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Liquid Phase Extraction and Determination of Chromium (III) Ion in Aqueous Solution Using Dithiocarbamate Derivative Reagent

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Abstract

The new reagent N-methyl-N-((((4-bromophenyl)diazenyl)thio) carbonothioyl) aniline was made by the reaction of (sodium N-methyl- N-phenyldithiocarbamate)with 4-bromobenzenediazoniume salts. UV-Visible spectroscopy, elemental analysis, Fourier-transform infrared spectroscopy, mass spectroscopy, proton nuclear magnetic resonance spectroscopy, carbon-13 nuclear magnetic resonance spectroscopy, magnetic susceptibility measurements, and conductivity measurements to characterize the prepared compound. Using analytical and spectroscopic data, stoichiometry was calculated, and it was discovered that the complex was 1:2 (metal: ligand). The complexes' molar conductivity was measured using dimethyl formide, and the results indicated that the produced complex was ionic. Results of elemental analysis and spectrum studies indicate that the compound has a tetrahedral structure. Cloud point extraction was created for the preconcentration and separation of Cr(III) in drug sample measurements utilizing flame atomic absorption and a UV-Visible spectrophotometer at a maximum wavelength is 536nm. The effectiveness of cloud point extraction is affected by pH at 7, 20 % triton X-114, interference, and salt out impact with 15 min of incubation time, and 70 Celsius of heating. The calibration curve of Cr(III) was linear in the extent from 0.1-2 ppm with a linearity coefficient is 0.988. The limit of detection and quantification is (0.124 and 0.377 ppm). The new method has been successfully applied to the extraction and assay of the metal ion Cr(III) under three pharmaceutical brands.

Keywords: Chromium ion, Dithiocarbamate compounds, Micro Liquid Extraction, Pharmaceutical metal brands, Spectrophotometric methods.

Introduction

Dithiocarbamates chemistry began in the early 20th century [1]. It is a soft donor ligand that can form chelates with the majority of the metal ions in the periodic table [2] and has a well-known property of forming stable complexes with transition metals in a variety of oxidation states by coordinating through one or both sulfur atoms, this class of compounds are strong metal chelators that bind the metal ions in a variety of coordination modes to create metal complexes with a variety of stereochemistry [3]. Studies of dithiocarbamate metal complexes continue to catch the interest of chemist researchers because of their numerous applications in catalysis [4], organic synthesis [5], an accelerator for vulcanization of rubber [6], medicine [7-10], pesticides [11] fungicides [12], and as a single source precursor for the creation of metal sulfide nanoparticles [13,14]. Analysis of trace heavy metals is difficult because of their very low concentrations in samples and the high complexity of sample matrices. Therefore, preliminary preconcentration and matrix removal steps are highly needed to ensure the accuracy and precision of the analytical results[15], a great number of pretreatment methods have been applied for the extraction and preconcentration including solid phase extraction[16], dispersive solid phase extraction[17], and cloud point extraction[18]. Cloud point extraction (CPE) is used for the preconcentration of inorganic and organic in natural and biological samples and is easily combined with spectroscopic or chromatographic methods [18, 19]. The conventional CPE method relies on the nonionic surfactant's ability to produce micelles in aqueous media when heated above a specific temperature (also known as the cloud point or cloud temperature) or by adding salt. Centrifugations are used to separate the mixture into two phases (an aqueous phase and a surfactant-rich phase) [20]. Cloud point extraction as a green method has become the best extraction method compared to other extraction processes due to its advantages such as high pre-concentration factors, sensitivity, accuracy, Low toxicity, inexpensiveness, environmental friendliness, reduced cost, quick operation, increased safety, ease of use, lack of need for significant quantities of harmful organic solvent, and simplicity in connecting to analytical instruments [21-23].

In this study, Cr(III) was extracted and determined from various local pharmaceutical samples by reacting with the reagent N-methyl-N((((4bromophenyl)diazenyl)thio)carbonothioyl) aniline through easy, low cost, and simple CPE coupling with UV-visible spectrophotometric method.

Materials and Methods

This project uses chemicals of grade (Sigma, BDH, and Fluka).

To record infrared spectra using a KBr disc, an FT-IR Shimadzu model 8400 device was employed (4000-400cm^{-1}). Using a BAMX400 MHZ Spectrophotometer, ^{1}H NMR spectra were recorded in DMSO-d^6, whereas CHNS was performed on (EuroEA Elemental Analyses). Mass spectra were described using the mass spectrophotometer (Shimadzu LCMS 2010 A), and Spectra of UV-Vis were recorded using (Shimadzu twin beam 1800 UV). The Digital Conductivity Series was used to determine the molar conductivity of the complex. Using the Gallen Kamp melting point, compounds' melting points were estimated. A magnetic susceptibility balance was used to calculate the magnetic susceptibility (Johnson Mattey). WTW (model 720) pH meter was used with a combined glass electrode. Separating the aqueous phase from the rich phase was performed by the German Hettich centrifuge, model D-78532, and vortex mixer 945307 (THE.U.S.A). FAAS (AA-6300 shemaduzu). For all CPE studies, a water bath model BS-11 NO. K109.125 (Korea) was employed.

Preparation standard solutions

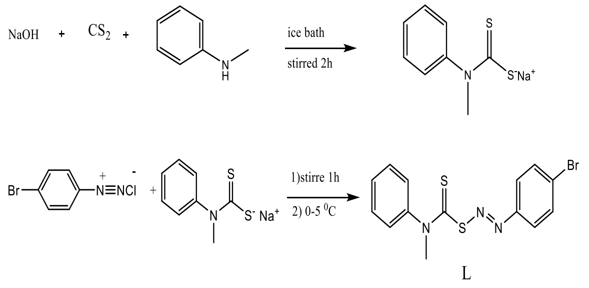
All chemicals used in this work have a purity of more than 98%. N-methyl-N-((((4-bromophenyl)diazenyl)thio)carbonothioyl)aniline (L) reagent 0.01mol L^{-1} was prepared by dissolving 0.1831g of reagent in 50mL absolute ethanol. To prepare a stock solution of 1000 ppm Cr(III), 0.4442g of $CrCl_3.6H_2O$ was dissolved in 100mL deionized water. A 0.1 mol L^{-1} of 37% w/w HCl solution was prepared 0.83mL diluted with 100mL deionized water. Also, prepare 0.1 mol L^{-1} of sodium hydroxide by dissolving 0.4000g in 100mL. 20% v/v of surfactants [TritonX-100 and TritonX-114] and (1% w/v) of surfactants [SDS and CTAB] were prepared by taking 5.00mL and 0.2500g from each and diluting by deionized water in 25 mL. 1000 ppm stock solution of interferences was prepared by dissolving (0.1598, 0.4577, 0.3112, 0.3104, 0.2683, 0.3602, 0.1574g and 0.1630g) from [$Pb(NO_3)_2$, $Cr(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$, $AgNO_3$, $CdCl_2$ respectively] in 100 mL deionized water. The following salts out were also prepared by dissolving 0.1 mol L^{-1} of [NaCl, KCl, NaF, Na_2CO_3, Na_2SO_4, $(NH_4)_2SO_4$ and NH_4Cl] (0.1461, 0.1863, 0.1049, 0.2649, 0.3551, 0.3303 and 0.1337g respectively) in 25mL of deionized water.

Synthesis of sodium N-methyl- N-phenyldithiocarbamate[24] (Nucleophilic addition of amines)

NaOH (2g, 0.05mol) dissolved in 5ml deionized water was let to reach an ice-cold temperature; (3.00 ml, 0.05 mol) of carbon disulfide was added to the cold solution. N-methyl aniline was then added (5.44 mL, 0.05 mol). The mixture was agitated for two hours and maintained a temperature below 4 °C. A solid yellowish-white substance was formed, separated, filtered, washed with ether, and finally recrystallized in warm acetone. Drying the white product under vacuum over $CaCl_2$ gave 1.6800g (yield=84%), m.p >300 0C. CHNS: Found (calc.) %: C;46.80(46.82), H;3.91(3.92), N;6.80(6.82), and S;31.22(31.24).

Synthesis of N-methyl-N-((((4-bromophenyl)diazenyl)thio) carbonothioyl) aniline(L)

para-bromoaniline (1.238g, 0.0072 mol) was dissolved in 10mL of hydrochloric acid :10 mL deionized water, then while cooling to a temperature of 0 to 5 ºC, the mixture was rapidly agitated. To this solution, gradually add the sodium nitrite (0.5000g, 0.0072mol) dissolving in 3.00 mL of deionized water. After 30 minutes of stirring at 0 to 5 ºC, a black solution was observed, this solution was added gradually to sodium N-methyl-N-phenyldithiocarbamate (1.5000g, 0.0072mol) dissolving in 6.60 mL deionized water, at temperature from 0 to 5 ºC, For an hour, the mixture was stirred. The precipitate that resulted was filtered and washed with cold water. Red precipitate, yield 73%, m.p 113 ºC. CHNS: Found (calc.) %: C; 45.91(45.80); H; 3.30(3.24); N; 11.47(11.33); S; 17.51(17.38). Scheme1 illustrates the procedures for reagent preparation. The general steps of reagent preparation are shown in Scheme 1.



Scheme 1. Illustration of the preparation N-methyl-N- ((((4bromophenyl)diazenyl)thio) carbonothioyl)aniline(L)

Synthesis of metal complex

A stirred mixture of the appropriate ligand (2 mol) in ethanol (5 mL) was added to the $CrCl_3.6H_2O$ (1 mol) in ethanol (5 mL). Refluxing the mixture for one hour. The colored precipitate is filtered and washed with ethanol with vacuum dried. Yellowish green color, yield 70%, m. p 114 ^{0}C.

Sample preparation

The method used for commercially available tablets includes choosing thirteen tablets from three distinct manufacturers. Each brand's tablets were weighed, then mortar-crushed and ground into a fine powder. A 1 ppm solution for Cr(III) was prepared by weighing an amount equal to the active component of each pharmaceutical preparation. In deionized water, the powder was dissolved. After that, it was filtered to get rid of any undissolved residue that might have impacted the response. The filtrate was completed to 100 mL. Further dilution was necessary to allocate the concentration within the linearity of the calibration graph Table 1 shows Samples of Cr(III).

Table 1. Samples of Cr(III)

	Cr(III)		
Samples Number	**Pharmaceutical drug company and claimed content of active ingredient**	**Wt of tablet (n=13)**	**Wt. of sample(g) of active of ingredient to obtain 1ppm in 100 mL**
D1	VITACED, Cedem AG, Switzerland, 0.025mg	1.5177	6.0708
D2	Sinturom, Elrazypharmacetical Co., Egypt, 0.04mg	1.0182	2.5455
D3	A-Z VITAL , Sanotact GmbH, Germany, 0.035mg	1.4165	4.2495

Cloud point extraction method

According to the cloud point procedure, aliquots of (10mL) of (10 ppm) of Cr(III) were added to (0.5 mL) of (0.01mol L^{-1}) of reagent, 0.5ml of 20% v/v Triton X-114 was then added, in a vortex mixer to thoroughly mix the solution. Place the tube in the 80°C water bath for 10 minutes. Centrifugation at 4000 rpm for five minutes was used to separate the phases. The aqueous phase was simply removed by decantation. The colored product's surfactant-rich phase was dissolved in 0.5mL of ethanol, and the product's absorbance was measured at λ_{max} 635nm in comparison to a blank reagent made under optimum conditions.

Results and Discussion

FT-IR spectroscopy

In Figs. 1 and 2, FT-IR spectrum of reagents and complexes shows, many important characteristic bands are noted such as NCS_2 and (-N=N-). A strong absorption band in the region 1253cm^{-1} is characteristic of the C-N of NCS_2 [9]. The stretching vibration of the polar -N-S bond appeared at 813 cm^{-1}, and a band assigned to the νasym (C-S) stretching is appeared at 1006cm^{-1} [9]. Further, the peaks observed at 1489 cm^{-1} and 628cm^{-1} assigned to the ν(-N=N-) and νasym (Br) stretching vibrations respectively. In the Chromium(III) complex, the C=S characteristic stretching frequency is shown at 1168cm^{-1}, and the asymmetric ν(C-S) stretching appears at 1099cm^{-1} shift to higher energy due to coordination. Additionally, new bands appeared in 466cm^{-1} indicating (Cr–S). An azo functional group at 1462cm^{-1} [25]. Bromo (-Br) functional group asymmetric stretch at 624cm^{-1}. A strong thioureide ν(C–N) band was found in the around 1253cm^{-1} [26].

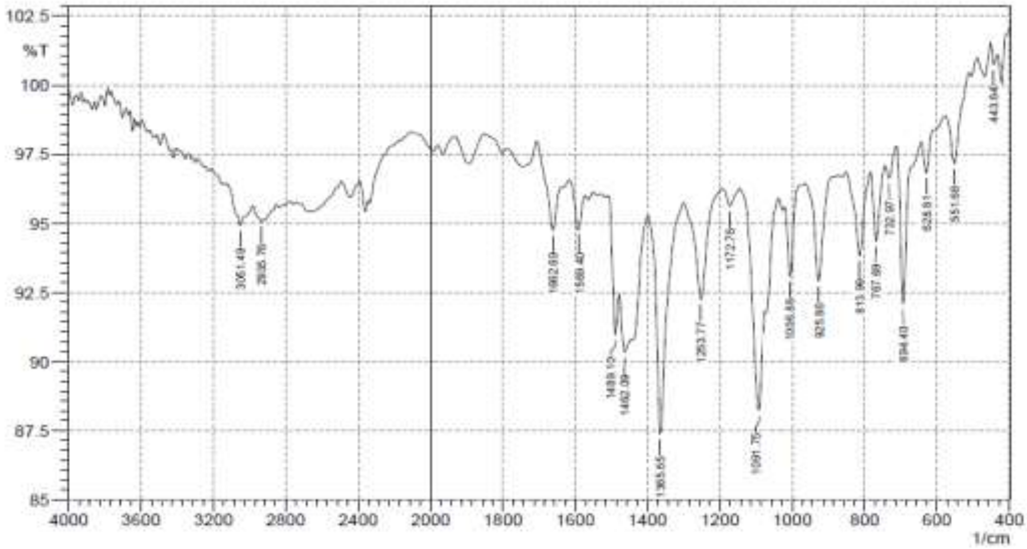


Figure 1. FT- IR Spectrum of reagent (L)

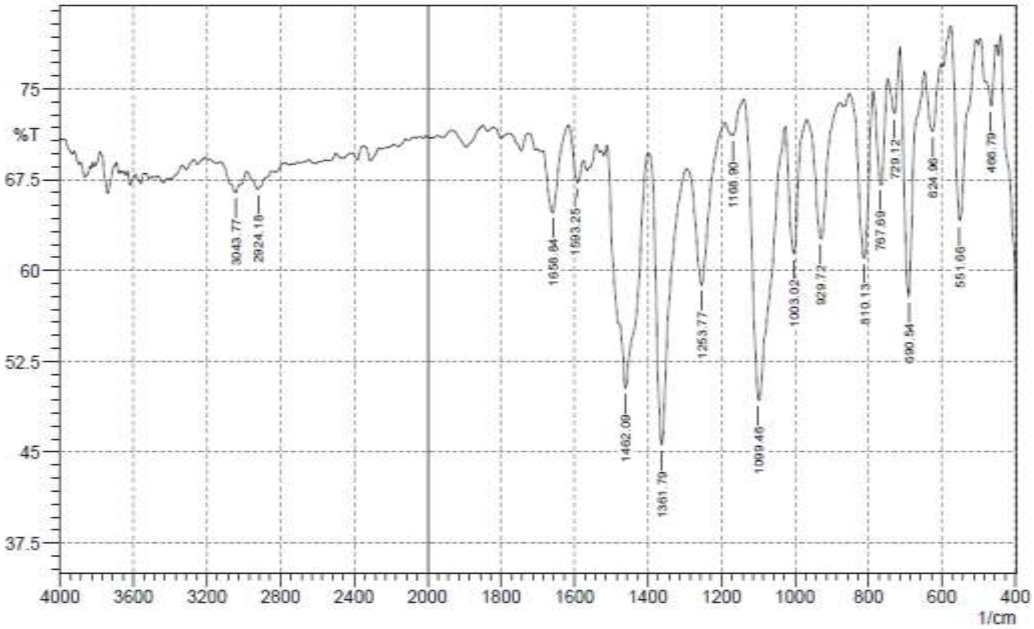


Figure 2. FT- IR Spectrum of complex

Mass Spectroscopy

As shown in Figs. 3 and 4, the mass spectrum of Reagent and Complex was obtained to determine their structural formula. The experimental parent molecular ion peaks of the prepared compound were (366.1), and (891.0) (m/z). Because they produce positive molecular ions and other positively charged fractions, azo, thioureido, and thiocarbonyl are the most important reagents, due to their significant relative abundance, reagent, and Complex have chosen a variety of fractionation processes [27].

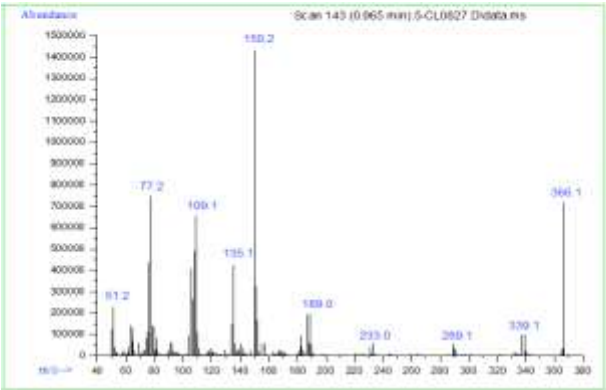


Figure 3. Mass spectrum of reagent(L)

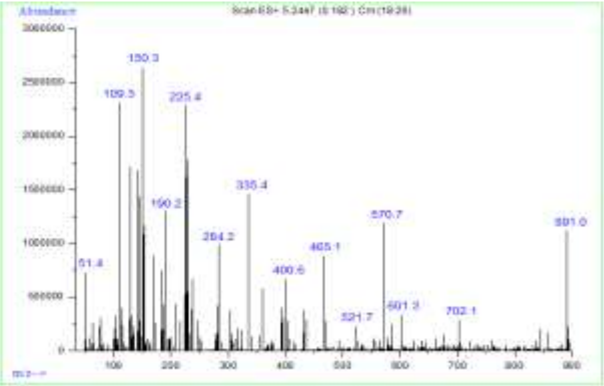


Figure 4. Mass spectrum of complex

^{1}HNMR and ^{13}CNMR spectroscopy

The reagent's ^{1}H NMR spectrum showed in Figs. 5a and 5b, showed a singlet peak at δ = 3.40 ppm equal to three methyl group protons in N–CH3, Several signals were seen in the region δ = 7.14–7.45 ppm are assigned to the N-phenyl rings protons following is: at the location δ= (7.14-7.16)ppm triplet peak assigned to the site's aromatic proton (b), the site δ= (7.33- 7.35) ppm a triplet peak corresponding to the aromatic proton in two sites (c) and the location δ= (7.44-7.45) ppm a duplet peak corresponding to the aromatic proton in the two sites (d) [28]. This indicates that the substitution took place on the sulfur atom during the interaction between sodium N-methyl-N-phenyldithiocarbamate and the diazonium salt to produce a reagent. A number of the signals seen in the area δ = 7.50–7.58 ppm is assigned to the protons of Azo-phenyl rings [9]. The ^{13}C NMR spectrum of the reagent is shown in Fig. 6. The dithiocarbamate substituent in the ^{13}C NMR spectrum is represented by a signal of thiocarbonyl carbon (C=S) in a weaker field at the site 193.95 ppm [24]. Signal observed in the site (35.05) ppm corresponds to methyl carbon attached to the nitrogen atom [29]. The reagent also showed a singlet peak at (δ =124.04, 127.43-127-71, 129.79, 130.35, 132.54, 138.96, and 156.39) ppm which belonging to carbons of aromatic rings.

In the ^{1}H NMR spectra of the complex shown in Figs. 7a and 7b, most proton signals were altered and displaced on complexation due to the coordination of the reagent with the metal ion. A singlet peak at δ = (3.31) ppm of the methyl group N–CH_3. The multiple singles that appeared in the site δ = (7.15–7.56) ppm are credited to the protons of N-phenyl rings [27]. The azo nitro benzene protons appeared sign in the location δ= (7.73-7.89) ppm [9,30]. ^{13}CNMR of the complex shown in Fig. 8, was recorded in DMSO-d^6, 52 ppm up field shifts are observed for the complex of NCS_2 carbon in comparison to the free reagent. This further supports the coordination via CS_2.

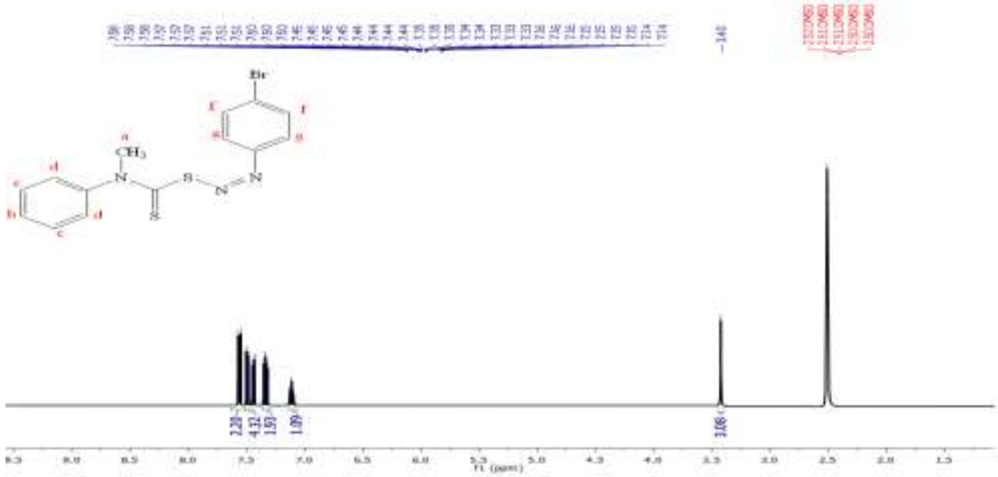


Figure 5a. ^{1}HNMR spectrum of reagent(L)

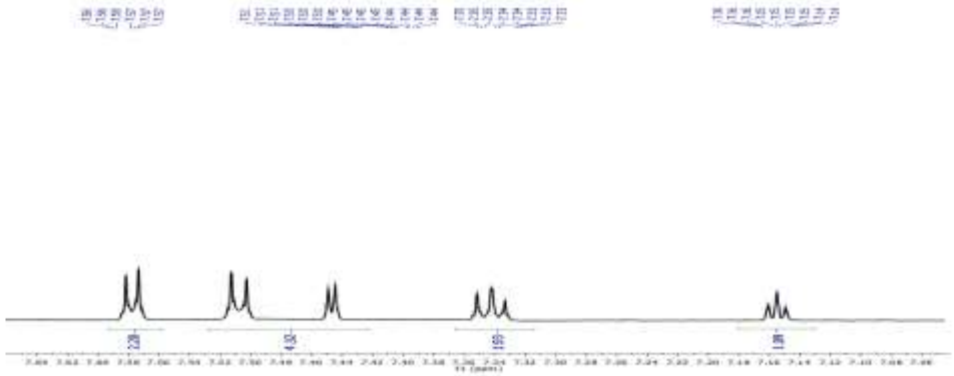


Figure 5b. ^{1}HNMR expansion of reagent(L)

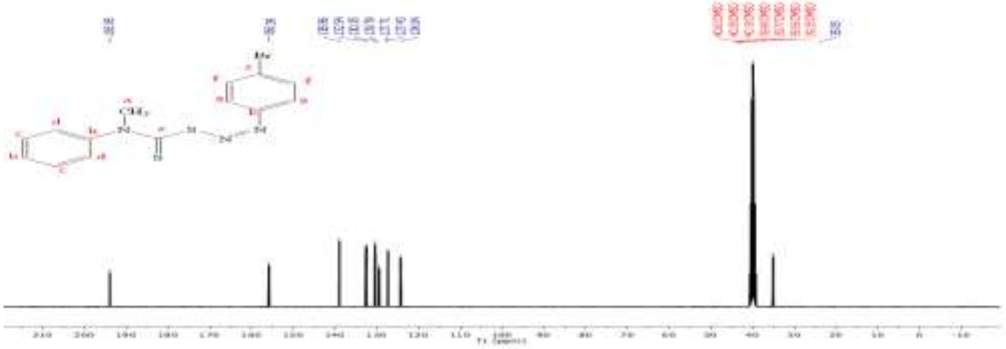


Figure 6. ^{13}CNMR spectrum of reagent(L)

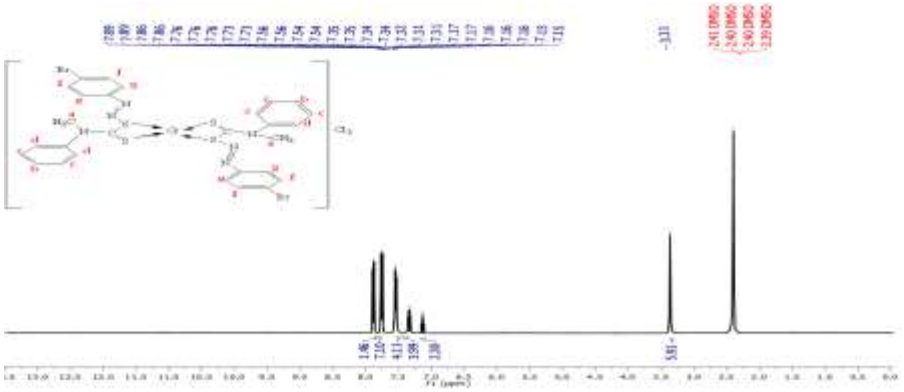


Figure 7a. ^{1}HNMR spectrum of complex

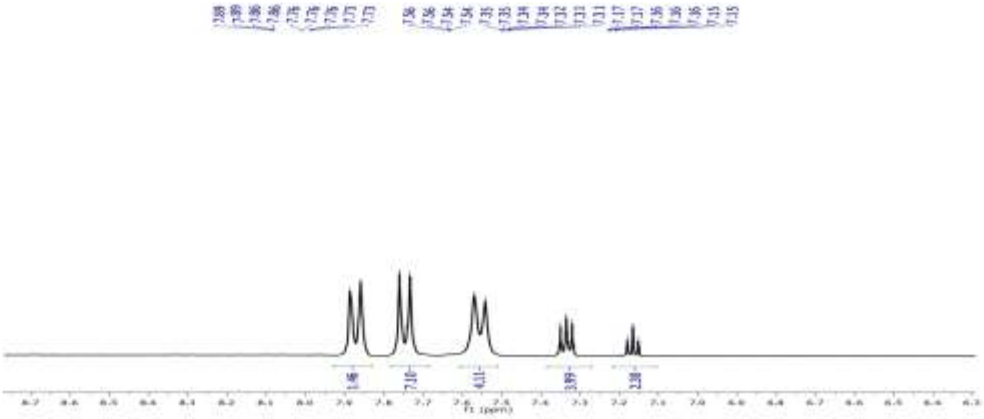


Figure 7b. ^{1}HNMR expansion of complex

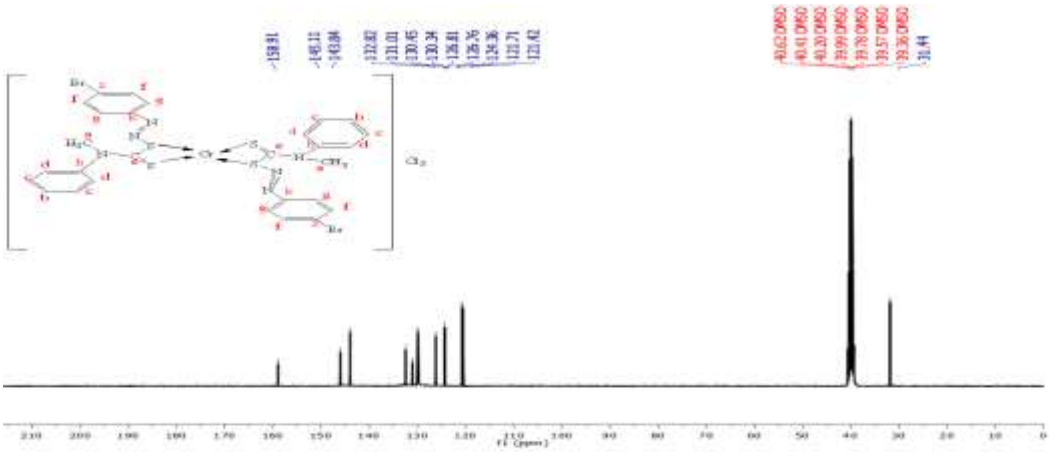


Figure 8. ^{13}CNMR spectrum of complex

Absorption spectra

Reagent and complex absorption spectrophotometry are shown in Fig. 9. After the complex formed, it was noticed that there was a movement toward the visible zone. where the reagent's wavelength is 413 nm belonging to the (n–π*) transition [31,32] and the complex's maximum wavelength is 536 nm.

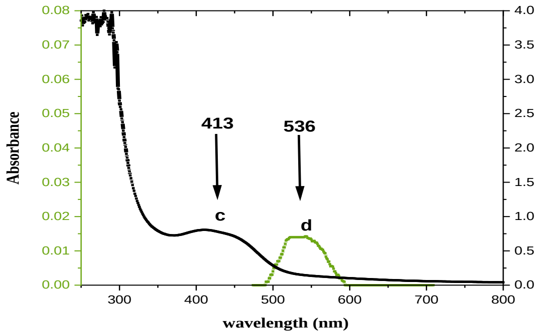


Figure 9. Absorption spectra for reagent (L) and Cr(III) complex

Optimization of the experimental conditions

Order of addition and pH effect

The add order is one of the most crucial variables examined. A change of order was observed in Cr(III) complex formation by using (10 ppm,10 mL) of Cr (III) and reagent (L) (0.01 mol L^{-1}, 0.5 mL) with 0.5 mL of 20% v/v Triton X-114. then heated for 5 min temperature of 75-80 ºC, followed by centrifugal separation, 0.5 ethanol addition to the rich phase, and UV-visible measurement, L-Cr(III)-TritonX114 was chosen as the addition order because it produced the best absorption results.

The pH plays the most important role in cloud point extraction by controlling how the target analytes for organic compounds partition in the micellar phase. The effectiveness of the extraction was examined in this work using a pH range of 1 to 10 by using pH solutions (0.1mol L^{-1} HCl and 0.1 mol L^{-1} NaOH) and the outcomes were acquired and afterward displayed in Fig. 10. The absorbance decreases at pH value greater than 7 due to hydrolysis of Cr(III) occurs.

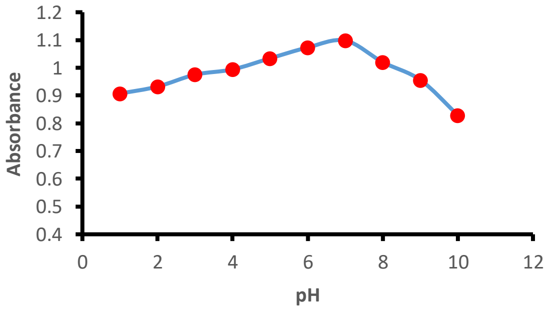
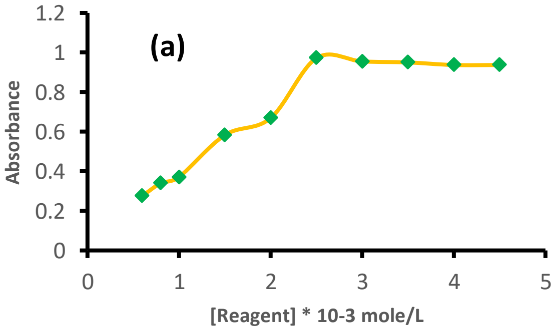


Figure 10. Effect of the pH for Cr(III) complex

Reagent concentration effect

One of the primary variables affecting the efficiency of extraction is the ligand concentration. The range of reagent concentrations used was 0.2×10^{-3} - 4.5×10^{-3} mol L^{-1}. The outcomes as shown in Figs. 11a and b. The better outcome is $2.5*10^{-3}$ mol L^{-1} of reagent.



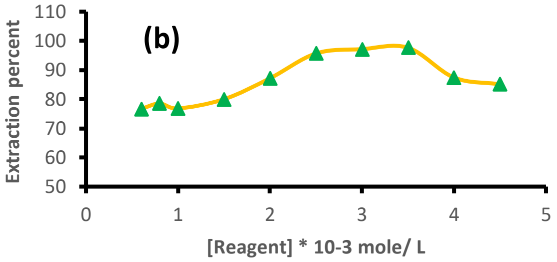


Figure 11. Effect of concentration reagent (L) for Cr(III) complex (a) variation of reagent concentration effect (b) Extraction percent estimation

Surfactant type and Triton X-114 concentration effect

The CPE efficacy determines the kind of surfactant utilized. Certain concentrations of various surfactant kinds were used in this study, including (TX-100, CTAB, TX-114, and SDS). When using various surfactant types, it was found that Triton X-114 delivered the best outcomes. The extraction efficiency is significantly impacted by the Triton X-114 concentration used as the extractant medium. To determine the ideal quantity, triton X-114 was used in various concentrations ranging from 0.50 - 4.00 mL. It was found that the complexes' absorbance rose when the amount of Triton X-114 was increased, reaching 3 mL. As shown in Figs. 12a and b.

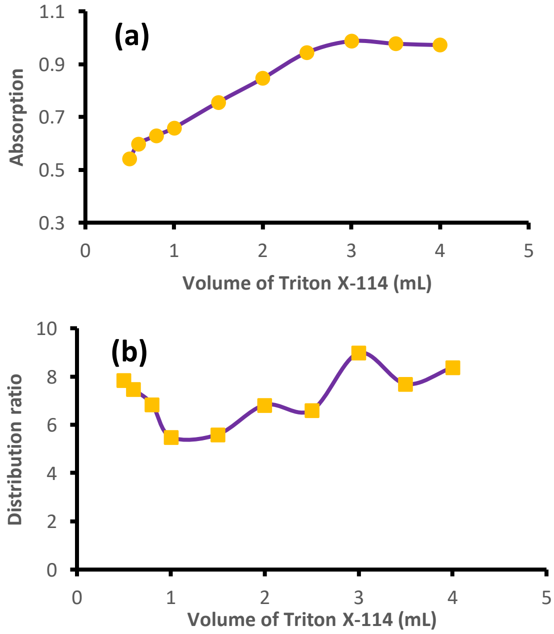


Figure 12. surfactant effect of complex (a) variation volume of surfactant (b)Distribution ratio

Temperature effect and incubation time

Cloud point extraction is a kind of equilibrium extraction. After determining the equilibrium temperature and incubation period, the best extraction efficiency was attained. The two factors were studied in the range of 50.0–85.0 ºC and 2.0–25.0 min, respectively, as shown in Figs. 13a and b. Maximum absorption was attained at a temperature of 75 ºC and for 15 minutes.

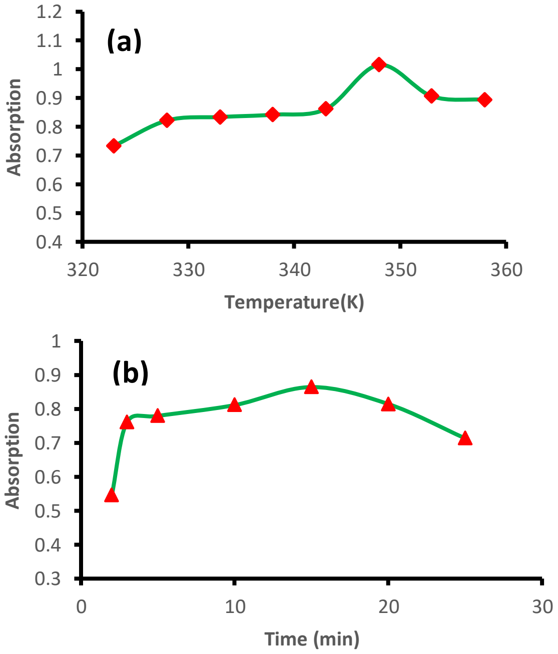


Figure13. (a) Temperature effect and (b) Time effect for Cr(III) complex

Salt out and interference effect

The addition of salt to the solution could affect the extraction procedure. A solution containing (0.5ml of 0.1 mol L^{-1}) of KCl, NaCl, NaF, NH_4Cl, $(NH_4)_2SO_4$, Na_2CO_3, and Na_2SO_4 was added to study the influence of salt on CPE. It was found that some salts, such as Na_2SO_4 and $(NH_4)_2SO_4$, induce a decrease in absorption value, while other salts cause an increase, as shown in Table 2. The approach selectivity under examination was determined by combining (0.5mL, 0.1 mol L^{-1}) from each interference [$Ni(NO_3)_2$, $Pb(NO_3)_2$, $CuCl_2.2H_2O$, $Cr(NO_3)_3$, $Co(NO_3)$, $MnCl_2.4H_2O$, $CdCl_2$ and $AgNO_3$] with (10mL of 10 ppm) Cr(III). It is noted that all interference interferes with metal and causes an increase in absorption, as shown in Table 3.

Table 2. Effect of salts out Cr(III)complex

Salt out	Abs filtrate	Abs rich phase	D	E%	Recovery%	Ere%
Abs. with out	0.017	0.882	51.882	98.109		
NaCl	0.026	0.892	34.307	97.167	101.133	1.133
KCl	0.028	0.973	34.75	97.202	109.080	9.080
NaF	0.029	1.087	37.482	97.401	111.716	11.716
Na_2CO_3	0.049	0.943	19.244	95.060	86.752	13.247
Na_2SO_4	0.026	0.708	27.230	96.457	75.079	24.920
$(NH_4)_2SO_4$	0.024	0.675	28.125	96.566	95.338	4.661
NH_4Cl	0.040	0.958	23.95	95.991	141.925	41.925

D: Distribution ratio = (conc. of analyte in rich phase/ conc. of analyte in aqueous phase), E%: Extraction percent= (D/1+D) *100, Re%= ((Measured Value/Actual Value)) *100, Ere%: Relative error percentage= (absolute error/Actual Value) *100, absolute error = Actual Value -Measured Value.

Table 3. Effect of interference Cr(III)complex

Interfering	Abs filtrate	Abs rich phase	Recovery%	Ere%
Abs. with out	0.017	0.882		
$Pb(NO_3)_2$	0.094	1.320	149.659	49.659
$Ni(NO_3)_2$	0.072	1.424	107.878	7.878
$Co(NO_3)_2$	0.03	1.466	102.949	2.949
$CuCl_2.2H_2O$	0.030	1.628	111.050	11.050
$MnCl_2.4H_2O$	0.047	1.733	106.449	6.449
Ag NO_3	0.023	1.434	82.746	17.253
$CdCl_2$	0.08	1.359	94.769	5.230

Re%= ((Measured Value/Actual Value)) *100, Ere%: Relative error percentage= (absolute error/Actual Value)*100, absolute error=Actual Value -Measured Value.

Calibration curve

Under the predetermined optimal circumstances, by adjusting the metal ion concentration to an extent of 0.3-2 ppm, the Cr(III) calibration curve was assessed. It was shown that absorption rises with increasing concentration, as it is a linear line. Absorbance and concentration were plotted on the calibration curve. Table 4. Results of the linear regression equation, linearity, slope, intercept, RSD%, r, r^2, LOQ, and LOD [33] for the estimation of Cr(III) using CPE and comparison with other published methods.

Table 4. Calibration Curve parameters

parameter	value CPE-UV-Vis new method	Value CPE-UV-Vis published method[34]
Regression equation	Y=0.363X-0.017	y = 0.0372x + 0.0237
r, r^2	0.994, 0.988	0.9904
Linear range (ppm)	0.3-2	$0–9 \times 10^3$
LOD (ppm)	0.124	2.5
LOQ (ppm)	0.377	------
Slope	0.363	0.0372
Intercept	0.017	0.0237
RSD% (n =5)	1.882	3.7

Application

After the metal study was completed of metal was studied on many medication models of drugs taken from various manufacturers, thirteen tablets of each kind were taken and the drug's content was assessed spectrophotometrically at λ_{max} 635 nm. By utilizing the t-test and F-test to compare the results of the new approach with a stock FAAS method for determining Cr(III) in the sample solutions, it was found that the concentration did not match the quoted value, therefore using the t-test and F- test, it appears that there is no significant difference between the new method and the FAAS method. As shown in Tables 5 and 6.

Table 5. Application for the determination of Cr(III) in pharmaceutical drugs

No. of Sample	**Quoted value and claimed content of active ingredient**	**Practical Content (Conc.) ppm**		**Rec% (New method)**	**Rec% (FAAS method)**
		New method	**FAAS**		
D1	0.1mg, (0.8 ppm)	0.81	0.78	101.25	97.50
D2	0.1mg, (0.8 ppm)	0.78	0.75	97.50	93.75
D3	0.1mg, (0.8 ppm)	0.83	0.85	103.75	106.25

Table 6. Statically data F- test and pair t- test for the determination of Cr(III) in pharmaceutical drug

No.of Sample	**X_d (ppm) New method with FAAS method**	**$\bar{X}_d$(ppm) ± Sd New method**	**RSD%**	**Paired t- test $\bar{x}_d\sqrt{n}/\bar{s}_d$ New method**	**$(\bar{X} \pm\sigma_{n-1})$ New method**	**$(\bar{X} \pm\sigma_{n-1})$ FAAS method**	**F cal.**
D1	0.03	0.04 ± 0.043	107.5	1.604	0.806 ± 0.025	0.793 ± 0.051	6.25
D2	0.03						
D3	-0.02						

F_{tab} at 95% confidence level, n-1=2 (19.00), t_{tab} at 95% confidence level, n-1= 2 (4.303)

$F_{cal} < F_{tab}$ non sig. difference, tcal. < t_{tab} non sig. difference.

Conclusion

N-methyl-N-((((4-bromophenyl)diazenyl)thio) carbonothioyl) aniline reagent synthesis by the reaction of (sodium N-methyl- N-phenyldithiocarbamate)with 4-bromobenzenediazoniume and used to prepare Cr(III) complex. According to elemental analysis (CHNS), FT-IR Spectra, UV-Visible spectra, ^{1}H NMR spectra, mass spectra, magnetic susceptibility, and molar conductivity, the structural formula of the complex was suggested. The molar conductance values of the Cr(III) complex indicate a 1:2 electrolytic natures.

Ecofriendly, sensitive, and selective spectrophotometric approach for determining the low concentration of Cr(III) using N-methyl-N-((((4 bromophenyl)diazenyl)thio) carbonothioyl) aniline reagent as complexing agent and CPE, the effectiveness of cloud point extraction is affected by pH at 7, 20 % triton X-114, incubation time 15 min, and 70 °C of heating. The suggested method was effective; the potential advantages of the current method are time savings, reducing the quantity of reagents used, and minimizing analyst effort. This method has been successfully applied to drugs such as (VITACED, A-Z VITAL, and Sinturom), and compared with the FAAS method, there were no significant differences, which indicates the possibility of using it as an alternative method.

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Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Karbala.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript

Author's Contribution Statement

The authors have participated in different roles as I. M. S. contributed an acquisition of data, drafting the MS and interpretation, A. F. K. participated for conception, design and acquisition of data and analysis while H. H. Mi. contributed for analysis and interpretation.

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استخلاص الطور السائل وتحديد أيون الكروم (III) في محلول مائي باستخدام كاشف مشتق داي ثايوكاربامات

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الخلاصة

تم تحضير الكاشف الجديد N-methyl-N - ((((4-bromophenyl) diazenyl) thio) carbonothioyl) aniline من تفاعل (sodium N-methyl- N-phenyl dithiocarbamate) مع (4-chlorobenzene diazonium salts). وشخص الكاشف الجديد بالطرائق الطيفية وهي، طيف الاشعة فوق البنفسجية، التحليل الدقيق للعناصر، طيف الاشعة تحت الحمراء، مطيافية الكتلة، مطيافية الرنين النووي المغناطيسي للبروتون والكاربون، التوصيلية المولارية والحساسية المغناطيسية. باستخدام البيانات التحليلية والطيفية، تم تحديد نسبة (الفلز: الكاشف)، ولوحظ أن المركب بنسبة1: 2 (فلز: كاشف). تم قياس التوصيلية المولية للمعقدات باستخدام DMF، وأظهرت النتائج أن المعقد الناتج كان أيونيا. تشير نتائج التحليل الدقيق للعناصر والدراسات الطيفية إلى أن المركب له بنية رباعية السطوح. تم تطوير الاستخلاص بنقطة الغيمة للتركيز المسبق وفصل الكروم الثلاثي في قياسات عينات الدواء باستخدام الامتصاص الذري للهب ومقياس الطيف الضوئي للأشعة فوق البنفسجية عند 536 نانومتر. تتأثر فعالية الاستخلاص بنقطة الغيمة بدرجة الحموضة، وتركيز Triton X-114 والكاشف، ونوع المادة الخافضة للتوتر السطحي، والتداخل، وتأثير الملح، والوقت، وتأثير درجة الحرارة. كان منحنى معايرة الكروم خطيًا في حدود 0.1-2 ميكروغرام مل-1 مع r2=0.9888. حد الكشف والتقدير الكمي هو (0.1246 و0.3777 ميكروغرام مل-1). تم تطبيق الطريقة الجديدة بنجاح لاستخلاص وفحص أيون المنغنيز الثنائي تحت ثلاث علامات تجارية دوائية.

الكلمات المفتاحية: ايون الكروم، مركبات الداي ثايوكاربامات، استخلاص السائل الدقيق، علامات تجارية فلزية صيدلانية، الطرق الطيفية.