the extraction yield for quantification purposes. The parameters related to the LLE namely the concentrations of ion-pair reagent, extraction pH and solvents, reaction duration, numbers of extraction cycles (repeated extraction), and sample preservation as the co-existence of Cr(III), were evaluated to discover the optimized analytical conditions for real wastewater application. Moreover, in this current study, the ion-pair reagent was prepared in the extraction organic solvent instead of in the aqueous phase to increase the extraction efficiency, minimize the interferences of co-existing ions and substances, and improve the recovery of the proposed analytical method for quantification purposes.

Materials and Methods

Chemicals and reagents

All chemicals and reagents, including a stock solution of 1000 mg L^{-1} chromium (III), methyl isobutyl ketone (MIBK), dichloromethane (DCM), and chloroform, were of the analytical grade and purchased from Merck (Germany). A stock solution of 1000 mg L^{-1} chromium (VI) solution was prepared from potassium dichromate (≥ 99.9%, Merck, Germany). Working standard solutions of Cr(VI) were prepared daily by appropriate dilution of the 1000 mg L^{-1} stock solution using deionized water (DIW, Millipore, USA) before each use. Ion-pair reagents of 0.05 mol L^{-1} tetrabutylammonium hydrogensulfate (TBAHS) in extraction solvents namely dichloromethane (DCM), methyl isobutyl ketone (MIBK), and chloroform were prepared by dissolving 7.608 g of TBAHS in 500 mL of each of these solvents to obtain three different solutions used as the extraction solvent. Sulfuric acid of 1.0 mol L^{-1} was prepared by properly diluting the concentrated sulfuric acid in DIW. The Cr(VI) standard solution of 1.0 mg L^{-1} was prepared and used for evaluating the effects of various analytical parameters in the LLE, including types of organic solvents, pH index in the aqueous phase, ion-pair reagent concentrations in the extraction organic solvent, shaking duration per each extraction cycle, and the numbers of extraction cycles (single or repeated extraction). For the assessment of sample preservation at the ambient temperature, primarily due to the effects of Cr(III) co-existence, Cr(III) and Cr(VI) standard solutions were spiked into real wastewater samples to obtain the concentrations of both species at 1.0 mg L^{-1}.

Liquid-liquid extraction

The single factor experiment of the standard solution was used for optimizing the liquid-liquid extraction (LLE). The LLE was set up as follows: 1.00 mL of 10 mg L^{-1} Cr(VI) was added to 40 mL glass vial with a cap. The solution pH was adjusted to different investigated values, namely below 1.0, 1.0, 2.0, and 3.0 using 1.0 mol L^{-1} sulfuric acid and sodium hydroxide solutions. Then, 5.00 mL of TBAHS with various concentrations of 0.02, 0.04, 0.05, and 0.05 mol L^{-1} in the extraction organic solvents was added to the sample liquids to carry out the LLE. Three different organic solvents of methyl isobutyl ketone or MIBK, dichloromethane or DCM, and chloroform were investigated to discover the most suitable extraction solvent. The extraction was carried out by shaking the sample glass vial for a certain duration (3, 5, 10, 15, 20, 25, and 30 minutes). Single, double, and triple extractions were evaluated to find out the number of repeated extractions required for the highest recovery. All the organic phases were collected and transferred to another glass vial before being evaporated to the volume of around 1 mL by gentle heating at 60-70 ºC. Next, approximately 1 mL of concentrated nitric acid was added. The mixture was continued to heat until the volume observed was nearly 0.3-0.5 mL (do not heat to dry). Finally, the residue in the reaction vial was dissolved carefully in DIW and transferred to a 10-mL volumetric flask. The solution was filtered through a 0.45-µm membrane before measurement at 357.9 nm on an atomic absorption spectrometer.

Flame atomic absorption spectrometry for determining Cr(VI)

Cr(VI) determination after LLE was performed on a flame atomic absorption spectrometer (AA-6650 Shimadzu, Japan), equipped with a chromium hollow cathode lamp, an air-acetylene flame atomizer. The wavelength, lamp current, and spectral bandwidth used were 357.9 nm, 10 mA, and 0.5 nm, respectively. The burner height was 12 mm and the gas flow rate were 3.0 L min^{-1}. The background correction using a Deuterium lamp was applied for all measurements. The calibration curve was developed based on the linear relationship between the Cr(VI) standard concentrations (i.e., 0.05, 0.10, 0.20, 0.40, 0.60, 0.90, 1.2, 1.5 and 2.0 mg L^{-1}) prepared in 0.5% (v/v) nitric acid and the respective absorbance. The method limits of detection and quantification (MLD and MLQ) were determined by simultaneously analyzing 11 blank samples using the optimized LLE and F-AAS measurement. The estimated average concentration value ($\bar{x}$) and standard deviation (SD) were calculated to apply in the following relationships [14, 15]: MLD = $\bar{x}$ + 3SD and MLQ = 10/3*MLD. The repeatability and reproducibility were evaluated by calculating %RSD_r and %RSD_R for intra-day (six replicates, n = 6) and inter-day (three separate days). The trueness of the method was evaluated based on the recovery of the spiked samples.

Application of the proposed method to determine Cr(VI) in real effluent samples

A total number of 10 wastewater samples or effluents were randomly collected from several industrial parks around Ho Chi Minh City, based on ISO 5667-3:2003 [16] and ISO 5667-10:2020 [17]. The effluents were collected from the wastewater drain pipes of textile and electronics factories. The samples were contained in acid-washed polyethylene bottles, filtered through a 0.45-µm membrane (GE Whatman Membrane Filters, GF/F), and stored at freezing conditions (−10 ºC) until further analysis. These samples were analyzed by the proposed analytical method using the LLE procedure for the selective determination of Cr(VI). Besides, the Cr(VI) standard solution was spiked to these collected effluents to carry out the recovery test based on the real sample matrices, which aimed to assess the matrix effects on the analytes of interest.

Results and Discussion

Effects of extraction solvents

There are two possible ways for the extraction of Cr(VI from the aqueous phase to the organic phase. A common approach is the formation of an ion-pair complex in the aqueous phase, using an ion-pair reagent in water. The formed complex was extracted using a suitable organic solvent. However, the produced TBA^+–$HCrO_4^-$ ion-pair complex is less polar, and therefore poorly interactive with water. The molecule has a large molecular size, and thus is less stable in water, lowering extraction efficiency. Another approach is to prepare the ion-pair reagent in organic solvents and carry out the LLE between aqueous and organic phases. In the present study, to enhance the extraction efficiency and minimize the interferences of co-existing ions and substances, the later approach was applied, i.e., the TBAHS was prepared in organic solvents, then used for LLE. The formation of an ion-pair complex could happen at the interface between the aqueous and organic phases (mostly in the aqueous phase) due to shaking effects. Such affects allow for the analyte of interest to be transferred into the organic solvent due to the stronger interaction formed by the ion-pair complex with organic solvents [8]. In the present study, three organic solvents were investigated for their potential use as extraction solvents, i.e., MIBK, DCM, and chloroform. The extraction yield (%) of Cr(VI) in the solvents (i.e., performing a single extraction within 10 minutes) is presented in Figure 1.

In descending order, the highest yield was obtained in DCM (97.4%), followed by chloroform (70.9%), and MIBK (26.9%). The differences in extraction yields could be due to the differences in the polarity of these solvents, of which MIBK has a relatively high polarity, and thus was less effective for extraction of Cr(VI). Meanwhile, DCM (polarity index of 3.1) and chloroform (polarity index of 4.1) are less polar than MIBK [18, 19], thus exhibiting higher extraction efficiency. Between DCM and chloroform, the former exhibited a better extraction efficiency, which may be due to the lower polarity and larger size of DCM molecules that allow for more favorable solvation for the ion-pair complex. The ion-pair complex is large in size, held by relatively weak electrostatic forces (Figure 3) but possesses enough stability to be effectively extracted to the organic phase [20]. Due to the large size of the formed complex, the organic solvents with larger molecule sizes may provide favorable conditions for better extraction yields than that of smaller molecule sizes under the same working parameters. Comparing between CCl_4 and $CHCl_3$ as the extraction solvent, CCl_4 with lower polarity was reported to perform higher extraction efficiency [21, 22]. Therefore, in this current study, an ion-pair reagent of TBAHS was prepared in DCM as a lower polar extraction solvent for further experiments and investigations to assure the highest extraction yield.

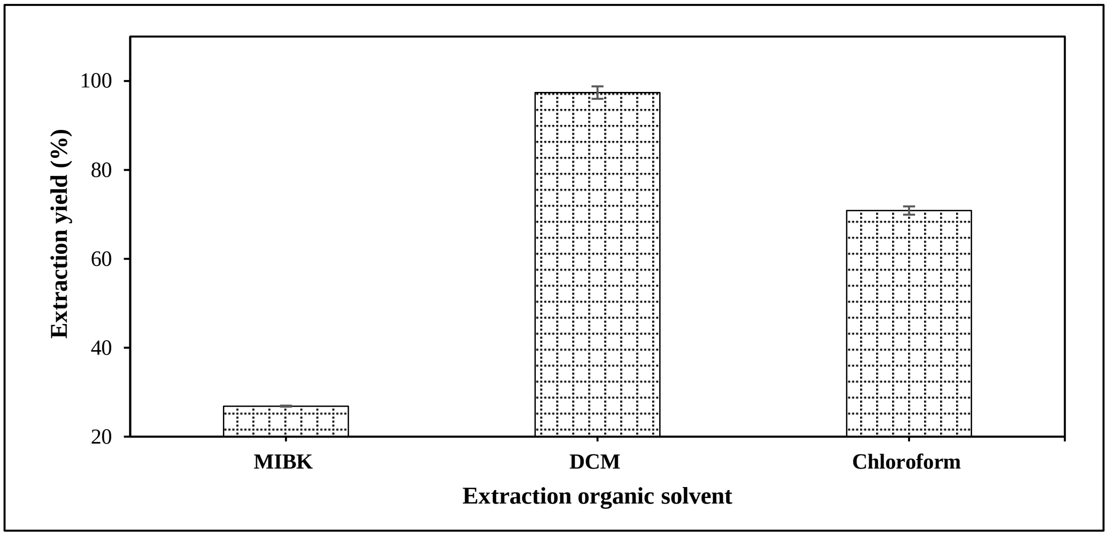


Figure 1. The Cr(VI) extraction efficiency using different extraction organic solvents

Effects of pH index in the aqueous phase

Depending on pH, predominant speciation of chromium could be changed to reach chemical equilibrium, which typically includes the formation of chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$), chromic acid (H_2CrO_4), hydrogen dichromate ($HCr_2O_7^-$), trichromate ($Cr_3O_{10}^{2-}$), and tetrachromate ($Cr_4O_{13}^{2-}$) [23, 24]. For instance, $HcrO_4^-$,

$Cr_2O_7^{2-}$, and H_2CrO_4 dominated the acid medium [25]. The different chromium species in water remarkably influence the extraction efficiency. The effects of pH on the extraction efficiency were investigated in the pH range from under 1.0 to 3.0. The extraction yield at different pH values is presented in Figure 2.

The results showed that the Cr(VI) ion quantitatively formed an ion-pair complex with TABHS at all the investigated pH, resulting in the extraction yields higher than 90%. Extraction yields generally remained unchanged within the ranges of pH tested in this current study (i.e., from less than 1.0 to 3.0). This phenomenon could be attributed to Cr(VI) mostly existing as $HCrO_4^-$ in the medium with a $pH < 4.0$, whereby the association was well-formed due to the big radius of $HCrO_4^-$[26]. The $TBA^+–HCrO_4^-$ ion association was formed in the interaction between the two phases (mostly in the aqueous phase) according to the following schematic representation (Figure 3). Therefore, the favorable pH for complex formation may vary in a relatively wide range, and pH adjustment in the sample preparation was not strictly (from very acidic, pH lower than 1.0, to pH of 3.0) [8, 20]. At $pH > 4$, lower extraction efficiency has been reported in previous publications, e.g., Ouejhani et al. [7], Baig et al. [21], and Kalihasan et al. [20]. The lower extraction yield of Cr(VI) in the alkaline medium could be explained due to the presence of dominant species, the CrO_4^{2-} and its potential hydrolysis [27]. In the present study, we did not investigate the extraction at high alkaline pH. The pH around 1.0 was chosen for further experiments and investigations due to the easy and convenient adjustment.

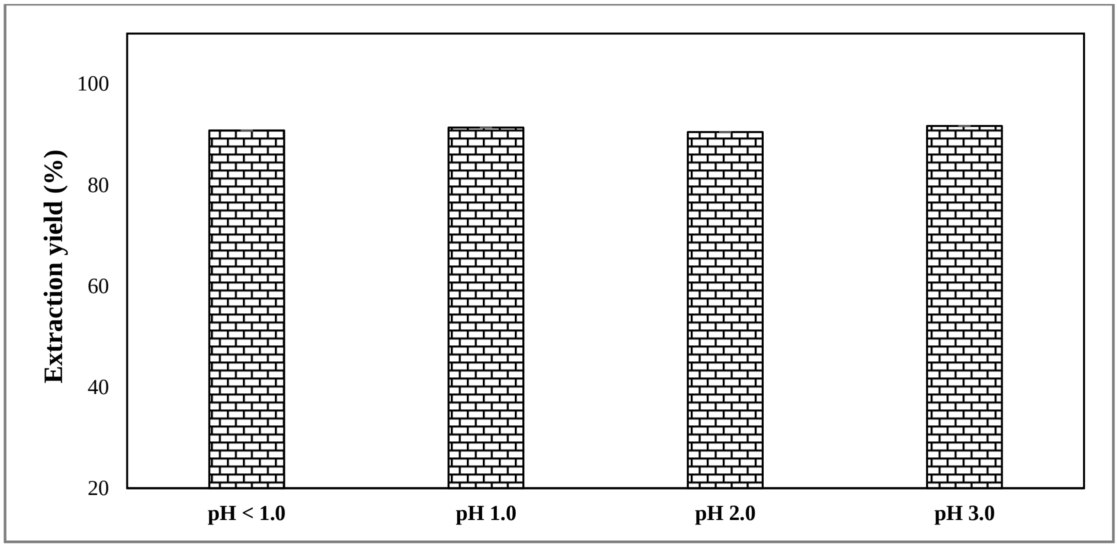


Figure 2. The Cr(VI) extraction efficiency at different pH

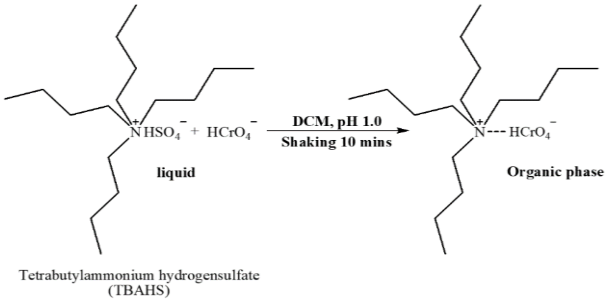


Figure 3. The chemical reaction for the formation of the ion-pair association

Effects of ion-pair reagent-TBAHS concentrations in DCM

As mentioned before, the ion-pair reagent of TBAHS was prepared in DCM to maximize the extraction efficiency [13]. The effects of TBAHS concentrations on the recovery were assessed, and the results are presented in Figure 4. It has been known that the formation of the ion-pair complex happens at the interface between two phases. However, the lower TBAHS concentration in the organic phase could lead to the lower concentrations of TBAHS as the ion-pair reagent at the interface, hence ineffective complexation between TBAHS and Cr(VI). Therefore, higher TBAHS concentrations were required to provide high TBAHS contents for favorable for ion-pair formation. Moreover, as shown in Figure 4, the chemical equilibrium was shifted forward to form the ion-pair complex when the concentrations of reactants (TBAHS) were higher. The increasing recovery as the concentration of TBAHS in DCM was increased was observed as the lowest (67.1%) and highest (103%) recovery was obtained at 0.02 mol L^{-1} and 0.05 mol L^{-1}, respectively. The TBAHS concentration of 0.04 mol L^{-1} resulted in relatively lower recovery (98.5%) and poorer precision (%RSD of 1.2%) than that of 0.05 mol L^{-1} (recovery of 103% and %RSDs of 0.68%). Based on the results, the 0.05 mol L^{-1} TBAHS in DCM was used for further experiments to ensure the most favorable recovery and precision.

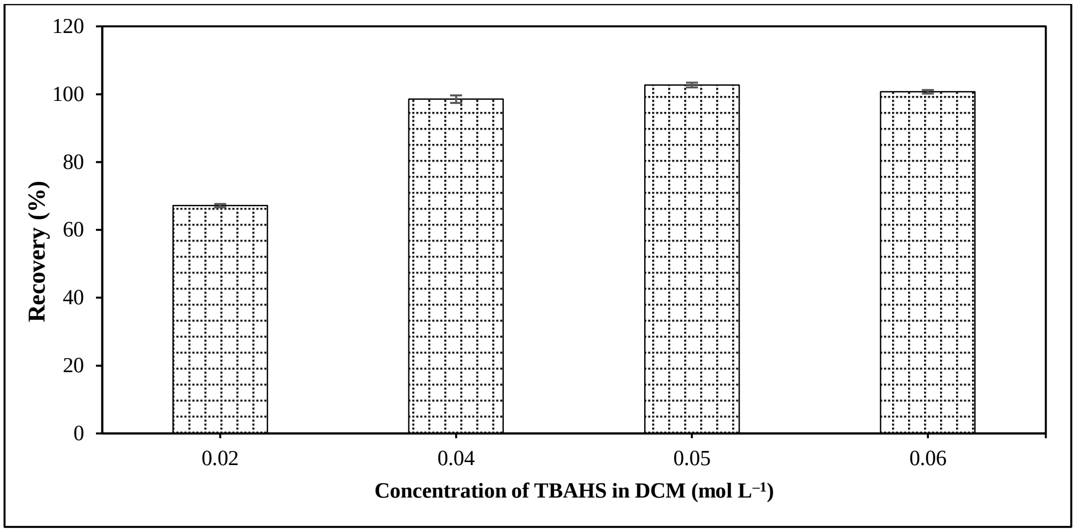


Figure 4. The extraction efficiency of Cr(VI) at different TBAHS concentrations in DCM

Effects of shaking duration and numbers of extraction cycles

During the extraction period, the shaking activity increases the interaction between Cr(VI) in the aqueous phase (wastewater samples) and the ion-pair reagents in the organic phase (DCM) at the interface of the two phases, and thus increases the chances for the formation of the ion-pair complex in the organic phase. The effects of shaking duration on the Cr(VI) recoveries are illustrated in Figure 5, which indicates that the longer shaking duration led to higher recoveries (i.e., 80.4% to 101%). We suggest that it is necessary to apply sufficient shaking for a certain duration to equilibriate the complex formation via a chemical reaction in the complicated wastewater matrices. In the present study, the recoveries mostly remained unchanged in the extraction performed for more than 15 minutes for each extraction cycle. Therefore, 15 minutes was determined as the shaking duration for each cycle of the extraction. In addition, to ensure the quantitative extraction of Cr(VI), the number of extraction cycles (i.e., repeated extraction) was investigated. Double and triple extraction procedures were compared for their respective recoveries. The results showed higher recovery in triple than double extractions (i.e., 89.6% and 104%, respectively), which reflected the high partition coefficient of the complex in the organic phase.

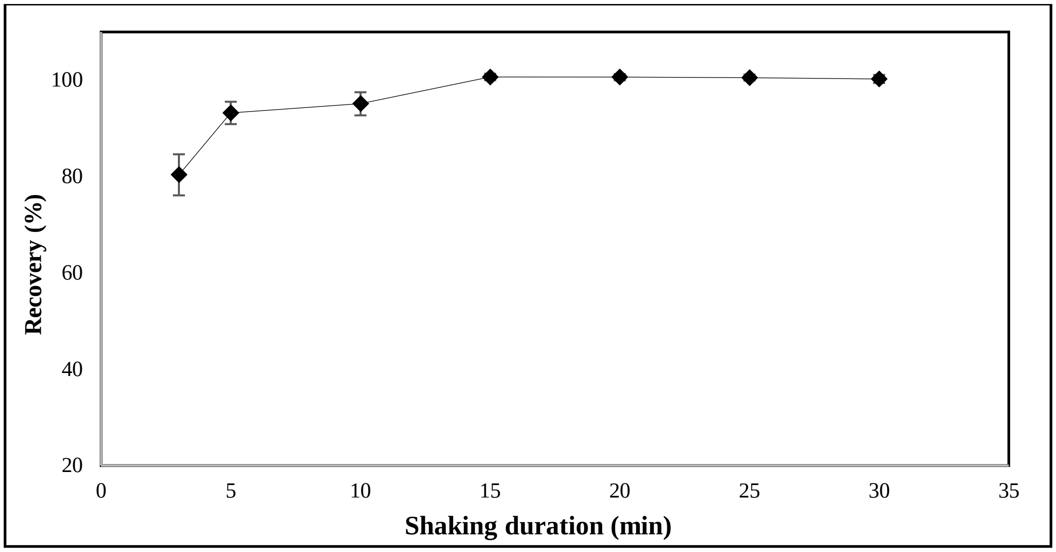
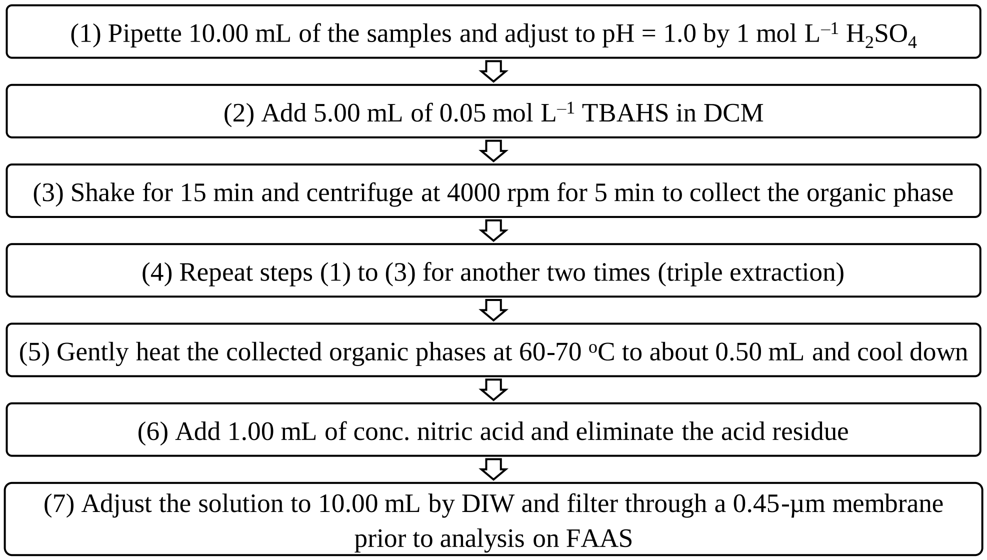


Figure 1. The variability of Cr(VI) recoveries at different shaking duration values (from 3 to 30 minutes), using 5.0 mL of DCM containing 0.05 mol L^{-1} TBAHS for 1.00 mg L^{-1} Cr(VI) standard solution

Effect of sample preservation on Cr(VI) analysis

The effects of sample matrices were investigated to obtain the most favorable sample preservation conditions at the ambient temperature. Cr(III) and Cr(VI) standard solutions were spiked into the real wastewater samples with free chromium to obtain the concentrations of 1.0 mg L^{-1} for both species to calculate the recoveries of Cr(VI) at different preservation duration values at the ambient temperature. The sample preparation for Cr(VI) analysis was carried out based on the optimized conditions, as shown in Figure 6.

The filtered sample solution endured FAAS measurement at 357.9 nm for quantification purposes. The results in Figure 7 showed that the immediate extraction within an hour resulted in no significant changes in the concentration of Cr(VI) as compared to its initial concentration, while the longer preservation duration resulted in lower recoveries (53.0% and 35.3% for 24-and 48-hour preservation, respectively). The result could be due to the presence of organic matters in the wastewater that may reduce Cr(VI) into Cr(III) [28, 29] and/or the presence of other substances that may interfere in the formation of Cr(VI) and the ion-pair reagent complexes. Therefore, to ensure reliable and accurate results, the wastewater samples should be analyzed right after being transported to the laboratory (within around one hour) or preserved at freezing temperature to minimize the conversion of Cr(VI) into Cr(III).



(1) Pipette 10.00 mL of the samples and adjust to pH = 1.0 by 1 mol L^{-1} H_2SO_4

(2) Add 5.00 mL of 0.05 mol L^{-1} TBAHS in DCM

(3) Shake for 15 min and centrifuge at 4000 rpm for 5 min to collect the organic phase

(4) Repeat steps (1) to (3) for another two times (triple extraction)

(5) Gently heat the collected organic phases at 60-70 °C to about 0.50 mL and cool down

(6) Add 1.00 mL of conc. nitric acid and eliminate the acid residue

(7) Adjust the solution to 10.00 mL by DIW and filter through a 0.45-µm membrane prior to analysis on FAAS

Figure 6. Optimized preparation procedure for Cr(VI) analysis

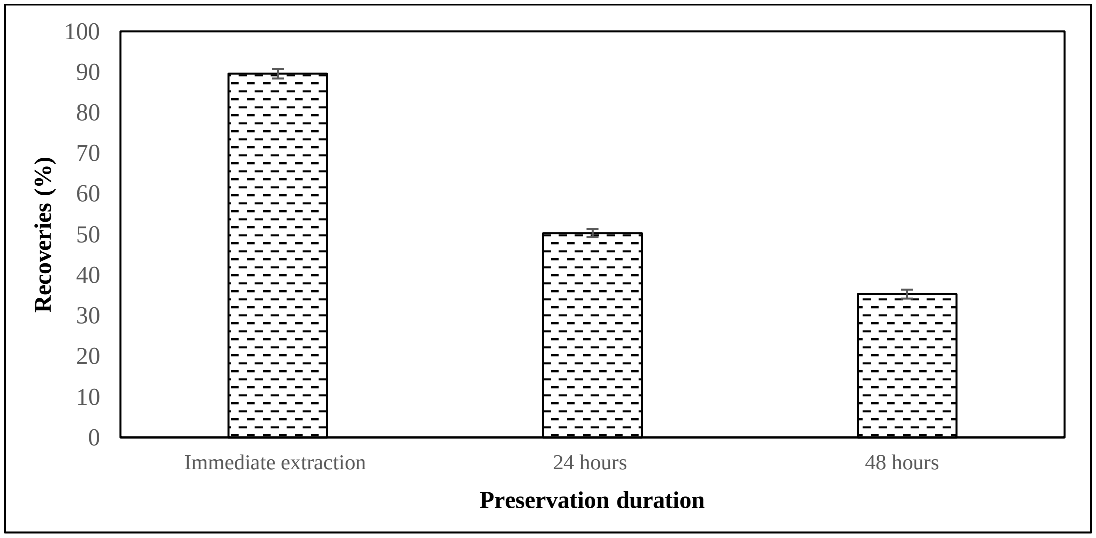


Figure 7. Recoveries of Cr(VI) in spiked samples with the co-existence of Cr(III) at different preservation duration values

Analytical method performance for analyzing Cr(VI)

The selective determination of Cr(VI) in wastewater following LLE with ion-pair reagent using FAAS was evaluated. The results are presented in Table 1. The estimated MDL and MQL were lower than regulated values in QCVN 24: 2009/BTNMT (National Technical Regulation on Industrial Wastewater) for industrial wastewater disposed to domestic and non-domestic water sources (0.05 and 0.1 mg L^{-1}) [30]. Therefore, the analytical method could be applied for industrial wastewater control and management of Cr(VI) content. The calibration curve was established based on the linear relationship between the chromium concentrations and their atomic absorption values, which exhibited goodness of linearity (R^2 = 0.9994). The %RSD_r and %RSD_R were used to evaluate the repeatability (within one day) and reproducibility (for three separate days) of the proposed analytical method, which proved favorable according to the Appendix F of AOAC (2016) [31]. Besides, the recoveries varied from 91.1 to 109%, demonstrating the result accuracy obtained via the proposed method.

Table 1. Parameters for analytical method performance

Regression Equation	**R^2**	**MDL (mg L^{-1})**	**MQL (mg L^{-1})**	**RSD_r (%)**	**RSD_R (%)**	**Recoveries (%)**
$y = 0.1068x + 0.0012$	0.9994	0.012	0.040	0.71	1.1	91.1-109

The variability of Cr(VI) in the effluents

The sample preparation for Cr(VI) analysis in real wastewater samples or effluents was carried out based on the optimized procedure in Figure 6. The results of Cr(VI) analysis in real effluent samples are shown in Table 2. Most of the wastewater samples exhibited remarkably low Cr(VI) (i.e., below MQL values of 0.040 mg L^{-1}). The highest Cr(VI) in wastewater was determined as 0.37 mg L^{-1}. The Cr(VI) standard solution was spiked into all these samples for the recovery test, which demonstrated favorable recovery values (91.1-109%) according to the Appendix F of AOAC (2016) [31]. The recovery test was conducted to examine the matrix effects (mostly from the co-existing ions and organic matters present in wastewater). Therefore, the obtained high recoveries obtained in the test demonstrated the effectiveness of the LLE using the ion-pair reagent (TBAHS) for selective determination of Cr(VI) in complicated sample matrices.

Table 2. Analytical results of Cr(VI) in wastewater samples and recovery tests

Sample code	**Cr(VI) (mg L^{-1})**	**Spiked Cr(VI) (mg L^{-1})**	**Recoveries (%)**	**RSD for Recoveries (%)**
S1	n.d	1.00	96.8	1.6
S2	n.d	1.00	91.1	2.1
S3	0.37	1.00	109	1.1
S4	n.d	1.00	102	1.8
S5	0.22	1.00	94.3	1.8
S6	n.d	1.00	95.3	1.8
S7	n.d	1.00	99.7	1.7
S8	n.d	1.00	96.8	1.1
S9	0.18	1.00	96.2	1.1
S10	n.d	1.00	96.8	1.4

n.d: not detected

Conclusion

The proposed analytical method for determining Cr(VI) in wastewater or effluents demonstrated its good sensitivity and selectivity. The measurement was performed on an inexpensive and common technique of FAAS following the liquid-liquid extraction with

TBAHS as the ion-pair reagent. The TBAHS was prepared in the organic solvent to improve the extraction efficiency due to the low potential of interferences. Dichloromethane (DCM) was found to be the most favorable organic solvent for the extraction process. Various analytical parameters related to the extraction procedure were investigated to discover the optimized working parameters, including 0.05 mol L^{-1} TBAHS as the ion-pair reagent in DCM, aqueous sample with pH index in the range of around 1.0 to 3.0 (i.e., before the extraction), triple extraction cycle or triple extraction, and 15 minutes of shaking duration for each cycle. The calibration curve was established using a standard solution with a concentration ranging from 0.05 to 2.0 mg L^{-1} based on the linear relationship between Cr concentrations and the respective atomic absorption values at the wavelength of 357.9 nm. The method limit of detection and quantification values were estimated as 0.012 mg L^{-1} and 0.040 mg L^{-1}, respectively. This proposed analytical method could serve as a simple and low-cost procedure to determine the severely low concentrations of Cr(VI) in wastewater samples or effluents, which indicated proper recoveries (91.1-109%) for spiked samples based on the Appendix F of AOAC (2016). Moreover, the LLE approaches coupled with the addition of ion-pair reagents may be applied for quantitative and qualitative analysis of other ion metals for trace analysis purposes.

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