Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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GJSFR-B Classification : FOR Code: 030599

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Abstract- A new trend in extraction and preconcentration of chromium (VI) using laboratory-made azo dye reagent 2-[benzenethiazolylazo]-4-benzenenaphthol (BTABN) after cloud-point extraction (CPE) and its determination by spectrophotometrically. The method involved the reaction of $Cr_2O_7^{2-}$ with BTABN in acidic medium forming a hydrophobic ion-association complex $[HBTABN][HCr_2O_7]$ which is entrapped into micelle-mediating solvent (Triton X-100) and the Cr(VI) detected spectrophotometrically at λ_{max} of 475 nm. The effect of the several factors on the CPE efficiency is optimized by one-factor-at-a-time (OFAT). Extensive thermodynamic study has been presented to understand the mechanism of extraction and solubilisation of ion-association complex in micelles. The interferences effect of divers ions is also considered. Under the optimized conditions, enrichment factor of 270 is achieved leading to limit of detection and limit of quantitation of 0.017 and 0.0568 $\mu g\ mL^{-1}$ respectively. The linearity of 0.1-2.0 $\mu g\ mL^{-1}$ and sensitivity in term of molar absorptivity is $4.47 \times 10^4\ L.mol^{-1}.cm^{-1}$ are obtained .The precision (RSD%; n=7) of the proposed method is of 0.31% % at 2.0 μg Cr (VI) mL^{-1}. This method is applied in the determination of Cr (VI) in various environmental and botanical samples.

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I. INTRODUCTION

Chromium (VI) is known to be a highly toxic metal and one of sources that drives to many cancer diseases namely, cancer of lung, oesophagus, and liver (1). Due to sever toxicity of Cr (VI), WHO and USEPA have set the guideline for drinking water with upper limit of 50 $\mu g\ L^{-1}$(2-4), whereas the Agency for Toxic Substances and Diseases Registry (ATSDR) classifies Cr (VI) as the top eighteenth hazardous substance and the Minimal National Standards (MINAS) upper limit of Chromium in industrial wastewater is of 100 $\mu g\ L^{-1}$(5). Consequently, the determination of Cr (VI) in an industrial effluent is necessary to control the level of Cr species in waste water, natural water, and drinking water. The determination of Cr (VI) in other environmental samples such as soils, plants and vegetables is also of prime importance to realize its concentration levels and extent of its impact on human health.

Trace amount of chromium determination in such complex matrices is a challenge and difficult analytical task, mostly due to the low concentration of metal in the samples, the existence of Cr (VI) as $Cr_2O_7^{2-}$ and CrO_4^{2-} species in most environmental matrices beside the matrix interferences, which should be required sensitive instrumental techniques and often a pre-concentration step.

Since its inception in 1985, cloud-point extraction (CPE) methodology has constituted an important theme in the analytical chemistry as promising procedure for the separation and preconcentration for the metal ions and organic compounds from the complex matrices samples. Nowadays, it has begun to take a large noteworthy position among the other modern separation methods in scientific research and applications fields on a high level due to its simplicity, rapidity, more precise and cheapness beside environmentally-friendly method. However, most applications of CPE dealt with extraction of metal ions after complexing with chelating agent forming chelate at a certain pH as a hydrophobic molecule which is easily extracted by nonionic surfactant. But, to the best of our knowledge, the separation and pre-concentration of inorganic anions such as metal halo anions (MX_4^-) metal oxyanions (MO_4^-) and metal cyanoanions $[M(CN)_6]^{3-}$, $[M(CN)_4]^{2-}$, $[M(CN)_2]^-$ or metal thiocynoanion $[M(SCN)_4]^{2-}$ into surfactant by CPE in a single-step extraction compared to the most common metal chelate extraction is so scanty and scarcely nonexistence so far since the commencement of CPE. Nevertheless, there were only two attemptts based on the above conception for the determination of Cd (II) as CdI_4^{2-} by CPE with flame atomic absorption spectrometry (6) and the reaction of CTAB with the heteropoly acid formed between MoO_4^{2-} and *o*-$PO_4^{2-}$to give a high molecular weight complex, which was quantitatively extracted in a non-ionic

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surfactant for the preconcentration and determination of orthophosphates (7) beside our two papers recently published elsewhere (8-9) for the determination of Cd(II) and Mn(VI) as inorganic anions by CPE-Spectrophotometry.

In the present study, an attempt has been performed to establish a new procedure for the separation and extraction of Cr (VI) by CPE methodology and its detection spectrophotometrically for the first time. The method is based on the formation of ion-association hydrophobic complex between $Cr_2O_7^{2-}$ and BTABN as a new synthesized reagent in acidic medium and subsequently extracted into the surfactant Triton X-100 at optimum conditions. The separated surfactant-rich phase is diluted with minimum amount of ethanol and Cr (VI) determined by UV-Vis spectromphotometry at λ_{max} of 475 nm. The proposed method was applied for the determination of Cr (VI) in different environmental matrices.

II. Materials and Methods

a) Apparatus

A Shimadzu double beam UV-Vis Spectrophotometer model UV-1700 (Japan) working at wavelength of 190-1100 nm (±0.3nm accuracy at D_2 peak 656.1 nm, 486.0 nm and ± 0.1 repeatability), spectral bandwidth of 1.0 nm (190 to 900 nm) equipped with 10-mm optical path cell was used for the scanning of absorption spectra of all reagents and complex throughout this study. While absorbance measurements in the optimization study and detection of metal was done with Single beam (UV-Vis) Spectrophotometer, TRIUP International Corp- TRUV. 74, S (Italy).

b) Reagent and materials

All analytical grade reagents were used without further purification as received from different company. Doubly distilled water was used for diluting the standard, reagents and samples. The nonionic surfactant (Triton X-100) whose chemical structure is $C_8H_{17}C_6H_4(OC_2H_4)n$ with *n* equal to 9-10 and an average molecular weight of 625 g/mol, was purchased from Sigma (Sigma Ultra , >99.6%). (UK) and. Potassium dichromate (98.0%) 2-aminobenozthiazol (99%), NaOH (99%) , HCl (37%), $NaNO_2$;(99%) were purchased from BDH(UK), p-benzenenaphthol(98%) from Fluka (Germany) and diphenylcarbazide(>98%) from Chem. Supply Pty limited(Australia). The stock solution of Cr (VI) at 1000 $\mu g\ mL^{-1}$ was prepared by dissolving of 0.2829 ±0.0010 g of $K_2Cr_2O_7$ in a minimum amount of water in 100 mL volumetric flask and completed to mark with water and mixed thoroughly. A stock solution of 2- [benzene thiazolylazo]- 4- benzenenaphthol (BTABN) reagent solution at concentration of $1x10^{-2}$ M was prepared by dissolving 0.3810 g in 0.5 mL of 1% Triton X-100 and minimum amount of water in 100 mL volumetric flask and diluted to mark with water. A 0.25% of Diphenylcarbazide solution was prepared by dissolving 0.25 g of 1, 5-diphenylcarbazide ($C_{13}H_{14}N_4O$) in 50 ml of acetone and quantitatively transferred to a 100 ml volumetric flask, diluted to the mark with water and mixed thoroughly. The solution was transferred to a brown bottle, cap tightly and keep in the refrigerator. The solution is stable for at least one month.

c) Synthesis and Characterization of Reagents

A 2- [benzene thiazolylazo] - 4-benzenenaphthol reagent was prepared according to the procedure published elsewhere (10) by dissolving (1.5 g 0.01 mole) of 2-aminobenzthiazol in a mixture containing 4 mL of concentrated HCl and 25 mL distilled water. After cooling this solution to 0 °C, 1.4 g of sodium nitrite dissolved in 10 mL distilled water was added with maintaining the temperature at 0 °C. The mixture was set aside for 15 min for complete diazotization process. Thereafter, the diazonium solution was poured drop by drop into beaker containing (2.2 g , 0.01 mole) of p- benzenenaphthol and 1.2 g sodium hydroxide dissolved in 150 mL ethyl alcohol with keeping temperature at 0 °C. After complete addition , the contents was left for two hours , then 150 mL of cooled distilled water was added and the pH of the solution maintained at 6, a brown powder were precipitated and left for 24 h. The solid product was filtered off, washed with cold water, crystallized twice from hot absolute ethanol and dried over $CaCl_2$ .Yield 77% ; mp 127-128°C ; anal calcd for $C_{23}H_{15}N_3OS$(382.48 g mol^{-1}); C ,72.23; H,4.22; N,10.98; S, 8.38; O,4.18; found C,72.65; H, 3.99; N,11.50; S,8.56;O,5.32; IR(KBr) ν_{max}/cm^{-1}, 3194.23(m, Ar-OH),3063.06 C-H aromatic, 2920(w,C-H aliphatic),1643(s,C=N) ,1514.17(m,N=N), 1367.58(m, C=C),1303.92(m, C-O),1249.91(m, C-N), 1180.47(m,C-S) 949.01 (s, δ, bend aromatic,C-H); ^{1}HNMR(DMSO-*d*6, 298 K,) d/ppm) 5.295 (m,1H, OH), 8. 515-8.492 (s,2 H, benzthiazole phenyl),7.575-7.559 (s, 2 H, benzthiazole phenyl),7.495, 7.524,7. 865, 7.891 and 7.931 (s,5H, p-phenoyl), 7.916 (s, H, phenol), 8.057, 8.485, 7.982, 7.931(s,4H, naphthol, phenyl). The chemical structure of 2- [benzene thiazolylazo]- 4-benzenenaphthol abbreviated as BTABN is shown in Figure 1.This reagent does not dissolved in water , but it dissolve in the organic solvents such ethanol, ethanol, chloroform, Acetone , DMF etc. However, to avoid for dissolving this reagent in organic solvents, it was prepared in 0.5% Triton X-100 before use.

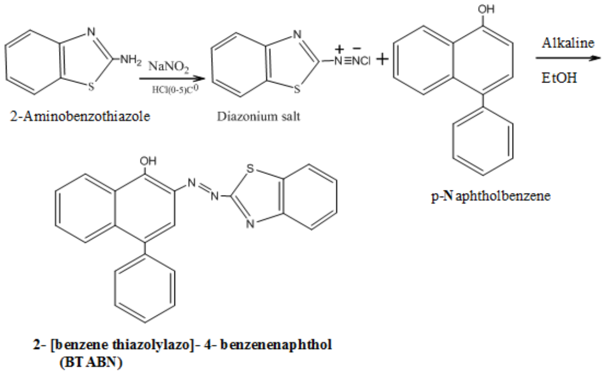

Figure 1 : Synthetic path of BTABN reagent

d) *General Procedure for CPE*

To an aliquot of 10 mL of a solution containing known amount of Cr (VI) as $Cr_2O_7^{2-}$ standard or sample solution in 0.1M HCl, $5x10^{-4}$ M of BTABN reagent solution, 0.4 mL of 1% Triton X-100 were mixed and allowed to stand for stand for 25 min in a thermostated bath at 80 °C to form cloud solution. Separation of the two phases were occurred immediately where the surfactant-rich phase became a highly viscous (without need of centrifugation and cooling) and settled down at the bottom of the tube making the aqueous phase easily discarded by simply inverting the tube. Later, the surfactant-rich phase in the tube was dissolved in minimum amount of ethanol and the absorbance of the resulting solution was measured at λ_{max} of 475 nm in a 1-cm cell against a reagent blank prepared in similar manner without analyte. The remaining quantity of Cr (VI) as $Cr_2O_7^{2-}$ in surfactant-poor phase (i.e. aqueous phase) was determined spectrophotometrically at λ_{max} of 540 nm by using the diphenylcarbazide method(11) for the purpose of determining the distribution ratio (D) and extraction efficiency (%E).

e) *Preparation of Samples*

A duplicate sample (soils, plants and vegetables) solution was prepared by transferring approximately 5 g of dried sample into a 250 mL conical flask and adding 10 mL of HNO_3. The contents of the flask were heated on an electric hotplate until the volume was reduced to 2-3 mL. After cooling,a further of 10 mL of concentrated HNO_3, 5 mL of concentration $H_2SO_4$and 4mL H_2O_2 were added and the content reheated to boiling until the volume became 2-3 mL , then 10 mL of water were added until colorless solution was obtained indicating of the oxidation of organic matter. The content was cooled and transferred into 100 mL volumetric flask and diluted to the mark with distilled water. An aliquot of 5 mL of sample solution was diluted into 25 mL conical flask and treated with 1 mL of 20% potassium sodium tartarate solution with continuous shaking and then filtered. The filtrated was transferred into 10 mL volumetric flask and diluted to the mark with water. The metal ions content was determined according to the recommended CPE procedure. The blank solution was prepared in the similar manner without analyte.

f) *Statistical analysis*

All mathematical and statistical computations were made using Excel 2007 (Microsoft Office) and Minitab version 14 (Minitab Inc., State College, PA, USA).

III. RESULTS AND DISCUSSION

a) *Absorption Spectra*

The absorption spectra of chromium as $Cr_2O_7^{2-}$ oxyanions with organic reagent of 2-[benzene thiazolylazo]-4- benzenenaphthol (BTABN) in acidic medium was recorded in the presence of surfactant against a reagent blank prepared under the identical conditions according to general CPE procedure. Figure 3 shows the overlaid spectra of (a) BTABN reagent and (b) its complex with $Cr_2O_7^{2-}$ oxyanion after CPE procedure. It has been evident that the oxyanion $Cr_2O_7^{2-}$ can form an ion-association complex with BTABN reagent in acidic medium as $[HBTABN]^+[HCr_2O_7]^-$ due to the appearance of another distinct absorption maximum at λ_{max} of 475 nm with molar absorptivity (ε) of $5.5x10^4$ L mol^{-1} cm^{-1} while the BTABN reagent alone gave the absorption maxima at λ_{max} of 452 nm as depicted in the spectra (a) and (b) of Figure 2

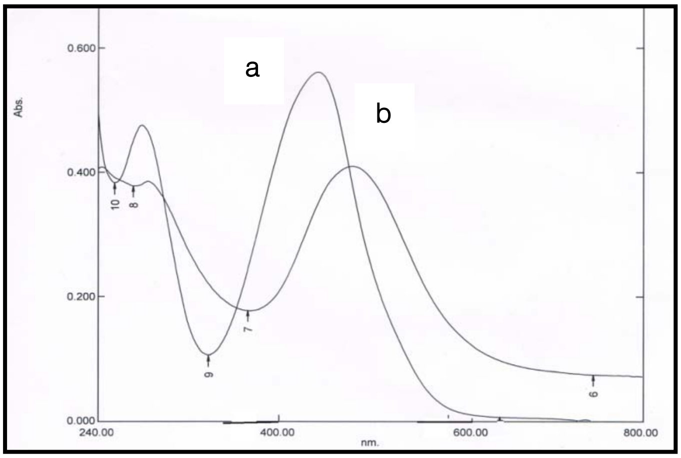

Figure 2 : Absorption spectra of (a) $5x10^{-4}$ M of (BTABN) 10 mL of 20 µg $Cr_2O_7^{2-}$, 0.1 M HCl, ($5x10^{-4}$ M) (BTABN) reagent and 0.5mL (1 % Triton X-100)].

b) *Optimization of CPE procedure*

Several factors affect the CPE procedure for Cr (VI) extraction such as, HCl concentration, Triton X-100 amount, BTABN concentration, heating time and equilibrium temperature by using classical optimization was investigated.

c) *Effect of HCl*

The separation of oxyanions such as $Cr_2O_7^{2-}$ by CPE method involves the formation of ion-association complexes between $Cr_2O_7^{2-}$ oxyanion and the protonated BTABN reagent in the presence of HCl, to get sufficient hydrophobicity that can be extracted into micelle medium thus obtaining desired enrichment. It is known that the HCl in aqueous medium will contribute most probably in converting $Cr_2O_7^{2-}$ ions into $HCr_2O_7^-$ species and the reagent BTABN into ion pair complex $(H\text{-}BTABN)^+$; Cl^-. Consequently, the effect of HCl concentration was studied by measuring the absorbance of 10 mL solution containing 20 μg $Cr_2O_7^{2-}$, $1x10^{-4}$ MBTABN and 0.5 mL of 1 % Triton X-100 and subjected to general CPE procedure. The results are depicted in the Figures 3. The results revealed that 0.1M of HCl was the optimum concentration giving highest percent extraction, indicating better thermodynamic equilbria can be reached and more stable ion pair complex extracted in micelles. Thus, the major effect of HCl was the formation of ion pair complexes as shown inthe following equations below;

$$\text{BTABN} + \text{HCl} \rightleftharpoons [\text{H-BTABN}]^+; \text{Cl}^- \quad \text{or}$$

$$\text{BTABN} + 2\text{HCl} \rightleftharpoons [2\text{H-BTABN}]^{2+}; 2\text{Cl}^-$$

Thereafter, an exchange of small anions Cl^- with large anions of $Cr_2O_7^{2-}$ may occur in micelles as the following;

$$\underset{\text{solution}}{[\text{H- BTABN}]^+; \text{Cl}^-} + \underset{\text{solution}}{\text{HCr}_2\text{O}_7} \rightleftharpoons \underset{\text{micelle}}{[\text{H–BTABN}]^+; \text{HCr}_2\text{O}_7^-} + \underset{\text{solution}}{\text{Cl}^-}$$

or

$$[2\text{H-BTABN}]^+;2\text{Cl}^- + \text{Cr}_2\text{O}_7^{2-} \rightleftharpoons [2\text{H-BTABN}]^+;\text{Cr}_2\text{O}_7^{2-} + 2\text{Cl}^-$$

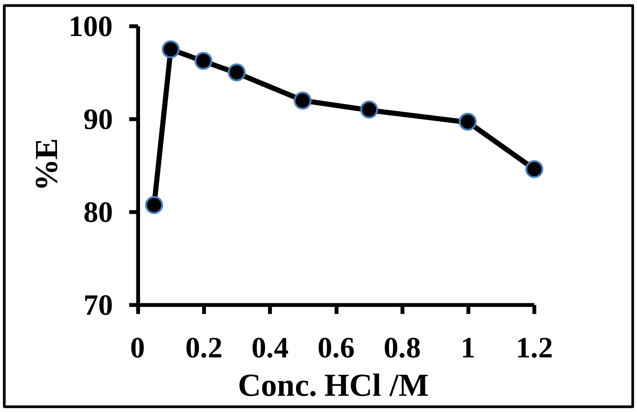

Figure 3 : Effect of HCl on extractability of Cr(VI)

Below 0.1M of HCl, it appeared that no favourable thermodynamic equilibria were reached leading to low extraction efficiency of complex. While at higher than 0.1M of HCl, there is a difficulty of exchange of $Cr_2O_7^{2-}$ as well as the smaller anion Cl^- to large cation $[H\text{-}BTABN]^+$ thereby led to increase their dissociation equilibrium. This behaviour led to decrease ion pair complex formation with $Cr_2O_7^{2-}$ and obvious depress the extraction efficiency (%E) as shown in Figure 3.

d) Effect of BTABN concentration

The extraction according to CPE methodology depends on the major step of complexation between organic reagent and Cr (VI) as $Cr_2O_7^{2-}$ which can be transferred to surfactant after formation cloud point phase. Therefore, the effect of BTABN concentration was carried out by taking 10 mL solution containing 20 μg Cr (VI) as $Cr_2O_7^{-2}$ or 0.1 M HCl, 0.5 mL of 0.1% Triton X100 plus various concentrations ($1x10^{-6}$-$1x10^{-3}$ M) of BTABN and subjected to the general CPE procedure. The results are shown in Figures 4.

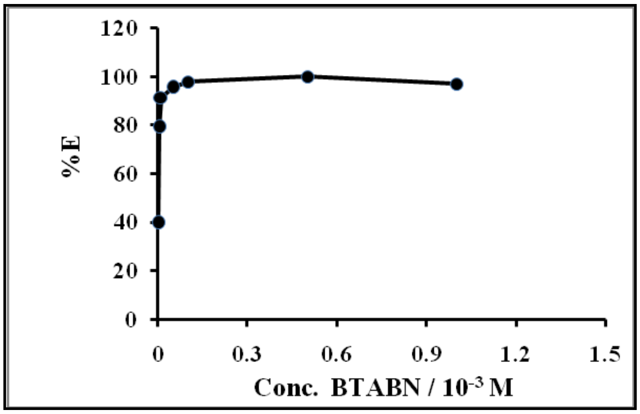

Figure 4 : Effect of BTABN concentration

It was appeared that the magnitude of the extraction efficiency increased sharply by increasing BTABN concentration and reached a plateau up to $1x10^{-4}$M. Therefore, a concentration of $5x10^{-4}$M was chosen as optimal. This may be gave thermodynamic equilibria favourable for the complexation because the rate of formation of ion pair complex for the extracted element Cr(VI) is probably much faster than back forward reaction at optimum concentration thereby a high extraction efficiency obtained. But at concentration of less than $1x10^{-4}$M., the rate of back reaction was predominated leading to the dissociation of ion pair complex and decreased in extraction efficiency.

e) Effect of TX-100 Amount

It is known that the amount of surfactant used in CPE process for the separation for any analyte is a critical factor and its success depends on obtaining a maximum extraction efficiency and minimum phase volume ratio so that to increase the preconcentation factor (12). The effect of Triton X-100 amount was conducted by taking 10 mL solution containing 20 μg $Cr_2O_7^{2-}$, $5x10^{-4}$ M (BTABN), 0.1 M HCl varying volumes of 0.1-2.5 mL of 1% Triton X-100 and the solutions subjected to general CPE procedure The results are seen in Figure 5.It was shown that the maximal extraction efficiency was achieved for ion-association complex extracted when the volume of 1% (w/v) Triton X-100 was of 0.4 mL. Thereafter the %E was decreased because of the increment in the overall analyte volumes and viscosity of surfactant-rich phase, or most probably due to incomplete dehydration of cloud point layer may be occur thereby the two phases cannot be formed leading to poor sensitivity and subsequently decreased in extraction efficiency. At volume less than 0.4 mL of 1% Triton X-100, on the other hand, a decrease in extraction efficiency of Cr (VI) has taken place due to insufficient extraction of ion pair complex formed. Accordingly, Triton X-100 concentration of 0.04% (i.e. 0.4 mL of 1% TX-100) was employed for the rest of this work.

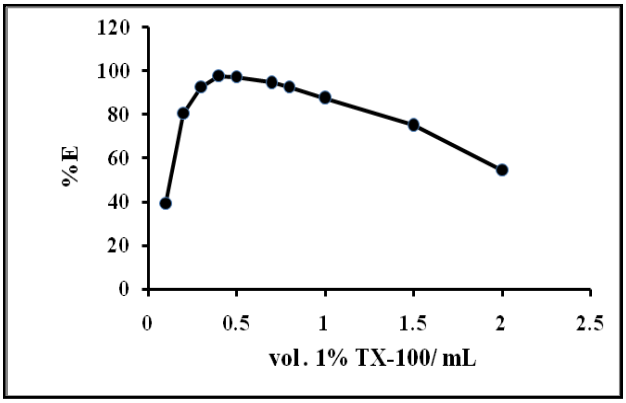

Figure 5 : Effect of Triton X-100 amount

f) Effect of Equilibrium Temperature and Incubation Time

The equilibration temperature and incubation (heating) time are very crucial and important parameters in CPE process for complete reaction to achieve easy phase separation and the preconcentration as efficient as possible. Therefore, the effect of temperature and time on the extraction of Cr (VI) was performed individually for solution containing 10 mL of 20 µg of $Cr_2O_7^{2-}$ by varying the temperature between 70-80 °C at 25 min and time between 5 and 40 min at 80 °C ,keeping other variables at optimal. A preliminary experiment has indicated that at temperature below 70 ^{0}C, no concrete phase separation (i.e. two phases cannot be formed) was observed due to very low number of micelles leading to difficulty in distinguishing the two phases thereby the ion-pair association complexe cannot be well separated. However, the results have shown that at temperature of 80 °C and time of 25 min gave a maximum extraction efficiency of 98.56% .But, at higher temperatures than 80 °C such problem has caused the instability of complex due to thermal decomposition of ion-association complex and as well as increase diffusion of micelles in aqueous solution which lead to increase in surfactant-rich phase volume resulting in decreasing the extraction efficiency.

g) Thermodynamic Study

It is useful to study the mechanism of phase separation by CPE which is still ambiguous and not yet intensively investigated. Therefore , in this study we were determined some thermodynamic data for [H–BTABN]$^+$;HCr$_2$O$_7^-$ system using Triton X-100 as a mediated extracting agent in order to understand a probable mechanism above the cloud point temperature (CPT). Depending on different operation temperatures and the distribution of target species between two phases via calculating the distribution ratios (D), the equilibrium extraction constants (K_{ex}) can be calculated. Table 1 summarize the variation of equilibrium extraction constants with temperature during CPE of the above ion-association complex system.

Table 1 : Variation of equilibrium constant with temperature during CPE for the extraction Cr (VI) as $Cr_2O_7^{2-}$ with (BTABN).

T °C	70	75	78	80
T °K	343	348	351	353
1/T	2.915	2.8735	2.849	2.8329
$K_{ex}x10^9$	1.9263	2.200	2.858	3.606

These thermodynamic equilibrium constants (K_{ex}) is actually represents all equilibrium constants that affect the separation process such as aggregation micelles constant with increasing temperature, complex transference constant from aqueous phase to surfactant phase , association constant of the complex and distribution constant of the surface between aqueous phase and surfactant (micelles) phase. From the results in Table 1, a plot of logarithm values of K_{ex} versus inverse temperature in Kelvin gave a straight line and from its slope, the enthalpy of extraction (ΔH_{ex}) can be calculated for CPE method as shown in Figure 6. While the values of entropy (ΔS_{ex}) and Gibb free energy (ΔG_{ex}) of this extraction process are determined from following thermodynamic relationships [$\Delta Gex=- RT \ln K_{ex}$] and [$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$] respectively. Once ($\Delta H_{ex}$) and ($\Delta G_{ex}$) are obtained, the$\Delta S_{ex}$ is calculated from second relationship and the results are summarized in Table 2.

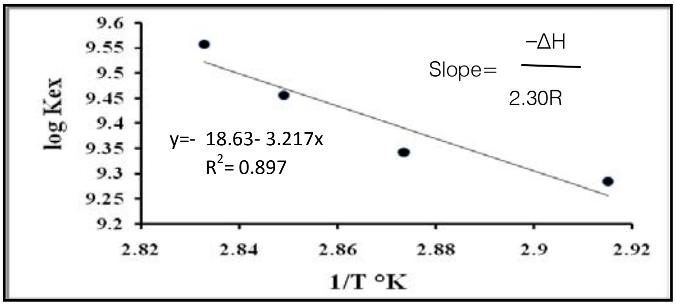

Figure 6 : Extraction constant K_{ex} as a function of equilibrium temperature for ion pair complex of $Cr_2O_7^{2-}$ with (BTABN)

Table 2 : Thermodynamic parameters for the extraction of $Cr_2O_7^{2-}$ ion-pair complex by CPE

T° (°K)	ΔH_{ex} (KJ mol^{-1})	$-\Delta G_{ex}$ (KJ mol^{-1})	ΔS_{ex} (J mol^{-1})
343	0.0544	60.9662	177.8151
348		62.2393	178.9186
351		63.5393	181.0932
353		64.5831	183.0192

It can be seen from Table 2, the enthalpy change (ΔH_{ex}) is quite low and equal to 0.0544 KJ mol^{-1}, indicating that the endothermic reaction for the solubilisation process of ion pair (H–$BTABN^+$; $HCr_2O_7^-$) complex is controlled by positive value of ΔH_{ex} which reflects a high efficiency of the extraction process of the complex that achieved thermodynamically into the surfactant-rich phase. This is explicates that a strong electrostatic association exists between Cr (VI) anion with cationic reagent beside the contribution of the complex itself in driving water molecules out of surfactant phase in which more of micelles are aggregated enabling the precise extraction of complex especially in extracting of trace amounts. Accordingly, the extraction of ion-pair complex is easy and thermodynamically favourable and due to the positive value of ΔH_{ex}, the dehydration of micelles (i.e. decrease the value of ΔH_{solv} and increase ΔH_{hyd}) is achieved resulting in increasing the phase-volume ratio thus extraction efficiency enhancement (13).

$$\Delta H_{ex.} = \Delta H_{solv.} - \Delta H_{hyd.}$$

The variation of ΔG_{ex} with temperature at optimum conditions of the extraction system (Table 2) was revealed that ΔG_{ex} increase with temperature and found to be negative, showing the extraction process is a spontaneous phenomenon because the complex transference and surfactant phase formation are synchronized processes occurs at the same time. Thus the more negative value of ΔG_{ex}, the large spontaneous process is. Accordingly, the spontaneity of ion pair complex extraction is governed by the negative value of ΔG_{ex} (14). The entropy (ΔS_{ex}) , on the other hand, was increased with increasing temperature and be positive values which shows a good affinity of ion-pair complex towards surfactant micelles and proves that the solubilisation of ion-association complex molecules are organized in more random fashion during extraction process (i.e. entropic in region).

h) Selection of Diluents

Since the surfactant-rich phase obtained after the cloud point preconcentration is a highly viscous layer containing analyte to be determined, it generally needs a little amount of solvent for transferring the solution into detection system. The effect of various organic solvents such as amyl alcohol, methanol, chloroform, acetone and ethanol, on the absorption behaviour of complex in the presence of surfactant was investigated. The results are summarized in Table 3.

Table 3 : Effect of organic solvent on absorbance

solvent	λ_{max}	Absorbance	Molar absorptivity (L mol^{-1} cm^{-1})
Amyl alcohol	443	1.037	$2.69\text{x}10^4$
Methanol	433	1.002	$2.60\text{x}10^4$
Chloroform	colloid	-	-
Acetone	445	0.140	$3.636\text{x}10^3$
Ethanol	475	0.855	$2.221\text{x}10^4$

It can been seen that all solvents gave a good solubility of complex in micelles phase, except chloroform which form a colloidal solution that is inconvenient for measuring the solution in the detection system used thus it can be ruled out, while the acetone gave poor sensitivity. Therefore, we chose ethanol as a diluent for many reasons because (1) it gave adequate sensitivity (i.e. good molar absorbitivity), (2) non toxic and (3) better for reducing the viscosity and facilitating the sample transference into a quartz cell.

i) Selection of surfactant type

In CPE, the type of surfactant plays a significant role in the separation and extraction process. Therefore, the experiments were conducted according to general CPE procedure via using different non-ionic surfactants such as, Tween-80 and Tween-20, Triton x-114 and one anionic surfactant like sodium dodecyl sulphate (SDS). Table 4 shows the behaviour of each surfactant on the extractability of (H–$BTABN^+$; $HCr_2O_7^-$) ion-pair complex. The results have been revealed that both Triton X-100 and Triton X-114 gave much better extraction efficiency than the rest surfactants. While the surfactants such as, Tween-20 , Tween-80 have shown that the formation of the separated surfactant-rich phase needs very high cloud point temperature which might be led to dissociation of ion pair complex and hence a poor extraction efficiency obtained as shown in Table 4. SDS, on the other hand, as anionic surfactant which contain sulphate ion in its structure seems indeed incompatible for solubilisation of hydrophobic ion-pair complex under study. Accordingly, Triton X-100 was chosen throughout this study despite Triton X-114 has too lower cloud temperature and gave easy phase separation than Triton X-100, but relatively less extraction efficiency obtained because of low solubility of Triton X114 in aqueous phase (15) .

Table 4 : Effect of surfactant type on CPE for the extraction $Cr_2O_7^{2-}$ with BTABN.

Surfactant	Tw-20	Tw-80	SDS	TX-114	TX-100
λ_{max}	473	475	472	472	475
Abs,	0.221	0.181	0.230	0.445	0.855
D	2.33	0.67	1.22	55.40	68.50
%E	69.96	39.97	54.99	98.22	98.56

j) Interference effect

The effect of some diverse ions that may be expected being in environmental samples on the determination of Cr (VI) was studied following the general CPE procedure. It is agreed that an extraneous ion deemed to interfere seriously when it gives a relative error percent more than ±10%. The selectivity of CPE for Cr(VI) ion as $Cr_2O_7^{2}$ was conducted by studying the effect of some salts containing , for example, both cations (Na^+ and K^+) and metal anions (I^-, WO_4^{2-} and $Mo_7O_{24}^-$) in addition to picrate, $C_2O_4^{2-}$, ClO_4^- ,$S_2O_3^{2-}$ and NO_3^- ions on the extraction efficiency of $Cr_2O_7^{2-}$ by CPE at the concentration of Interferent/ Cr(VI) ratio of 13 fold. The results are presented in Table 5. It can be seen that most of interfernts have no appreciable effect on the Cr(VI) extractability expect I^- and MoO_4^{2-} ions which have exceeded the allowable limits of interferences for Cr(VI) . Therefore, these anions should be removed first, if present, by using suitable masking agents before determination of Cr (VI) in any samples.

Table 5 : Interferences effect of some salts on extractability of $Cr_2O_7^{2-}$ with BTABN (percent extraction = 98.56%).

Interferent	Percent extraction (%E) found	$\%E_{rel}$
$KClO_4$	92.21	-6.4
$Na_2C_2O_4$	96.68	-1.9
Picric acid	92.63	-6.0
NaI	83.09	-15.6
$(NH_4)_2MoO_4$	74.83	-24.0
Na_2WO_4	97.48	-1.1
$Na_2\,S_2O_4$	95.28	-3.4

k) Stiochoimetry of the Extracted Complex

It is reported that the analysis of the dependence log D = *f* (log $C_{REAGENT}$) permits the determination of the stiochoimetry in the extracted complex (16). Consequently, the slope in the Figure 7 for log D = *f* (log C_{BTABN}) coordinates is nearly equal to less than one (i.e. 0.71), indicating the ion pair complex with ratio 1:1 is extracted into the surfactant-rich phase. Thus the most probable composition of the complex extracted in the forms of $[H\text{-}BTABN]^+;HCrO_4^-$.

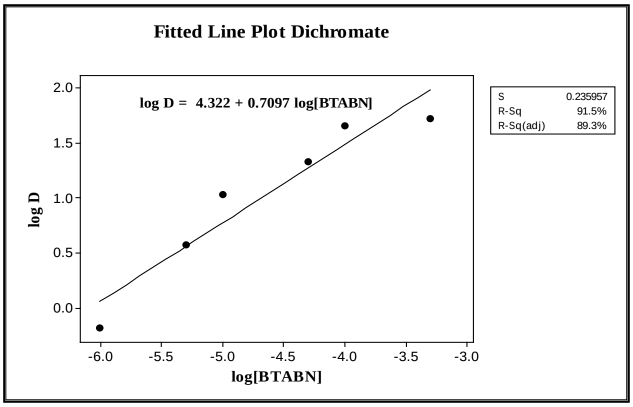

Figure 7 : log D = *f* (logC_{BTABN})

l) Analytical Figures of Merit

Under the optimized conditions established by CPE procedure, a series of standard Cr (VI) solutions ranging from 0.1-2.0 μg mL^{-1} were taken and subjected to the general CPE and the Cr (VI) was determined spectrophotometry at λ_{max} of 475 nm in order to test the linearity of the method. The analytical figures of merit are presented in Table 6. The statistical evaluation of calibration curve has shown that a strong correlation between absorbance and Cr (VI) concentration may exist (R^2=100%).The analysis of variance (ANOVA), On the other hand, also proved the linear regression equations [y= (0.428±0.003534) x-(0.0016±0.00389] was statistically valid. This because of the ratio (MS_{reg}/ MS_{error}] for 1 and 6 degree of freedom (*DOF*), larger than critical values (F16 = 5.987 at 95% CI), indicating that the prediction based on the regression is satisfactory (Table 7).

The limit of detection (LOD= 0.017 μg mL^{-1}) and limit of quantitation (LOQ= 0.0568 μg mL^{-1}) obtained for Cr (VI) with the prepared ligand (BTABN) by developed CPE-Spectrophotometry were based on the standard deviation of the response and the slope of the calibration curve using the following equations; LOD = 3 σ_B/s; LOQ = 10 σ_B/*s*, where (σ_B) is the standard deviation of the calibration line and (*s*) its slope.

Concerning the detection limit, our findings was generally in harmony with that obtained by Madhuchandr et al (17) and Suvardhan et al (18) who used the combined CPE-ETAAS and FAAS, respectively. But, it was worse than that obtained by Li et al (19) and Shemirani et al (20) who employed the sophisticated instrumentation such as EV-ICP OES and FAAS combined with CPE respectively. However, by considering 5 g of the analyzed sample in 100 mL and 17 μg L^{-1}, the detection limit was of 0.34 μg g^{-1}, thus the adopted method was applied for the determination of Cr (VI) in various environmental samples in order to test its applicability and reliability.

Table 6 : Figures of merit for the determination of $Cr_2O_7^{2-}$ by the proposed method

Parameter	value
λ_{max} (nm)	475
Regression equation	y = 0.428x - 0.0016
Correlation coefficient(r)	0.9999
Coefficient of determination (R^2)	100%
C.L. for the slope (b± tsb) at 95%	0.428±0.003534
C.L. for the intercept (a± tsa) at 95%	-0.0016±0.00389
Concentration range (μg mL^{-1})	
Limit of Detection (μg mL^{-1})	0.1-2.0
Limit of Quantitation (μg mL^{-1})	0.0170
Sandell's sensitivity	0.0568
(μg cm^{-2}/0.001A.U)	1.16 x 10^{-7}
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	
Composition of complex (M: L)*	4.47x10^4
RSD% (n=7) at 2 μg mL^{-1}	1:1
Preconcentration factor**	0.31
Enrichment factor***	250
	270

*obtained by slope analysis method ** calculated as the ratio of the original sample volume to that of extracted volume ***Calculated as the ratio of slope of calibration curve obtained by CPE to that obtained without preconcentration

Table 7 : Analysis of Variance of regression line of Cr (VI)

Source	DOF	SS	MS	F	P
Regression	1	0.5195	0.51954	87824	0.00
l Error	6	0.00004	0.00001		
Total	7	0.51958			

DOF=degrees of freedom, SS: sum of squares, MS: mean of squares, F (Fisher F-test). P: probability at 0.05

m) Determination of Cr (VI) in Real Samples

The developed method was applied for the Cr (VI) detection in various environmental and botanical samples and the results were statistically compared with standard flame atomic absorption spectrometry (FAAS) that had done in our laboratory under the conditions outlined by company's manual. The method involved the determination of Cr(VI) in two types of soils collected near the roadside streets, most of near of the rivers (agriculture street) , water collected from different point of Al-Forat river and water purification projects, plant and vegetables from local market used for human consumption, and wastewater from Leather Tanning Company in Al-Zuafraina/ Baghdad . The results are presented from Table 8 to Table 12. All statistical results performed by the paired t- test [21] for comparison of means between the proposed and standard FAAS methods for all samples (Tables 8 to 12) have shown that all p values [P(T<t) two tailed] based on the 5% critical values (t -two tailed) were more than the |t| calculated values indicating acceptance of null hypothesis (H_o) which specified that there appears insufficient evidence to suggest the accuracy of the established CPE- Spectrophotometry differs with that of standard AAS method(i.e. there is a good agreement between the results obtained by the two methods).

From the environmental point of view, the means and concentration range of Cr(VI) were entirely different depending on the site of collection in both non agriculture and agriculture soils and found to be of 5.18(4.88-7.20) and 1.57(0.72-3.44) as μg g^{-1} respectively. This indicated that the extent of chromium pollution of soil in some places selected in the Al-Najaf city was slightly high, but appears naturally more significant than in non-agriculture soil due to its location in the vicinity to the roadsides which might be contaminated by congestion of the traffic. In fact, there is no guideline level for Cr (VI) in agricultural soils approved by Iraqi body. However, the international and/or national guidelines regarding Cr (VI) in soil are not firmly established so far and varied from country to the other; for example, the quality guideline for Cr (VI) in Canadian soils is of 0.4 μg g^{-1} [22] while the permissible limit for Cr in Dutch standards is 100 µg g^{-1}[23]. In Poland, it is accepted that the natural content of chromium in the surface layer (0-15 cm depth) of sandy soil is 2.0-30.0 µg g^{-1} and in dusty and loamy soil is of 14.8 – 81.0 µg g^{-1} [24].In conclusion, the concentrations of Cr (VI) were found to be low in agriculture soil of Al-Najaf city, which is below the plant toxicity threshold value of 5 µg g $-^1$ [25].

The Cr (VI) levels in water (river and water projects) samples of the Al-Najaf city were also determined by the proposed method. The results have revealed that the average concentration of Cr (VI) in water sample was of 1.01 µg g^{-1} with concentration range of 0.24 to 2.72 µg g^{-1}. Unfortunately, most limits, guidelines and criteria for water are based on total chromium levels. Thus the standards based on total chromium do not recognize the significant differences between the health and environmental impacts of Cr (VI). However, the dissolved Cr(VI) content in freshwater and marine water according to UK environmental quality standard are of 0.0043 and 0.0006 µg g^{-1} respectively, indicating that all water samples analyzed were mostly above the maximum permitted concentration for protection of aquatic life and drinking [26].

The results have shown , on the other hand ,that the concentration of Cr(VI) in some plant and vegetables with mean value of 1.283 μg g^{-1} and ranged from 0.40 to 2.65 μg g^{-1}. The results in Table 12 shows the Cr (VI) content in different sites of the General Company of Leather (Tanning site) in Al-Zuafrania / Baghdad, before, after removal of chromium by chemical process and in leather piece too. It can be seen that the content of Cr (VI) after chemical treatment of wastewater (0.8±0.055 μg g^{-1}) in Tanning site of the company is still high in accordance to the Agency for Toxic Substances and Diseases Registry (ATSDR) which classified Cr (VI) as the top eighteenth hazardous substance and assessed that the Minimal National Standards (MINAS) upper limit of Chromium in industrial wastewater is 100 μg L^{-1} (27).

Table 8 : Cr (VI) content (μg g^{-1}) in the non-agriculture soil samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t test
1	5.69±0.168	5.09±0.364	$\bar{X}_d$ = 0.0160 S_d=0.035777 $t_{cal(n=5)}$= 1.0 $t_{crit.}$at95% df;4=2.78 P-value=0.374
2	5.84±0.161	4.98±0.136	
3	7.20±0.451	6.90±0.368	
4	4.88±0.205	5.33±0.311	
5	5.44±0.417	5.21±0.224	

1) Al-Muthana street near street; 2) Al-Ashreen street; 3) Al-Mufeed street; 4) Al–Rawan street; 5) Al-Muthana street far–off street.

Table 9 : Cr (VI) content (μg g^{-1}) in the agriculture soil samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	2.24±0.209	2.10±0.523	$\bar{X}_d$=0.115714 S_d= 0.144897 $t_{cal(n=8)}$= 2.11$t_{crit.}$at 95% df;7=2.36 P-value=0.079
2	1.00±0.903	0.97±0.341	
3	0.80±0.168	0.77±0.624	
4	1.20±0.569	1.10±0.335	
5	BDL*	BDL*	
6	1.60±0.611	1.55±0.258	
7	0.72±0.187	0.69±0.038	
8	3.44±0.420	3.01±0.492	

**BDL= below detectable limit; 1) Near Kufa river; 2) Al-Huria; 3) Al-shamia; 4) Shamia; 5) Abarat; 6) Abasia;7) Heara;8) Al-Mashkab.*

Table 10 : Cr (VI) content (μg g^{-1}) in water samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	0.73±0.581	0.65±0.444	$\bar{X}_d$=0.236000 S_d =0.455006 $t_{cal(n=5)}$= 1.19 $t_{crit.}$at95% df;4=2.78 P=0.301
2	0.56±0.127	0.52±0.627	
3	0.80±0.519	0.81±0.253	
4	2.72±0.492	1.69±0.085	
5	0.24±0.620	0.20±0.710	
6	BDL*	BDL*	
7	BDL*	BDL*	

**BDL= below detectable limit;1) Old kufa bridge;2) River(water project);3) Al- Abasia river;4) Kary saad;5) Meesan; 6) Alamam Ali bridge;7) New project water.*

Table 11 : Cr (VI) content (μg g^{-1}) in plants and vegetable samples withstatistical paired t-test at 95% confidence level.

Sample	Proposed method	AAS method	Paired t -test
1	BDL	BDL	$\bar{X}_d$= 0.323333 S_d= 0.456216 $t_{cal(n=3)}$= 1.23 $t_{crit.}$at95% df;2=4.30 P-value=0.344
2	2.65±0.400	1.8±0.059	
3	BDL	BDL	
4	BDL	BDL	
5	BDL	BDL	
6	0.40±0.625	0.35±0.026	
7	0.80±0.183	0.73±0.53	
8	BDL	BDL	

**BDL= below detectable limit; 1) Solanum melongena; 2) Potato; 3) Tomato;4) Aplum gravealens;5) Iraqi dates; 6) Cucumbers;7) Capsicum sp;8) Vicitoria regia.*

Table 12 : Cr (VI) (μg g^{-1}) content in wastewater of leather tanning plant and saffron Sheep leather and statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	7600±0.6	7598.5±0.82	$\bar{X}_d$= 0.992500 S_d=0.710557 $t_{cal(n=4)}$=2.79 $t_{crit.}$at 95% df;3 =3.18 P-value=0.068
2	3360±0.2	3358.4±0.17	
3	500.0±0.3	499.2±0.26	
4	0.8±0.05	0.730±0.17	

1) Before chemical treatment;2) Tanned leather piece;3) Outside after saturated leather ;4) After chemical treatment.

IV. CONCLUSIONS

In this work, a new essay for the extraction and detection of Cr (VI) as $Cr_2O_7^{2-}$ was examined using a new synthesised organic reagent, for the first time, in an attempt to extent the analytical capability of CPE technique in conjugation with spectrophotometry for inorganic anions analysis. The results we have attained are promised that enough to continue ahead to carry out further works that concerning the development more sensitive methods in this field. Though there has been a marked improvement in most analytical figures of merits, the thermodynamic study is still needs much work to investigate the effect of other parameters such as the variation of surfactant amount added and the concentration of the reacting species abreast with temperature for the formation an ion-association complex to fully understand the mechanism of solubilisation of this type of molecules in micelles. However, it should be borne in mind that the implementation of inorganic anion analysis by CPE is not as straightforward as anticipated as with metal ions in the form of chelates due to the limitations such as interfering species, surfactant type and electrolytic salts which can expect be solved in future works. These limitations have been alleviated to some extent by careful optimization of the chemical variables in this study. However, the proposed procedure permits to increase the popularity of UV-Vis speectrophotometric technique after CPE beside the solvent-free extraction for metal anions from complex matrices which proved to be fairly simple, sensitive, precise and accurate thereby it might be considered as an alternative for atomic spectrometric techniques.

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