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RESEARCH ARTICLE

A New Approach for Extraction and Determination of Manganese in Environmental Samples Using Cloud-Point Extraction Coupled with Spectrophotometry

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Abstract: A new and versatile procedure for the spectrophotometric determination of manganese using micelle-mediated extraction was developed. The method involved the formation of an ion association complex between manganese oxyanion (MnO_4^-) and brilliant green in acidic solution and the complex was extracted into the surfactant Triton X-100 at optimum conditions. The surfactant-rich phase which contains manganese complex was mediated with solvent and the Mn content measured spectrophotometerically at absorption maximum (λ_{max} = 657 nm). The effects of the several variables which impact the CPE efficiency were optimized by one-factor-at-a-time (OFAT). Under the optimized conditions, enrichment factor of 282 was achieved leading to limit of detection and limit of quantitation of 0.086 and 0.242 μg mL^{-1} respectively, with linearity of 0.2-3 μg mL^{-1}. The precision (RSD%) of the proposed method was of 1.07% . The interferences effect of such ions was also studied. This method is applicable in the determination of manganese in environmental and vital samples.

Keywords: Manganese oxyanion, Brilliant green, Cloud-point extraction, Spectrophotometry

Introduction

Manganese is well-known as both an essential and toxic trace element. As an essential, it is considered one of most important element in biochemistry which plays as co-factor for several enzymes. Mn contributes to maintain healthy nerves and immune system, helps in blood sugar regulation, involved in utilization of vitamins B1 and E and required for normal bone growth or for avoiding blood clotting defects[1-2]. Mn deficiency in human is rarely occurring owing to its widespread presence in the human diet, but if it is happening, causes the bones and cartilages deformation, destroys platelet aggregation, ataxia, osteoporosis, epilepsy and impaired growth[3]. However, at elevated Mn concentration, neurotoxicity occurs due to an accumulation of the metal in brain tissue causing an irreversible neurological

syndrome similar to Parkinson's disease[4]. In this context, WHO recommends that the intake of Mn can be as high as 20 mg/day without apparent ill effects, *i.e*. with an intake of 12 mg/day adult (60 kg) would receive 0.2 mg/kg of body weight per day[5]. Therefore, the determination of trace amounts of manganese in various samples is very significant for some fields, such as water, environmental and food matrices.

Trace manganese determination in such complex matrices is a challenge analytical task, mostly due to the low concentration of metal in these samples beside the matrix interferences, which requires sensitive instrumental techniques and often a pre-concentration step. Hence, separation and pre-concentration procedures before detection is a must to avoid the above dilemmas. Several separation and enrichment protocols coupled with different instrumental techniques for manganese assay have been developed include, precipitation/ FAAS[6], solvent extraction/FAAS[7], solid phase extraction/FAAS[8] or solid phase extraction/ spectrophotometry[9]. Despite that each procedure has its merits and drawbacks, but the choice depends by virtue of analytical problem.

Recently, cloud point extraction (CPE) has intensively highlighted by many authors as a versatile and promising methodology for the separation and enrichment for metal ions and organic compounds from various matrices. Simply, in CPE, hydrophobic analytes is distributed between surfactant and aqueous phases and when the solution heated over a critical temperature of nonionic surfactant, called cloud point, the hydrophobic species are in a position to interact with the micelles thus being separated and concentrated in the small volume of surfactant-rich phase[10]. This phase acts as an organic solvent with the extracted analyte partitioned between this phase and the aqueous solution containing only very small amounts of the dissolved surfactant[11].

Since last decade, few articles have appeared in the chemical literatures reflect the applications merit of CPE coupled with atomic spectrometers for manganese extraction and preconcentration from water, saline water and food matrices. In all these attempts, the determination of manganese as a metal ion is based on the formation of hydrophobic chelates with commercial organic agents and extracted into micelle-mediated solvent , such as 1-(2-thiazolylazo)-2-naphthol(TAN)[12], 1-(2-pyridylazo)-2-naphtol (PAN) and 1-(2-pyridylazo) -2-naphthol (PAN)[13-14], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)[15-16], 2-(2´-thia-zolylazo)- resorcinol (TAR)[17], 2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol((Me-BTABr)[18], nitrophenylazoresorcinol (Magneson I)[19] and dithizone[20].

The extraction and enrichment of metal ions as anionic metal complexes such as metal halo anions (MX_4^-) and/or metal oxyanions (MO_4^-) via the formation of ion-pairing complex with chromogenic reagents rather than chelating agents by using CPE coupled with UV-Vis spectrophotometry is a new trend toward establishing and developing in analytical methodology which will open the vast manners in easy, simple and inexpensive routine analysis instead of using costly instrumentations in this field. To the best of our knowledge, there is only one article was appeared in the chemical literatures based on the above concept for the determination of Cd (II) as CdI_4^{2-} by combined CPE/ flame atomic absorption spectrometry since establishing of CPE [21].

In this piece of work, a new approach was developed for the determination of manganese in soil, plant vegetable and meat samples by using CPE combined with UV-Vis spectrophotometry. The method is based on the formation of ion-paring hydrophobic complex between MnO_4^- and Brilliant green (cationic dye) in acidic solution and subsequently extracted into the surfactant Triton X-100 at optimum conditions. The separated surfactant-rich phase was diluted with minimum amount of ethanol and manganese determined by UV-Vis spectromphotometry at λ_{max} of 657 nm. The proposed method was applied for the determination of Mn in environmental and botanical samples

Experimental

A Shimadzu double-bean UV-visible Spectrophotometer model UV-1700 (Japan**)** equipped with 10 mm optical path cell is used for the scanning study of absorption spectra of the complexes formed, while absorbance measurements were performed with Shimadzu single-beam UV-Vis model UV-100.02 spectrophotometer model UV-100.02 (Japan). A Shimadzu atomic absorption spectrophotometer model AA6300 (Japan) is also used for the determination of manganese in the samples.

Reagent and materials

All analytical grade reagents were used without further purification as received from different company. Doubled 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 used without further purification. Potassium permanganate (purity 99.0%) and Brilliant green were purchased from CHEM-SUPPLY Pty limited (Australian) and Merck respectively.

The stock solution of Mn (VII) at 1000 μg mL^{-1} was prepared by dissolving of 0.2877 g of $KMnO_4$ in a minimum amount of water in 100 mL volumetric flask and completed to mark with water. Brilliant green solution of $1x10^{-2}$ M was prepared by dissolving 0.4827 g of Brilliant green in minimum amount of water in 100 mL volumetric flask and completed to mark with water. A 1% (w/v) of triton x-100 was prepared by dissolving 1g of reagent in 100 mL of water.

General CPE procedure

10 mL aliquots containing a proper amount of permanganate (MnO_4^-) standard or sample solution in 0.5 M HCl, 0.5 mL Brilliant green ($1x10^{-2}$ M) and 0.5 mL of 1% triton x-100 were allowed to stand for 10 min in a thermostated bath at 80 ^{0}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 5 mL of ethanol and the absorbance of the resulting solution was measured at 657 nm in a 1 cm cell against a reagent blank. The distribution ratio (D) and percent extraction (%E) were determined after the measurement of remaining quantity of MnO_4^- in aqueous to that extracted in micelle phase by using spectrophotometric method published elsewhere[22].

Preparation of samples

Duplicate sample (soil, plant and meat) solutions were prepared by transferring approximately 2 g of dried sample into a 250 mL conical flask. Then, 4 mL of distilled water, 5 mL concentrated H_2SO_4 and 10 mL concentrated HNO_3 were added. The content of the flask was heated gently on an electric hotplate for 10 min to ensure the destruction of all organic compounds in the sample. After cooling the solution, a little of water was added and then filtered. To each filtrated solution, 3 mL of concentrated sulfuric acid, 2 mL of concentrated phosphoric acid and 0.1 g of KIO_4 were added and the contents heated to boiling for 10 min to oxidize all Mn(II) in the sample solution to Mn(VII). Thereafter, the contents were transferred into 50 mL volumetric flask and diluted to mark with water.

An aliquot of 5 mL of each sample solution was pipetted into 10 mL conical flask and treated with 0.1 mL of $1x10^{-2}$M potassium thiocyanat solution as a masking agent and then

filtered. The filtrated was transferred into 10 mL volumetric flask and diluted to mark with water from which the manganese content was extracted according to the general CPE procedure and determined by spectrophotometry at λ_{max} of 657 nm. The blank solution was prepared in the same manner without analyte.

Statistical analysis

All statistical calculations, such as basic statistics, significance tests, regression equations and correlation coefficients for the calibration curves, were implemented using Minitab version 14 (Minitab Inc., State College, PA, USA) and Excel 2007(Microsoft Office®).

Results and Discussion

Absorption spectra

Figure 1 shows the absorption spectra of the reagent brilliant green solution and its ion-association complex with manganese oxyanion (MnO_4^-) in surfactant-rich phase against blank solution prepared under similar conditions were recorded using Shimadzu UV1700 equipped with 1 cm matched quartz cell. It was appeared that the absorption maximum (λ_{max}) of $[MnO_4^-][BG^+]$ ion association complex occurs in visible region at 657 nm while the reagent BG solution alone displays an absorption maximum at λ_{max} of 633 nm. Therefore a wavelength maximum at 657 nm for the complex was used throughout this work.

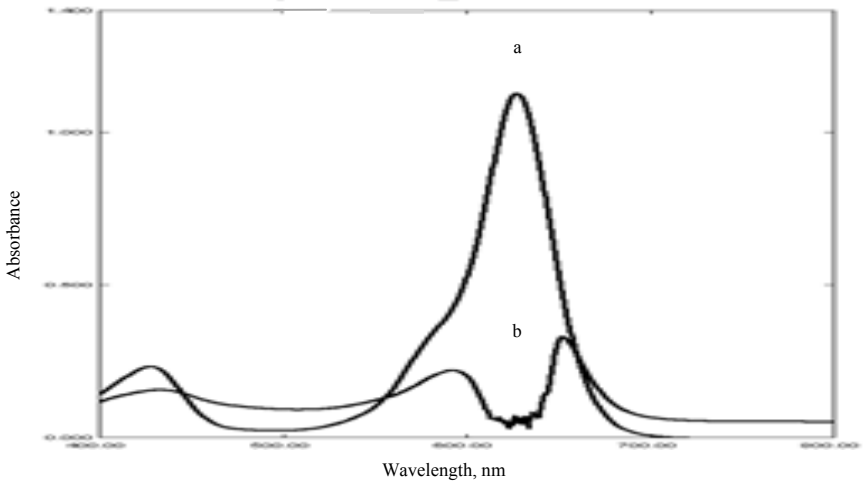

Figure 1. Absorption spectra of (a) $5x10^{-4}$ M Brilliant green (b) Mn-BG complex in micelle dissolved in ethanol.(Conditions: 20 µg Mn(VII) 0.5 M HCl ;0.5 mL Brilliant green ($1x10^{-2}$ M); 0.5 mL of 1% triton x-100)

Optimization of CPE procedure

The effects of several experimental parameters which impact the CPE efficiency were carried out by classical optimization (one-variable-at-a-time). In this approach, we observe the effect of one factor at a time (OVAT) on an experimental response. While only one factor is changed, others are kept at a constant level. Although, the "optimization" performed by OVAT[23] does not ensure at all that the real optimum will be conformed, but it would be valid only if the variables to be optimized would be totally independent from each other (*i.e.* no interactive effects among the variables). Nevertheless, the classical optimization certainly leads at least to an improvement of the analytical method. In as much

as the extraction efficiency of the CPE depends on dual factors, some of regarding the prior formation of a complex with sufficient hydrophobicity and the other for the formation of micelles to obtain the desired separation and pre-concentration. Consequently, the effects of HCl, concentration of Brilliant green, nonionic surfactant Triton X-100 concentration and equilibration temperature and heating time were selected in this study.

Effect of HCl concentration

The separation of oxyanion (MnO_4^-) by CPE method involves the formation of ion-association complex between (MnO_4^-) and the protonated Brilliant green in the presence of HCl, with sufficient hydrophobicity and extracted into micelle medium thus obtaining desired enrichment. In this study, 10 mL solution containing 20 µg Mn as MnO_4^-, Brilliant green ($5x10^{-4}$ M) and 0.5 mL of 1% Triton x-100 and varying concentration range of 0.1-1.0 M HCl was subjected to general CPE procedure. The results depicted in Figure 2 (a, b) show the influence of HCl concentration on the absorbance and extractability of ion-association complex into the surfactant-rich phase. The absorbance signal reaches a maximum at 0.5 M HCl. At higher concentrations of HCl, the absorbance suddenly decreases which most probably due to the reduction of permanganate(VII) ion to Mn(II) thus preventing the formation of ion-pair complex in micelle-mediated phase (Figure 2a) . On the other hand, the distribution ratio (D) was also maximum at 0.5 M HCl, indicating an adequate extraction efficiency of [MnO_4^-][BG^+] ion-pair in water -nonionic surfactant phase system (Figure 2b).

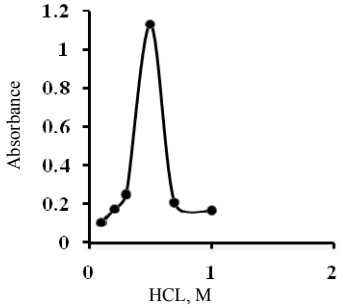

Figure 2a. Effect of HCl concentration on absorbance values

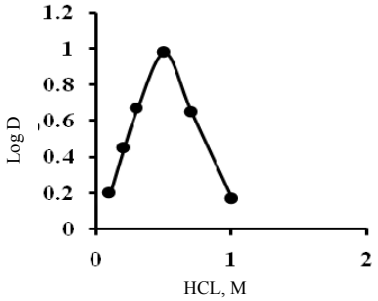

Figure 2b. The dependence of log D= *f* [HCl]

Effect of brilliant green concentration

The variation of absorption signal as a function of Brilliant green amount was investigated for 10 mL solution containing 20 µg Mn(VI), 0.5 mL of Triton x-100 (0.1%), 0.5 M HCl and varying volumes of 0.01-5 mL Brilliant green ($1x10^{-2}$M) during CPE procedure. The results illustrated in Figure 3a have shown that the analytical response increased linearly with increasing in the amount of BG reagent and reached maximum up to 0.5 mL of $1x10^{-2}$ M BG which is equivalent to $5x10^{-4}$ M BG, indicating sufficient for ion-pair complex formation. Thus a concentration of $5x10^{-4}$ M of BG was selected as optimum. This experiment was also conducted to obtain the distribution ratio (D) from the reminder quantity manganese as MnO_4^- by spectrophotometric method[22] and amount of transferred manganese as MnO_4^- to form ion-pair complex into surfactant at the selected concentration of the reagent as shown in Figure 3b. The results also reveal that the concentration of $5x10^{-4}$ M BG provides a high distribution ratio (D) with highly stable ion pair complex formation extractable into surfactant. At lower than $5x10^{-5}$ M BG, unstable ion-pair complex was formed which led to depress the extractability of ion pair complex into surfactant.

It is also reported that the analysis of the dependence log D = *f* (log C_{BG}) permits the determination of the stiochoimetry in the extracted complex[13]. Consequently, the slope on the Figure 3b in log D = *f* (log C_{BG}) coordinates is nearly equal to one, indicating the ion pair complex with MnO_4: BG ratio 1:1 is extracted into the surfactant-rich phase.

$$MnO_4^- + C_{27}H_{33}N_2^+ HSO_4^- + H^+ \xrightarrow{\text{TX-100}} [MnO_4^-][C_{27}H_{33}N_2^+] + H_2SO_4$$

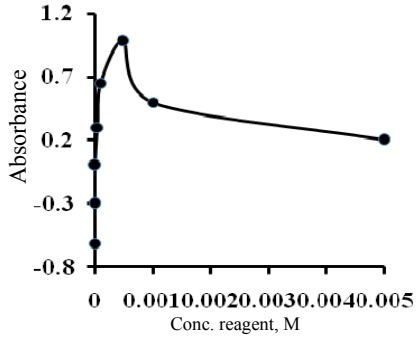

Figure 3a. Effect of BG concentration on extractability of ion-pair complex

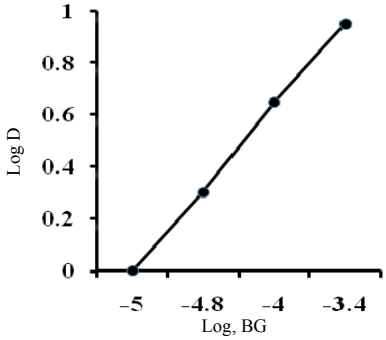

Figure 3b. log D = *f*(logC_{BG})

Effect of surfactant concentration

The effect of the surfactant amount on CPE of 10 mL containing 20 µg Mn (VII) with $5x10^{-4}$ M BG at 0.5 M HCl in the presence of 1% Triton x-100 varying from 0.1 to 1 mL has been optimized in order to obtain maximum extraction efficiency via minimizing the phase volume ratio. Figure 4a reflects the influence of Triton x-100 amount on the preconcentration of Mn (VII). It was shown that the absorbance signal increases dramatically and reach maximum at 0.5 mL of 1% TritonX-100 and decreases suddenly thereafter. At low amount of surfactant, the absorbance and hence the distribution ratio (Figure 4b) for ion pair complex are low, perhaps due to the insufficiency of assemblies formation entrapping the complex quantitatively. Whilst at higher amount of surfactant, the extraction efficiency is low, probably due to the increase in surfactant-rich phase volume at which the analyte become more diluted resulting in poor sensitivity and thus valueless extraction efficiency. Consequently, optimum volume of 1% (w/v) Triton x-100 at 0.5 mL volume (equivalent to 0.05% Triton x-100 in 10 mL test solution) was used in all experiments.

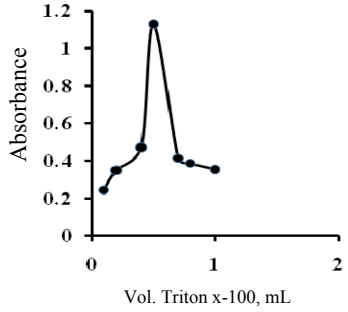

Figure 4a. Effect volume of Triton x-100 on absorbance

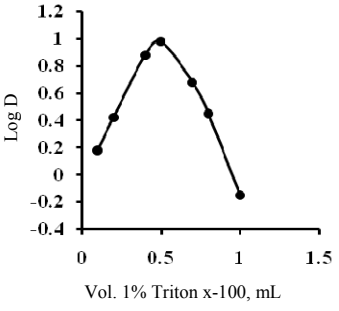

Figure 4b. Effect volume of Triton x-100 on distribution ratio

Effect of the equilibration temperature and incubation time

To ensure phase separation and preconcentration of an analyte efficiently, optimal equilibration temperature and time are very crucial parameters for complete reaction. The effects of the equilibrium temperature and the incubation time were examined due to their importance for the reaction completion and efficient separation of the phases, which reflect certainly the magnitude of preconcentration factor of an analyte. The temperature was varied from 70 to 80 °C in a search of optimum value. It was shown that the highest absorbance signals were obtained when the temperature at 80 ºC achieving quantitative extraction (Figure 5). Unreasonably high temperatures are not suitable for the CPE procedure because higher temperatures could cause problems to the stability of complex due to thermal decomposition of ion-association complex. In this study, 80 °C was chosen as the optimized temperature for subsequent experiments. It was also observed that the incubation time of 10 min is sufficient for the maximum absorbance of manganese complex (Figure 6). Thus, the temperature of 80 °C for 10 min was selected to fulfill efficient separation conditions.

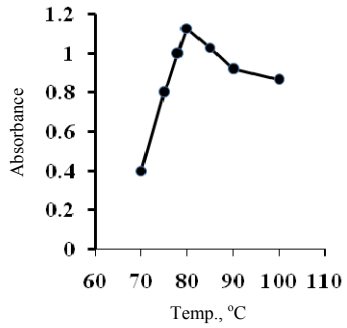

Figure 5. Effect of Temperature

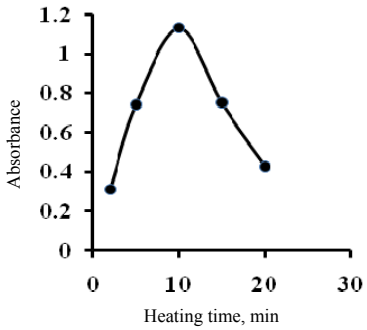

Figure 6. Effect of incubation time

Thermodynamic study

The equilibrium extraction constants (K_{ex}) and thermodynamic parameters for the extraction of [MnO_4^- : BG^+] complex during the cloud point extraction using Triton x-100 as a mediated extracting agent at various temperatures were determined. The equilibrium constants (K_{ex}) at the selected temperature were calculated from equation below and the results are shown in Table 1 and Figure 7.

$$K_{ex} = \frac{D}{[Mn(VII)]_{aq.}[BG]}$$

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 transportation 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.

Table 1. Variation of equilibrium constant with temperature during CPE

T C^0	70	75	78	80
T K^0	343	348	351	353
1/T	2.92	2.87	2.85	2.83
K_{ex}	$1.9054x10^8$	$3.4674x10^8$	$4.1687x10^8$	$5.248x10^8$

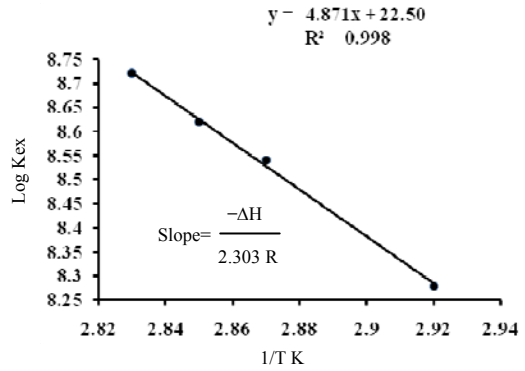

Figure 7. Effect of the equilibration extraction temperature on ion pair complex formation by CPE

Thermodynamic parameters were also calculated from the relationships mentioned elsewhere[24]**.** The results are summarized in Table 2. The value of enthalpy change (ΔH_{ex}) was obtained from the plot of log K_{ex} *versus* 1/T (Figure 7) and found to be 0.091 kJ mol^{-1} while the values of Gibb's free energy (ΔG_{ex}) and entropy change (ΔS_{ex}) were obtained at different temperatures from thermodynamic relationships.

Table 2. Thermodynamic parameters for the extraction of ion-pair complex by CPE

T, °K	ΔH_{ex}, kJ mol^{-1}	ΔG_{ex}, kJ mol^{-1}	ΔS_{ex}, J mol^{-1}
343		-54.3688	158.7749
348	0.091	-56.8932	163.5718
351		-57.9215	165.2777
353		-58.9116	167.1461

It can be seen from Table 2 that the enthalpy change (ΔH_{ext}) is quite low and equal to 0.091 KJ mol^{-1} indicating a high efficiency of the extraction process of complex was achieved thermodynamically into the surfactant-rich phase. This is because (1) a strong electrostatic association exists between MnO_4^{2-} anion with the reagent cation and (2) contribution of the complex in driving water molecules out of surfactant-rich phase in which more of micelles are aggregated enabling the precise extraction of complex especially in extracting of trace amounts. As for ΔG_{ex} is negative in all cases, indicating the extraction process is a spontaneous phenomena because the complex transportation and surfactant phase formation are synchronized processes occur at the same time. Thus the more negative value of ΔG_{ex}, the large spontaneous process is. The positive values of ΔS_{ex} prove that the solubilized ion-association complex molecules are organized in more random fashion during extraction process. Therefore, the extraction process is endothermic in nature, which is also verified from the positive value of ΔH_{ext} (Table 2).

Effect kind of surfactant

10 mL of aqueous solution containing 20 µg Mn (VII), $5x10^{-4}$M Brilliant green, 0.5 M HCl and 0.5 mL of 1% of the selected surfactants is subjected to general CPE procedure. Figure 8 highlights the effect of different kinds of surfactants on the extractability of $[MnO_4^-]$ $[C_{27}H_{33}N_2^+]$ complex. The results show Triton X-100 was the best non ionic surfactant for CPE of ion pair complex of MnO_4^- with BG. From the other hand the, the presence of ether groups on structure of Triton x-100 is more probable by sharing lone pair electron of which making

the hydrogen bonding leading to significant increase of the micelles which reflect higher distribution ratio of the ion-pair complex in Triton x-100 than in the other surfactants studied. While the other surfactants such as, Tween-80 and Tween-20 and SDS have shown that the formation of the separated surfactant-rich phase needs a higher temperature than 80 ºC and 15 min for Tween-20 and Tween-80 except that SDS needs approximately 63 ºC and 15 min.

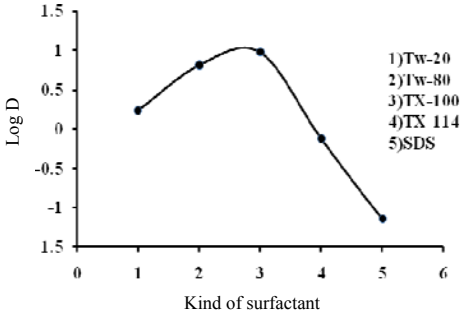

Figure 8. Effect of surfactant kinds on D value

Effect of electrolyte salt

It is known that the behavior of some electrolyte salt solutions lie in increasing the extraction percent during CPE process due to their act in increasing the dehydration of surfactant-rich phase. Table 3 reveals that some of electrolyte salts such as LiCl, $MgSO_4$, $NaNO_3$, $Na_2C_2O_4$, $CaCl_2$ and KNO_3 except NH_4NO_3 behave variably in decreasing the distribution ratio of ion association complex under extraction by CPE.

Table 3. Effect of some electrolyte salts on extractability of ion-association complex (D=9.5 and Abs= 1.13) upon addition of 0.2 M of each salt

Electrolyte salt	Abs. at 657 nm	D value
LiCl	0.432	3.60
$MgSO_4$	0.767	7.66
$NaNO_3$	0.568	5.30
NH_4NO_3	1.29	16.5
$CaCl_2$	0.921	8.45
KNO_3	0.525	4.80

This may be ascribed to the competition anions of these salts in formation of ion-association complex with brilliant green cation rather than MnO_4^- anion which lead to depression in extractability of $[MnO_4^-][BG^+]$. On the contrary, ammonium nitrate gave a remarkable increment in the distribution ratio of interested complex because this salt has a great effect on dehydration of surfactant-rich phase due to the nature of electrolyte solution which may organize their ions inside surfactant-poor phase, leaving the ions of complex are more approaching together which contribute to concentrate ion-association complex in surfactant-rich phase and thereby the extractability was increased markedly.

Method validation

Under the optimized conditions, a linear calibration graph was obtained by plotting the absorbance signal against the concentration of Mn(VII). The calibration data are summarized in Table 4. The following regression equation was obtained:

$$y = (0.565\pm0.0064)\ x - (0.027\pm0.0115)\ r = 0.9995 \text{ and } n = 7$$

Where y is the absorbance and x is the manganese concentration in $\mu g mL^{-1}$. This regression line had a coefficient of determination (R^2) of 99.9%, which suggests it is statistically valid. Analysis of variance (ANOVA) for the regression line was also carried out as shown in Table 5. ANOVA analysis supports that there is a strong significant relationship between the concentration of the analyte and absorbance units as $F_{tab}= F_{1, 6}=10.01 << 7909.44$. Beer's law was obeyed over the concentration range 0. 2–3 $\mu g\ mL^{-1}$. The limit of detection (LOD) and limit of quantitation (LOQ) were of 085 and 0.282 $\mu g\ mL^{-1}$ respectively, 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 plot and (*s*) its slope. The limit of detection obtained was better than that obtained by Soto-Neira *et al.* (22 $\mu g\ mL^{-1}$) using a new reagent (Cadmium(II) meso-Tetrakis (4-sulfophenyl) porphyrin complex) and derivative spectrophotometric method[25]. It is approximately close to that obtained by Kargosha and Noroozifar (0.031 $\mu g\ mL^{-1}$) for speciation of manganese in aqueous solution by using flow injection-spectrophotometric method[26]. But, it was generally worse than that obtained by AAS, FI-AAS and ICP-OES coupled with CPE[14-15,17-18,27].

Table 4. Figures of merit for the determination of Mn by the proposed methods

Parameter	value
λ_{max}, nm	657
Regression equation with CPE procedure	y = 0.565x - 0.027
Correlation coefficient(r)	0.9995
Coefficient of determination (R^2)	99.9%
C.L. for the slope (b± tsb) at 95%	0.565±0.01632
C.L. for the intercept (a± tsa) at 95%	-0.027±0.02945
Concentration range, $\mu g\ mL^{-1}$	0.2-3
Limit of detection, $\mu g\ mL^{-1}$	0.086
Limit of quantitation, $\mu g\ mL^{-1}$	0.282
Sandell's sensitivity, $\mu g\ cm^{-2}$/0.001A.U	$1.16x10^{-7}$
Molar absorptivity, $L.mol^{-1}.cm^{-1}$	$5.5x10^4$
Composition of complex (M: L)*	1:1
RSD% (n=7) at 2 $\mu g\ mL^{-1}$	1.07
Preconcentration factor**	200
Enrichment factor***	280

**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 5. Analysis of Variance of regression line

Source	DF	SS	MS	F
Regression	1	2.05227	2.05227	7909.44
Residual Error	5	0.00130	0.00026	
Total	6	2.05357		

DF=degrees of freedom, SS: sum of squares, MS: mean of squares, F(Fisher F-test)

This is evident due to the detection restrictions of UV-Vis spectrophotometry comparing with above the most sensitive techniques. By considering a limit of detection of 86 $\mu g\ L^{-1}$ and 2 g of sample in 50 mL, the LOD of the method would be 2.15 $\mu g\ g^{-1}$. On that

basis the proposed method was applied for the determination of manganese in various samples including soils, plants (vegetable and leaves) and meat selected randomly from different areas of the Najaf City (middle of Iraq) in order to test its applicability and reliability.

Determination of manganese in real samples

The proposed method was applied to the determination of manganese in soil, vegetables, crops and meat samples. Each sample was treated according to digestion procedure explained in experimental work and all manganese was oxidized into Mn(VI), preconcetrated by recommended CPE procedure and detected spectrophotometrically at 657 nm. The samples were also analyzed by a standard atomic absorption spectrometry (FAAS) method and the results were compared. The results are presented from Table 6 to Table 9.

Table 6. Mn content (μg g^{-1}) in the non-agriculture soil samples from different areas of the Najaf City (middle of Iraq).

Sample	Proposed method	AAS method
Al-Muthana street near street	56.0±0.135	55.0±0.236
Al-Ashreen	42.4±0.166	39.9±0.122
Al-Mufeed street	48.0±0.141	45.6±0.179
Al–Rawan street	54.2±0.085	53.3±0.311
Al-Abasiat	65.0±0.189	66.0 ±0.231
Al-Muthana street far –off street	54.4±0.147	53.7±0.056
$\overline{X}_d$	0.867	
S_d	1.461050	
$t_{cal(n=6)}$	1.45	
$t_{crit.}$at 95% DF=5	2.57	
P-value	0.206	

Table 7. Mn content (μg g^{-1}) in the agriculture soil samples (most of near of the rivers) of the Najaf City (middle of Iraq)

Sample	Proposed method	AAS method
Near Kufa river	66.0±0.162	65.0±0.214
Al-Huria	76.0.±0.233	74.5±0.198
Al-shamia	64.0±0.264	65.0±0.209
Shamia	58.0±0.186	56.0±0.322
Abarat	60.0±0.067	60.0±0.259
Abasia	24.0±0.125	23.0±0.147
Heara	16.0±0.269	15.0±0.359
Al-Mashkab	72.0±0.311	71.5±0.402
$\overline{X}_d$	0.750	
S_d	0.925820	
$t_{cal(n=6)}$	2.29	
$t_{crit.}$at 95% DF=7	2.36	
P- value	0.056	

Table 8. Mn content (μg g^{-1} in plants and vegetable samples of the Najaf City (middle of Iraq).

Sample No.	Proposed method	AAS method
Solanum melongena	13.6±0.413	12.5±0.266
Potato	46.0±0.287	45.0±0.373
Tomato	56.0±0.258	55.0±0.421
Aplum gravealens	80.0±0.228	78.4±0.277
Iraqi dates	56.0±0.319	55.0±0.139
Cucumbers	20.0±0.309	18.8±0.212
Capsicum sp	4.0±0.1099	3.30±0.227
Vicitoria regia	10.0±0.157	12.0±0.355
$\overline{X}_d$	0.700	
S_d	1.119949	
$t_{cal(n=6)}$	1.77	
$t_{crit.}$ at 95% DF=7	2.36	
P-value	0.120	

Table 9. Mn content (μg g^{-1}) in meat samples

Sample No.	Proposed method	AAS method
Beef(Indian)	12.8±0.288	11.9±0.214
Beef (Iraqi)	12.2±0.328	12.0±0.056
Chicken(Brazilian)	9.2±0.328	8.7±0.0940
Tween-20	5.8±0.244	5.2±0.208
Chicken(Iraqi)	2.8±0.269	2.0±0.361
fish(Iraqi)		
$\overline{X}_d$	0.400	
S_d	0.353553	
$t_{cal(n=5)}$	2.53	
$t_{crit.}$ at 95% DF=4	2.78	
P- Value	0.065	

All statistical results performed by the paired *t*-test[28] for comparison of means between the proposed and standard AAS methods for all samples (Table 6-9) 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-spectrophtometry differs with that of standard AAS method (*i.e*. there is a good agreement between the results obtained by the two methods).

Conclusion

In this piece of work, a new avenue has been exploited for the extraction and determination of manganese in the form of oxyanion that reacts with an organic reagent to form ion-association complex by combined CPE-spectrophotometric method, for the purpose of developing the features and analytical capability of CPE in inorganic anion analysis rather than that of the previously reported for metal chelate extraction by using CPE. Although, thermodynamic study and effect of some parameters gave encouraging results, but more

works would require investigating the behavior of solubilization of inorganic anions in the micelle phase. The proposed procedure also permits to increase the popularity of UV-Vis speectrophotometric technique after CPE beside the solvent-free extraction for metal ions from complex matrices which proved to be fairly accurate and thereby it might be considered as an alternative for atomic spectrometric techniques.

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