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RESEARCH ARTICLE

Selective and Sensitized Spectrophotometric Determination of Cr(III) Ion using 2-(Phenyl)-4,5-di(4-methoxyphenyl)imidazole, Ligand for Speciation of Chromium Ion in Triton X-100 as Surfactant

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Abstract: Highly interference-free sensitized and sensitive spectrophotometric method for the determination of Cr(III) ion is described. The method is based on the reaction between Cr(III) ion and benzyl dioxime in micellar in the presence of non-ionic surfactant Triton X-100 has been performed. The absorbance is linear from 0.1 up to 25.0 μgml^{-1} in aqueous solution. The repeatability (RSD) is 1.3% at a concentration of 1 $\mu g\ mL^{-1}$ with molar absorption coefficient of 68,600 $Lmol^{-1}cm^{-1}$ and detection limit of 0.12 $ngmL^{-1}$. The influence of reaction variables including pH, amount of 2- (phenyl)-4,5-di(4-methoxyphenyl)imidazole (PDMPI), type and amount of surfactant, complexation time and the effect of interfering ions, were investigated. The proposed methods have been applied to the rapid and simple determination of Cr(III) ion in the real samples successfully with recovery yield of almost 100%. The method does not need any separation or organic solvent extraction.

Keywords: Cr(III), Surfactant Triton X-100, separation, Determination, Spectrophotometry

Introduction

Chromium is one of the most abundant elements on Earth. The amount of chromium in the environment has gradually been increased predominantly by industrial activities especially from tanneries, mines and incinerators[1]. Chromium is stable in Cr(III) and Cr(VI) oxidation states in aqueous solutions[2]. The spectrophotometric and extraction method have been described for chromium determination according to coordination with different ligands[3-6]. Several methods require complicated and expensive instrument and are time consuming, low reproducibility of results is another restriction. Meanwhile there is trace chromium(III) ion in real samples, so that new methods for selective, sensitive rapid and convenient determination should be developed[7]. The spectrophotometric determination and organic

micellar media are employed as powerful tools in analytical application[8,9]. Environmental or real samples has low concentration and matrix effects with detection limit of metal[10]. Micellar systems are convenient to use because they are optically transparent, readily available and stable[11]. In the field of metal ion complexation, micelles form a ternary complex at concentrations below or above the critical micelles concentration (CMC) which has advantageous properties, such as hyperchromic and bathochromic displacements, so that sensitivity of the method can be modified by affecting the interferences of matrix[12]. Micellar system has an important ability to solubilize slightly insoluble or even very insoluble complexes and/or ligands which introduces it as a typical manner[13–15]. The ability of micelles to solubilize complexes in aqueous solution eliminates non-aqueous extraction step in a given analysis[13,16,17]. Many of these methods require complicated and expensive instrument and are time consuming, some of them has low repeatability and need more care for sensor preparation. However, the spectrophotometric method still has the advantages such as simplicity and requires no expensive or complicated test equipments. So that a wide variety of spectrophotometric method for the determination of chromium have been reported[18-23]. Due to the well known effect of surfactants in extraction system which emerged from their ability in phase separation, solvent extraction, especially in surfactant media have been successfully applied in the extraction, preconcentration and purification of many species especially in the separation of metal ions[24,25]. Thus, analytical methods which is based on sensitized spectrophotometric reagents permit measurements in the nano to micro molar range because they are often sufficiently sensitive and show an intense absorbance peak, and determination of trace ions is possible by conventional spectrophotometry. In the present work highly selective, simple and sensitive spectrophotometric method for determination of chromium(III) ions using PDMPI in surfactant media (Triton X-100) was established. The effect of various parameters such as pH, type and amount of surfactant and amount of 2-(phenyl)-4,5-di(4-methoxyphenyl)imidazole[26], ligand were examined. Time dependency of complex and effect of interference of other metal ions were evaluated. The method successfully has been used for determination of Cr(III) ion content in real samples, due to wide linear range, low detection limit, high sensitivity, selectivity and high repeatability.

Experimental

The UV/Vis spectra a Perkin-Elmer, model Lambda 2 was used to measure the absorbance of complex in Triton X-100 media. a Genway model 3510 pH/Ion meter with a combined glass and calomel electrode has been applied to adjust the pH and prepare the buffer solution. The Cr(III) ion determinations was carried out on a Perkin-Elmer 603 atomic absorption spectrometer outfitted a hollow cathode lamp and a deuterium background corrector, at an air–acetylene flame under the recommended conditions.

Reagent and solution

All chemicals such as nitrate of Cr(III) ion and other cation were purchased from Merck Company with analytical grade. All surfactant with 0.5% (w/v) were from Merck company including Triton X-100, sodium dodecyl sulfate (SDS), Brij58, cetyltrimethylammonium bromide (CTMAB), n-dodecyltrimethylammonium bromide (DTMAB) was prepared by dissolving 0.5 g of surfactant in a volumetric flask with stirring. The 2-(phenyl)-4,5 -di(4-methoxyphenyl)imidazole[26] was purchased from Merck company and used without further purification.

Synthesis of 2-(Phenyl)-4,5-di(4-methoxyphenyl)imidazole (PDMPI)

A mixture of 4-methoxybenzaldehyde (1 mmol), benzyl(1 mmol), and ammonium acetate or primary amine (6 mmol) in ethanol (5 mL) was added to silica-bonded *N*-propylsulfamic acid (0.0025 g) and heated at 130 ^{0}C in an oil bath. The reaction process was checked by TLC, after completion the reaction mixture was filtered and remaining washed with warm acetone (20 mL). After cooling and purification by recrystallization from hot ethanol, the corresponding products were obtained. The recovered catalyst for subsequent runs was used again. The product was synthesized according to the literature[26] and purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:5)] to give pure 2-(phenyl) -4,5-di(4-methoxyphenyl)imidazole, ligand in 94% yield, Figure 1.

MP: 110-112 ºC ^{1}H NMR (DMSO-d_6, 400 Hz) δ: 3.77 (s, 6H), 6.95 (d, 4H, J=8.1 Hz), 7.35 (t, 1H, J=7.3 Hz), 7.44-7.48 (m, 6H), 8.07 (d, 2H, J=7.3 Hz), 12.54 (brs, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 55.1, 113.8, 125.0, 127.0, 128.6, 128.9, 130.5, 144.8, 158.3, 172.0.

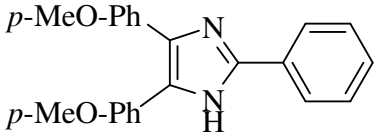


Figure 1. 2-(Phenyl)-4,5-di(4-methoxyphenyl)imidazole (PDMPI)

Calibration curve procedure

Standard Cr(III) solutions were prepared in the range of 0.05–30.0 µg mL^{-1}. Several aliquots of Cr(III) ion were added to 10 mL volumetric flask, and 0.8 mL of 1mM PDMPI and 1mL of 0.55mM Triton X-100 were added to each flask, then 2 mL 0.01M NaOH was added and filled to the mark and calibration curve of Cr(III) was constructed using a UV–Vis 160 spectrophotometer.

Pretreatment of real samples

Water samples

For determination of Cr(III) ion content in water samples, analysis was performed as following: In a beaker includes 8 mL concentrated HNO_3 and 3 mL of H_2O_2 of 30% to elimination and decomposition of organic compound were added to 200 mL of samples. The samples were heated to one tenth volume while stirring. All samples were performed according to general described procedure[27] after adjustment of samples pH to desired value.

Blood sample

20 mL of homogenized blood sample was weighed accurately and was added in a beaker with an oxidizing agent and 10 mL concentrated HNO_3 and 2 mL $HClO_4$ 70 %, the content of the beaker was heated for 1 h, then filtered through a Whatman No. 42 filter paper into a 250 mL calibrated flask, after adjustment of pH to desired value, it was diluted to mark with de-ionized water. Amount of Cr(III) ion was found by standard addition method[28] for all of real and synthetic samples.

Vegetable sample

Spinach sample bought from Shiraz, Iran was taken in small mesh. A 40 g sample was heated in silica crucible for 3 hours on a hot plate, the charred material was transferred to

furnace to heat overnight at 650 ^{o}C. After cooling the residue, it was treated with 10 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 hours at the same temperature so that all organic traces compounds are left. The final residue was treated with 2-4 mL 70% perchloric acid and 3 mL hydrochloric acid then evaporated to fumes, so all the metals change to respective ions. The solid residue was dissolved in water, filtered and kept at pH 8.0[29].

Results and Discussion

Metal ions with complexing agent constitute stable compounds in surfactant media and formed aggregates that cause an improvement in sensitivity and detection limits.

Absorption spectra of Cr(PDMPI)$_3$ in Triton X-100 media

After Cr(III), PDMPI and Triton X-100 were added to a 10 mL volumetric flask and the solution was diluted to the mark at pH=10 so the concentrations of these reactants were changed to 2.0×10^{-6} M, 8.0×10^{-3} M and 5.5×10^{-4} M respectively. Then, the absorption spectrum of $Cr(PDMPI)_3$ in the presence and absence of Triton X-100 was obtained, which is shown in Figure 2. Examinations in micellar media has higher sensitivity need to extraction of complex to organic phase. The studies focused on complexation of Cr ion and PDMPI in micellar media and the aim is evaluating optimum conditions for its sensitized spectrophotometric determination. The stability and decomposition rate of complex seriously depend on pH and time which is confirmed by low sensitivity and omitting spectra in acidic media. The time dependency and rate of complex formation was investigated at the optimum pH. The effect of various parameters such as pH, type and amount of surfactant and amount of ligand were examined. Time dependency of complex and effect of interference of other metal ions were evaluated. Complexation with PDMPI has been successfully in aqueous media in the presence of surfactant, the method has wide linear range, low detection limit, high sensitivity and selectivity and high repeatability which has high dependency to the reactant addition order (Addition of surfactant before ligand lead to orange color and addition of Cr(III) ion in the end lead to a red color). The desired complex has high time dependency and has high solubility in alkali media with pH = 10, although the sensitivity can be improved by addition of suitable surfactant. After adding Cr(III), PDMPI and Triton X-100 to a 10 mL volumetric flask which their concentrations were 8.0×10^{-3} M, 5.5×10^{-4} M and 8×10^{-3} M respectively, they were diluted to the mark with 0.01M KOH. The absorption spectrum of complex in the presence and absence of Triton X-100 was obtained, which is shown in Figure 2. A red color complex of chromium ion was formed after stirring for 8 min quantitatively which used for spectrophotometric determination of Cr(III) ion. A red complex formed after stirring the solution for about 8 min and spectrophotometric determinations of Cr(III) ion were done on this complex. The method has advantages including simplicity, speedy, no need to extraction of complex to organic phase and no need to harmful.

pH effect on sensitivity

The absorbance of desired complex in 5.5×10^{-4} M Triton X-100 media for its quantitative determination with the PDMPI in micellar media was investigated over the range 3–10 of pH. The complex was surveyed for acidity effect on the absorbance which are shown in Figure 3. The results indicate that $Cr(PDMPI)_3$ has maximum absorption in alkaline pH 8.0. At pH <8.0 the intensity of the desired complex decreases most probably due to partial hydrolysis of chromium ion. We assume that complex formation could have competed against ligand protonation at lower pH which lead to incomplete complex formation and lower sensitivity.

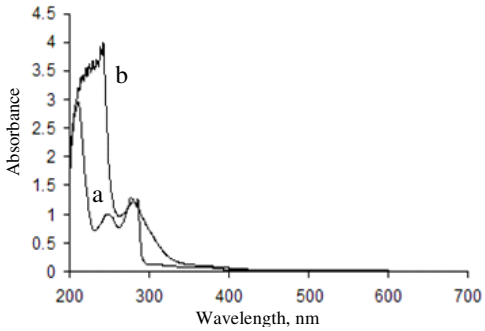


Figure 2. The absorption spectra of 10 µgmL^{-1} Cr(III) complex with PDMPI in the presence (a) and absence (b) of surfactant at optimum condition of reagents (mentioned concentrations at pH=10) organic solvent

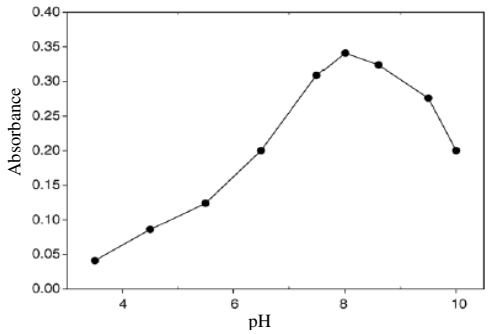
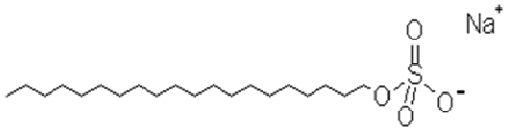


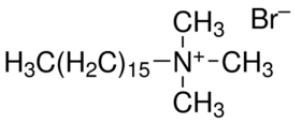
Figure 3. Effect of pH on sensitivity of Cr(III) in micellar media according to the conditions

Effect of surfactant on sensitivity

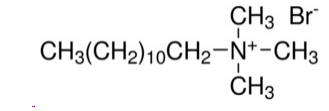
The desired complex and PDMPI has good water solubility in alkaline media, but sensitivity of its complex in the absence of surfactants is low. In order to increase the sensitivity, different types of surfactants with different concentrations were examined. The structures of them have been shown in Figure 4. To ensure the effect of types of surfactants, Triton X-100 and Brij 58 as non-ionic, sodium dodecyl sulfate (SDS) as anionic surfactant and cetyl-trimethylammonium bromide (CTMAB) and *n*-dodecyltrimethylammonium bromide (DTMAB) as cathionic surfactant on the absorbance of the complex were studied. As shown in Table 1, Triton X-100 5.5×10^{-4} M media below its critical micelle concentration[30,31], could be constructed the calibration curve with high sensitivity and red shift and its slope was approximately c.a. which is two times more than in the absence of surfactant. In other media, the spectra shows lower sensitivity, so Triton X-100 was selected for further studies. This observation illustrated a non-ionic surfactant could increase sensitivity, on the other hand it shows the complex interacts with the Triton X-100 as non-ionic surfactant by hydrophobic solvation of the chelate. Besides the electrostatic interactions can have a significant effect on solubility**.** It seems that PDMPI combines with Cr(III) ion to form a more polar complexes, and the complexes is extracted instantaneously in the local polar environment of micelle of non-ionic surfactant. The desired complex was homogenously dissolved in micellar media with molar absorptivity of 68,600 L moL^{-1} cm^{-1}. It seems Brij 58 due to long nonpolar chain, prevents applying electrostatic interactions. Without any surfactant, the absorbance is very low.



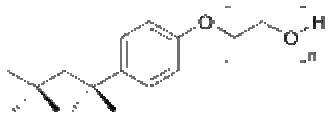
Sodium dodecyl sulfate(SDS)



Cetyltrimethylammonium bromide(CTMAB)



N-dodecyltrimethylammonium bromide (DTMAB)



Polyoxyethyleneoctylphenyl ether (Triton X-100)

$HO(CH_2CH_2O)_{20}C_{16}H_{33}$ Polyoxyethylen (23) dodecanol (Brij-58)

Figure 4. Structures of different types of surfactants

Table 1. The effect of the surfactant types on method sensitivity according to the conditions

Surfactant	Absobance	Maximum wavelength (nm)
SDS	1.95	287
Brij 58	2.22	293
CTAB	1.26	284
DTAB	1.46	284
Triton X-100	3.27	295

The effect of Triton X-100 concentration

Sensitivity of the complex was examined with various concentrations of Triton X-100. The Results are shown in Figure 5. Triton X-100 surfactant with less than its critical micelle concentration (CMC), can form the homogeneous solution at a point where Cr(III) – PDMPI complex can be well dissolved. The CMC is an important characteristic of a surfactant, it is a concentration in which micelles are performed, in this concentration micelles are produced from about 200-400 activating monomer. When the concentration of Triton X-100 increases from 1.5×10^{-4} to 6.5×10^{-4} at pH 8.0 for PDMPI, the absorbance of desired complexes at concentration of 10 µg ml^{-1} Cr(III) ion, increases sharply with increasing in Triton X-100 concentration up to 5.5×10^{-4}M concentration of Triton X-100.

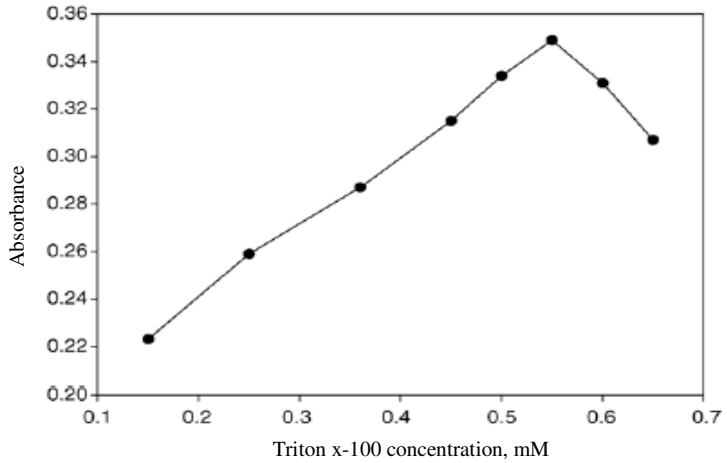


Figure 5. The effect of Triton X-100 concntration on sensitivity of Cr(III) ion according to the conditions

The effect of PDMPI concentration on sensitivity

The concentration of PDMPI has a deep effect on the absorbance of the chromium complex. For this evaluation at fixed value of other parameters, for a 10 µg ml^{-1} Cr(III) ion, various amount of ligand was added to similar solutions at optimum conditions. Results which has been shown in Figure 6 describes that maximum absorbance was happened at ligand concentration higher than 8 mM. So we added PDMPI more than 20 times Cr(III) concentration to reduce fluctuation in measurement.

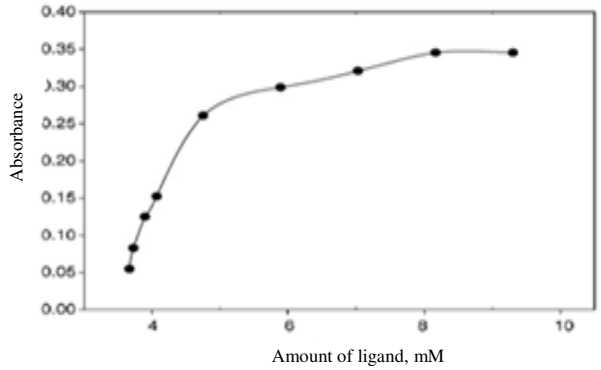


Figure 6. Effect of PDMPI concentration on sensitivity at optimum conditions

Investigation of the composition of complex and the order of reactants integration

Reactants order and the rate of complex formation were examined. They are no significant effects on reaction rate at temperature about 15 ^{o}C. Thus once at fixed concentration of reactant and then with variety of concentrations, the order of reactants integration was calculated as 1:1:2 for Triton X-100: Cr(III): PDMPI at room temperature after 5 min. It shows that the order of addition of reagents are very important. If the chromium ion and ligand were poured at first and then Triton X-100 was added, an orange complex was formed, while the reverse order lead to the formation of a red complex. It is clear that the surfactant and ligand are formed a suitable groundwork for metal acceptance. The choice of suitable complexation time requires a trade-off between sensitivity, speed and selectivity. The various complexation time on method sensitivity was examined, which results shown in Figure 7. Express that reaction time maximum sensitivity can be obtained after 5 min.

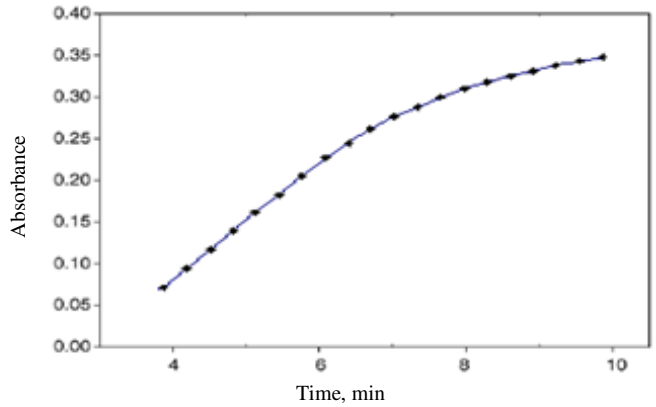


Figure 7. Effect of complexation time on sensitivity at optimum conditions

Calibration curve and detection limit and reproducibility

By using the sensitized spectrophotometric method with various concentration of the chromium ion, a calibration plot for the determination Cr(III) ion was prepared according to the general procedure under the optimum conditions. The dynamic range of Cr(III) was 0.1–25.0 μg ml^{-1} with correlation coefficient (R_2) of 0.9989 shows the good linearity of calibration curve. It was found that the detection limit was 0.12 ngmL^{-1} based on the signals of ten blank solutions and the slope of calibration curve. To assurance of reproducibility of method at optimum condition five experiments has been performed and results can be obtained at optimum conditions that indicate repeatable results. The result of repeatability as RDS for 10 μg mL^{-1} Cr(III) ion is 1.3%.

Interference effect

The effect of potential interfering ions on the determination of Cr(III) ion at optimum condition were investigated by addition known concentrations of each ion to a fixed Cr(III) ion concentration and the absorbances with various amount of common interfering ions that concomitant with chromium in real samples were measured. If the sensitivity and extraction efficiency does not differ more that 5% analyte signal in the absence of the interfering ion, that ion does not interfere. Therefore various amount of interfering ion was added to 1 μg mL^{-1} of Cr(III) ion and results are shown in Table 2. Results display among the ions studied, several ions could be tolerated up to the mg level. The method has good selectivity even in the presence of copper, iron and cadmium ions. This unique selectivity is due to high pH.

Table 2. The effects of the matrix ions on the recoveries of the examined chromium(III) ion (N=6)

Ion	Added as	Tolerance Limit, mM L^{-1}
Cl^-, K^+, Na^+	KCl, NaCl	13.4, 17.1
Mg^{2+},Ca^{2+}	Chloride salts	95.3, 111
Cu^{2+}	Nitrate salts	0.37
HCO_3^-	$NaHCO_3$	11.9
SCN^-	KSCN	10.3
PO_4^{3-}	Na_3PO_4	2.4
Fe^{3+}	Nitrate salts	0.12
CO_3^{2-}	Na_2CO_3	3.8
Mn^{2+}	Nitrate salts	0.84
Cd^{2+}	Nitrate salts	0

Analytical application in real samples

To distinguish the applicability of the method to real samples with different matrices, containing various amounts of diverse ions, some studies were performed. Especially spiking experiments and independent analysis were used in order to increase accuracy and reliability of proposed method. The proposed method was applied for water, blood and vegetables samples and total chromium(III) in them was determined. The results are shown in Table 3, and compared with those obtained by atomic absorption spectrophotometry. The examinations show the level of the analyte ions are below the detection limit of related element. Due to importance of replicability, three analyses of each sample were performed and show that the ions recoveries are almost quantitative with a low RSD. The recovery of spiked samples is reasonably satisfactory and was confirmed using standard addition method, which indicates it is a reasonable method for determination of trace amounts of these elements in different samples.

Table 3. Recovery of trace chromium(III) from water, vegetables and blood sample after application of presented procedure (N=6)

Sample	Added,ng L^{-1}	Founded, ng L^{-1}	RSD %	Recovery %
Tap water	0	0.110	1.1	-
	1.0	0.160	1.8	103
River water	0	0.061	1.1	-
	1.0	0.164	1.3	95.3
Spring Water	0	0.068	2.1	-
	1.0	0.165	1.5	97.8
Vegetable	0	0.067	1.7	-
	1.0	0.228	2.7	100.8
Blood	0	0.064	1.9	-
	1.0	0.170	2.3	102

Table 4. Investigation of method repeatability according to Table 3

Parameter	Optimum value for Cr(III) ion
Ligand concentration (M)	8.0×10^{-3}M
pH	8.0
Linear range (μg mL^{-1})	12.0
Regression equation	$A = 0.0934C_{Cr} - 0.0046$
Surfactant and its concentration (M)	5.5×10^{-4}M Triton X-100
Equilibration time (min)	8.0
Solvent	Water
Selectivity	High
Detection limit (ngmL^{-1})	0.12
Accuracy and precision	High
Advantages	High sensitivity, selectivity, wide linear range, repeatability, and no need to organic solvent
Disadvantages	Do not preconcentrate

Conclusion

The optimum value of parameters is presented in Table 4. The proposed method has premium such as simplicity, selectivity and high sensitivity for the determination of Cr(III) ion without the need for organic solvent extraction. It does not need preconcentration or pre-separation[30-33]. An efficient analytical method for determination Cr(III) was successfully developed by using a sensitized spectrophotometric using PDMPI. The method because of advantages such as high selectivity and sensitivity, low detection limit, low cost, simplicity, and no need to extraction and without any harmful organic solvent is a good alternative method for chromium determination with respect to previously reported methods.

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