Pergamon

Talanta, Vol. 41, No. 2, pp. 179–185, 1994

0039-9140/94 $6.00 + 0.00

SPECTROPHOTOMETRIC DETERMINATION OF COPPER(II), NICKEL(II) AND COBALT(II) AS COMPLEXES WITH SODIUM DIETHYLDITHIOCARBAMATE IN CATIONIC MICELLAR MEDIUM OF HEXADECYLTRIMETHYLAMMONIUM SALTS

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(*Received* 24 *May* 1993. *Revised* 12 *August*, 1993. *Accepted* 19 *August* 1993)

Summary—The determination of copper(II), nickel(II) and cobalt(II) was carried out as diethyldithiocarbamate (DDTC) complexes in presence of aqueous solutions of cationic surfactants of hexadecyltrimethylammonium bromide, chloride and hydroxide (CTAB, CTAC, CTAOH). The presence of micellar systems avoids the previous step of solvent extraction necessary to the formation of the DDTC complexes in absence of micelles. The influence of the different micellar counterions on the analytical characteristics (sensitivity and detection limits) of the proposed method for spectrophotometric determination of Cu(II), Ni(II) and Co(II) was studied.

Micelles are dynamic aggregates of amphiphylic molecules, called surfactants, that possess both polar or ionic and unpolar moieties. In very diluted aqueous solutions, surfactants are dissolved and exist as monomers but, when their concentration exceeds a characteristic value known as the critical micelle concentration (cmc), they spontaneously associate to form aggregates called micelles.[1-5]

These organized molecular assemblies are used in spectroscopic measurements due to their possible effects on the system of interest. In the field of metal ion complexation, at concentrations above the cmc, micelles form a ternary complex with advantageous properties, such as hyperchromic and bathochromic displacements, that can modify sensitivity and selectivity of the method by affecting the interferences and matrix effects.[6-12] The ability of micellar systems to solubilize slightly insoluble or even very insoluble complexes and/or ligands has been used to enhance the analytical merit of given methods.[6,8,13,14] Most research in micellar metal ion determination studies cationic and nonionic surfactants due to direct anionic surfactant–metal ion interactions which inhibit metal ion–ligand complex formation.[10]

Diethyldithiocarbamate (DDTC) is one of the most widely used photometric reagents for copper and, less often, other elements like nickel or cobalt. Metal–DDTC complexes are water insoluble and thus, the determination requires a prior solvent extraction step into chloroform or carbon tetrachloride.[15,16] This complication can be avoided either by using dithiocarbamates containing hydrophilic groups or by the addition of large amounts of alcohol or another water-miscible solvent such as acetic acid.[15,17]

Nevertheless, the addition of surfactants in concentrations above the cmc to the aqueous medium to form a micellar solution is the most commonly preferred procedure nowadays. Nonionic surfactants like Triton X-100, have been used for the spectrophotometric determination of Cu(II) with DDTC[18] and Hg(II) and Ag(I) by displacement of Cu(II)–DDTC complexes.[19]

This paper describes a procedure to determine Cu(II), Co(II) and Ni(II) with DDTC in the presence of cationic micelles, hexadecyltrimethylammonium salts (CTAX) with the purpose of studying the influence of micellar counterions ($X = Br^-$, Cl^-, OH^-) upon sensitivity and detection limits.

EXPERIMENTAL

Reagents

All reagents used were from Merck and of analytical grade. Stock solutions of nickel(II),

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cobalt(II) and copper(II) were prepared from nitrate salts. The sodium diethyldithiocarbamate solutions were freshly prepared in distilled water just before use to avoid acid decomposition. The surfactant hexadecyltrimethylammonium hydroxide, CTAOH, was synthesized by an ion exchange method, from hexadecyltrimethylammonium bromide (CTAB), with the anionic resin Amberlite 21K, 20–50 mesh.

Apparatus

A Hewlett-Packard Diode Array Spectrophotometer, model HP8452A, equipped with 1 cm quartz cells was used to record the absorption spectra and to measure the calibration absorbance data at chosen wavelengths.

Flame atomic absorption spectrometric measurements were carried out in a Perkin-Elmer instrument model 2380.

A Metrohm pH-meter, with a Metrohm combined electrode was used to measure the pH of solutions and all cmcs were determined using a Crison 522 conductimeter.

Spectrophotometric UV–Vis and conductimetric measurements were carried out at 25 ± 1°C with a Braun thermostatic bath model Thermomix BU.

Synthesis of hexadecyltrimethylammonium hydroxide

In order to have the ion exchange resin in hydroxide form, it was placed in a column and prior to use, several ion exchange cycles were conducted (OH^-–Cl^-) that left the resin in hydroxide form. The column was also thermostated at 37 ± 1°C to avoid CTAB precipitation and then a $0.12M$ CTAB solution was slowly passed through the resin where an ion exchange between bromide of CTA^+ and hydroxide of resin occurs. The effluent was collected in a flask closed in a nitrogen atmosphere, because CTAOH is unstable in oxygen air. After obtaining the CTAOH, it was titrated in the following form to know the actual concentration. The CTA^+ was precipitated with $HClO_4$ (Merck 70%) $0.1M$ previously titrated with standardized NaOH. The excess of $HClO_4$ was titrated with NaOH and CTAOH concentration of $0.07M$ was obtained. The CTAOH solution was stored in a refrigerator.

Procedure

Conductimetric determination of surfactants' cmc at different DDTC concentrations. The values of cmc for CTAB and CTAC in absence and in presence of different DDTC concentrations (5×10^{-5}–$5 \times 10^{-4}M$) were obtained from conductivity measurements. The surfactant concentration was ranged 1×10^{-4}–$2.5 \times 10^{-3}M$ for CTAB and 2×10^{-4}–$2.2 \times 10^{-3}M$ for CTAC. The occurrence of sharp inflexion point in the plots of specific conductivity *vs* surfactant concentration indicates the cmc's values.

Spectrophotometric metal ion determination in micellar solutions. Appropriate quantities of stock metal ion solutions, DDTC and the chosen surfactant were added to a series of 25 ml volumetric flasks and made up to volume with distilled water. The metal concentration was ranged from 2×10^{-6} to $3 \times 10^{-5}M$ for Ni(II), from 5×10^{-6} to $5 \times 10^{-5}M$ for Co(II) and from 1×10^{-5} to $8 \times 10^{-5}M$ for Cu(II). DDTC concentrations were $2 \times 10^{-4}M$ for nickel and cobalt complexes and $4 \times 10^{-4}M$ for the copper complex. Surfactant concentrations, pH values and analytical wavelengths, are indicated in Table 1.

Spectrophotometric metal ion determination after extraction with CCl_4. Appropriate volumes of stock metal and DDTC aqueous solutions were placed into an extractive funnel and 10 ml of CCl_4 were added. The organic layer was transferred to a 25 ml volumetric flask. In order to obtain complete extraction, the process was repeated twice, the first time with 10 ml and the

Table 1. Experimental conditions for metal ion determination with DDTC in cationic micellar medium (CTAX) and by solvent extraction in carbon tetrachloride

Surfactant		CTAB $0.020M$	CTAB $0.096M$	CTAC $0.022M$	CTAC $0.111M$	CTAOH $0.015M$	CTAOH $0.060M$	CCl_4
Co(II)	Wavelength	324 *nm*	324 *nm*	324 *nm*	324 *nm*	NC*	NC	322 *nm*
	pH	7.7	8.0	6.0	6.2	NC	NC	8.0
Ni(II)	Wavelength	326 *nm*	326 *nm*	326 *nm*	326 *nm*	NC	NC	328 *nm*
	pH	6.5	7.5	6.3	6.5	NC	NC	6.7
Cu(II)	Wavelength	440 *nm*	440 *nm*	436 *nm*	436 *nm*	436 *nm*	436 *nm*	436 *nm*
	pH	7.7	8.0	6.5	6.7	12.2	12.7	7.6

*NC: No complex formation.

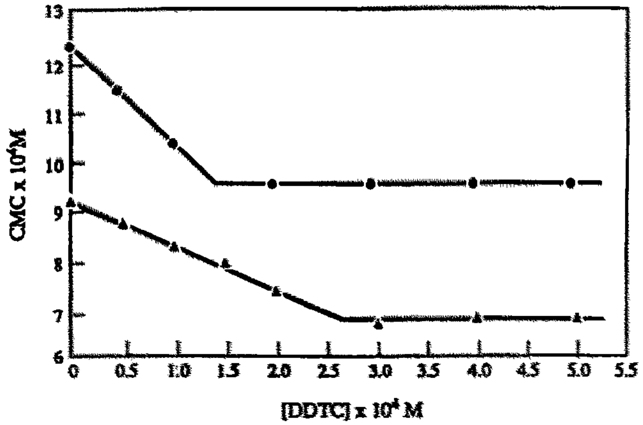

Fig. 1. Variation of critical micelle concentration (cmc) of hexadecyltrimethylammonium salts (bromide ▲ and chloride ●) with the sodium diethyldithiocarbamate concentration (DDTC).

second time with 5 ml of CCl_4. For the 25 ml total volume of the organic layer, absorbances were measured at the appropriate wavelength for each metal (Table 1).

Determination of Cu(II) in a mixture of Ni(II), Co(II) and Cu(II) by Flame Atomic Absorption Spectrometry (FAAS) and by the spectrophotometric method in presence of CTAOH. Acidic aqueous standard solutions of Cu(II) in the range concentration of 1–5 ppm were prepared to make the analytical calibration curve. An acidic aqueous sample containing 2.4 ppm of each metal was prepared. Copper standards and sample were introduced into an air–acetylene flame and their absorbances at 325 nm were measured.

In order to compare spectrophotometric method and FAAS, an aqueous sample, $4 \times 10^{-4}M$ DDTC, 0.06*M* CTAOH, and containing the metal ions at the above mentioned concentrations was prepared. Absorbance of Cu(II) at 436 nm was measured.

Sensitivity and detection limits. Sensitivity of the spectrophotometric method was calculated in this paper as the slope of the analytical calibration curve and was expressed as the molar absorptivity.

The detection limit was defined as the sample solution concentration giving a signal equal to the blank signal, y_B, plus three standard deviations of the blank, s_B, so that the probability of either of two kinds of error (type 1 error or type 2 error) occurring is only 5%. A value of $y_B + 10\ s_B$ has been used to define the limit of determination.[20]

The method of least squares was used to calculate the linear relationship between the analytical signal (absorbance) and the concentration. The line of regression thus calculated was used to estimate sensitivity, the detection limit and the determination limit in accordance with the literature.[20]

RESULTS AND DISCUSSION

Variation of surfactants' cmc as a function of DDTC concentration

The determination of the cmc for CTAB and CTAC for different values of the DDTC concentration in solution has been achieved by conductivity measurements as indicated in the Experimental section. For CTAOH it was not possible to determine the cmc by conductivity measurements due to the high value of ionic conductivity of hydroxide ion.

Figure 1 shows the results obtained for the variation of cmc for CTAB and CTAC when DDTC concentration in solution increases. The values obtained for CTAB and CTAC in pure aqueous solution, that is, in absence of DDTC, were $9.20 \times 10^{-4}M$ and $1.24 \times 10^{-3}M$, respectively, in agreement with the literature.[21] For both surfactants, the cmc values were lower for any DDTC concentration than those obtained in pure aqueous solution. However, cmc values decrease when DDTC concentration increases until it reaches a constant value of $6.60 \times 10^{-4}M$ for CTAB and $0.94 \times 10^{-3}M$ for CTAC which were independent of added DDTC quantities.

The results indicate that the presence of DDTC improves the micellization process for both cationic surfactants, also, the micelles formation is favoured for CTAB than CTAC for any DDTC concentration.

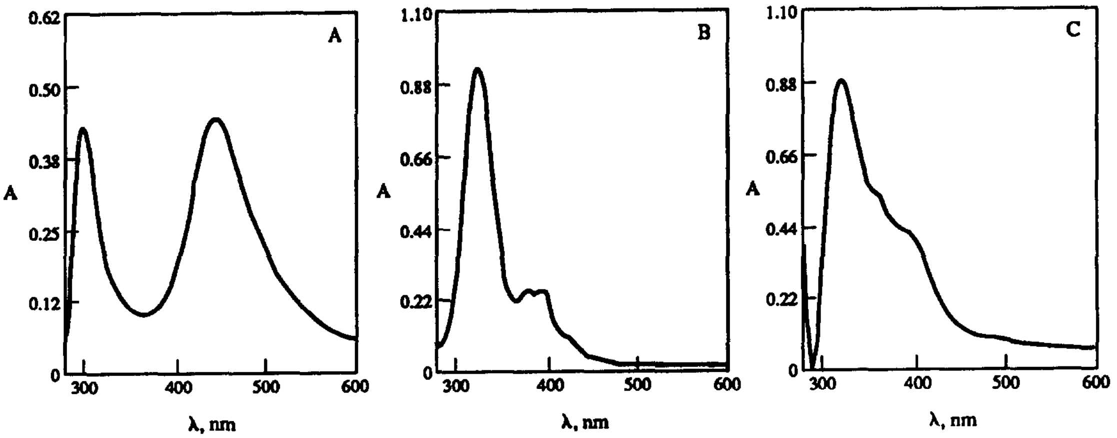

Fig. 2. Absorption spectra of metal ions with DDTC in micellar solutions of hexadecyltrimethylammonium bromide (CTAB) at concentration 0.02M: (A) [Cu(II)] = 4 × $10^{-5}M$, [DDTC] = 4 × $10^{-4}M$; (B) [Ni(II)] = 3 × $10^{-5}M$, [DDTC] = 2 × $10^{-4}M$ and (C) [Co(II)] = 4 × $10^{-5}M$, [DDTC] = 2 × $10^{-4}M$.

A 2 × $10^{-4}M$ DDTC concentration was chosen for CTAB and CTAC in solution to achieve the spectrophotometric determination of Ni(II) and Co(II) in micellar media. This concentration allows to obtain the minimum value of cmc for CTAC and a CMC value for CTAB close to the minimum. In the case of Cu(II), a 4 × $10^{-4}M$ of DDTC concentration in CTAC and CTAB was used in solution to improve sensitivity in the determination of this metal ion. Figure 1 shows that this concentration allows us to obtain the minimum value for CMC in the case of CTAC as well as in the case of CTAB. Therefore, both concentrations chosen for DDTC, favour the micellization process in the experimental conditions for the determination of metal ions.

The decrease observed in the cmc values for CTAC and CTAB in the presence of DDTC was previously observed for several micellar systems when some additives such as alcohols and salts were added to the solutions.[22,23]

Spectrophotometric characteristics of Ni(II), Cu(II) and Co(II) complexes with DDTC

In order to optimize the experimental conditions to determine metal ions as DDTC complexes, the absorption spectra for Cu(II), Ni(II) and Co(II) DDTC complexes were obtained. Figure 2 shows the results obtained in presence of CTAB cationic micelles at a concentration of 0.02M. Similar spectra were obtained for three metal ion complexes in presence of CTAC. However, in CTAOH micellar media the Ni(II) and Co(II) DDTC complexes were not formed and therefore only Cu(II) can be determined as DDTC complex in this medium. Absorption spectra of DDTC complexes after extraction in CCl_4 were also obtained. Table 1 groups the analytical wavelength values of the different metal–ligand–surfactant systems studied and the wavelength of the metal–ligand complexes after solvent extraction. Since a buffer to fix the solution's pH was not used, the different pH

Table 2. Detection limits (D.L.), determination limits (DT.L.) and molar absorptivity (ϵ) obtained in metal ion determination with DDTC in cationic micellar medium (CTAX) and in carbon tetrachloride

Surfactant		CTAB 0.020M	CTAB 0.096M	CTAC 0.022M	CTAC 0.111M	CTAOH 0.015M	CTAOH 0.060M	CCl_4
Co(II)	D.T.(ppb)	37.7 ± 8.2	136.3 ± 5.9	53.5 ± 0.4	46.2 ± 1.4	NC*	NC	47.5 ± 2.4
	DT.L.(ppb)	123.4 ± 31.9	455.9 ± 20.3	178.5 ± 1.12	154.4 ± 4.3	NC	NC	159.3 ± 8.1
	$\epsilon.10^{-3}$(l/mol/cm)	21.7	22.1	22.5	22.8	NC	NC	23.3
Ni(II)	D.L.(ppb)	81.7 ± 7.9	22.5 ± 5.1	18.5 ± 0.6	15.9 ± 0.3	NC	NC	24.3 ± 1.5
	DT.L.(ppb)	264.5 ± 16	74.9 ± 17.2	61.8 ± 1.8	53.0 ± 1.0	NC	NC	81.0 ± 5.2
	$\epsilon.10^{-3}$(l/mol/cm)	31.6	29.7	33.4	32.7	NC	NC	32.1
Cu(II)	D.L.(ppb)	71.9 ± 6.5	277.6 ± 82.1	63.1 ± 1.1	40.6 ± 2.1	86.5 ± 2.5	55.7 ± 2.1	117.3 ± 3.5
	DT.L.(ppb)	229.6 ± 20.8	920.8 ± 271.1	210.5 ± 3.7	135.7 ± 6.9	288.3 ± 8.2	185.8 ± 7.1	423.9 ± 17.2
	$\epsilon.10^{-3}$(l/mol/cm)	11.9	12.7	11.9	12.2	11.3	12.3	14.9

*NC: No complex formation.

values obtained in the solution have also been included in Table 1. It was observed that the solution's pH in CTAB micellar media are always higher than or equal to the solution's pH in CTAC micellar media and for the three metal ions. In order to explain this behavior it is necessary to study the differences that can exist between both micellar solutions. One reason is that it could be the different acid–base character of micellar counterion, but in this case, the similar acid–base character for Br^- and Cl^- does not allow the counterion nature as the reason for the difference in pH. However, the micellar systems have different characteristics. The cmc of CTAC is always higher than the cmc of CTAB, as shown in Fig. 1, and the dissociation degree of CTAC is also higher than CTAB according to the literature.[1,2,21] For these reasons, it is possible to think that CTAC favoured the formation of an ionic couple with DDTC, CTA^+DDTC^-, so that the ligand with negative charge protonation is avoided when the counterion is Na^+. According to this, in micellar media of CTAC, the pH of the solutions must be lower because DDTC has captured less H^+ of the bulk solution than in CTAB media.

The study of wavelength values for each metal–DDTC system on the Table 1, shows that the presence of cationic micelles of the type CTAX ($X = Br^-, Cl^-, OH^-$) did not produce significant displacements in the wavelengths of the absorption bands of the studied complexes in relation to the bands obtained in an earlier extraction with carbon tetrachloride.

As is shown in Fig. 1, Ni(II) and Co(II) can interfere in the Cu(II) determination due to the presence of absorption bands at wavelengths close to 440 nm.

It must be remarked (as indicated in Table 1), that the presence of CTAOH micelles (pH = 12.2 – 12.7) inhibits the formation of Ni(II) and Co(II) complexes with DDTC. This fact permits as will be shown later, the determination of the Cu(II) concentration in the presence of the other two metals and avoids their spectral interferences.

About the reasons for no complex formation of Ni(II) and Co(II) with CTAOH micelles, we suppose that at the pH of the CTAOH solution (pH 12) the complex formation constants are very low. Additionally, on the basis of some data founded in the literature,[16,24] it is possible to calculate very approximate complex formation constants for Cu(II)–DDTC and Ni(II)–DDTC at the pH considered but it has not been possible for Co(II)–DDTC as there has not been data in the literature. These approximate values show a low formation constant for Ni(II) in comparison to Cu(II), the values that we have found are $\log K_f = 19.5$ for Cu(II)–DDTC and $\log K_f = 6.21$ for Ni(II)–DDTC.

Table 3. Results obtained for Cu(II) determination in a synthetic sample by UV–Vis spectrophotometry with DDTC in CTAOH medium and by FAAS

Method	pH	[Cu(II)],ppm
UV–Vis (CTAOH 0.060*M*)	12.7	2.4178 ± 0.0021
FAAS	2.2	2.4106 ± 0.0347

Spectrophotometric determination of Ni(II), Cu(II) and Co(II) as DDTC complexes in presence of cationic micelles of CTAB, CTAC and CTAOH

The detection limit, the determination limit and the sensitivity of the method, defined as indicated in the Experimental section of this paper were determined for each metal ion in any micellar system and in CCl_4. Six independent values for each of these parameters were obtained and the average values are grouped in Table 2. Also, the standard deviation for these six values is included in Table 2 for the detection and determination limits.

From the results shown in Table 2, it is possible to deduce that the sensitivity of the spectrophotometric method in presence of CTAB, CTAC and CTAOH micelles, expressed as molar absorptivity for each of the metal ions, is very similar and independent of micelle counterion nature (Br^-, Cl^-, OH^-), and surfactant concentration. In concordance with molar absorptivity values, the sensitivity of the method follows the order Ni(II) > Co(II) > Cu(II). In the same way, it can be indicated that the sensitivity of the method in the presence of cationic micelles is also similar to the sensitivity obtained in the metal ion determination with DDTC after extraction with carbon tetrachloride (Table 2).

In regards to detection limits, Table 2 shows that Ni(II), Co(II) and Cu(II) can be determined as DDTC complexes in micellar media at ppb levels. In fact, the lowest detection limit obtained corresponds to Ni(II) in CTAC 0.111*M* (15.9 ppb) and the highest detection limit corresponds to Cu(II) in CTAB 0.096*M* (277.6).

Another question is the influence of the surfactant nature and concentration over the detection limits values. As is shown in Table 2, the micelle counterion nature does not seem to be a determinant factor over the detection limit values, although the presence of CTAC micelles did decrease these values. It must also be noted that the precision in the determination of detection limits, expressed as standard deviation, is higher in CTAC (and CTAOH in the case of Cu(II)–DDTC complex) with relation to CTAB micelles.

The influence of surfactant concentration on detection limit values can be related to a general behaviour that when the surfactant concentration increases, the detection limit values decrease with the exception of Cu(II) and Co(II) with CTAB. Micellar media do not allow to obtain better detection limits than solvent extraction with CCl_4 but avoid the previous step of extraction and eliminate the use of organic solvents which are toxic, expensive and environment pollutants.

Determination of Cu(II) in presence of Ni(II) and Co(II) as DDTC complexes in CTAOH medium

As was commented above, the presence of cationic CTAOH micelles only allows formation of the Cu(II)–DDTC complex and the resulting detection limits are lower than those obtained after the carbon tetrachloride extraction process while molar absorptivity values are similar in both instances (Table 2). Due to the special selectivity offered by CTAOH, the spectrophotometric determination of Cu(II)–DDTC was carried out in a mixture which also contained Ni(II) and Co(II) in the presence of CTAOH at a concentration of 0.06*M*. In order to verify the spectrophotometric method, the result obtained by this method was compared with the result found by flame atomic absorption spectrometry (FAAS) method using the same Cu(II), Ni(II) and Co(II) sample in an acid medium and in the absence of both the ligand and the surfactant. Table 3 shows the results with the standard deviation of four measures obtained for Cu(II) concentration with both methods, and these had good concordance. It is important to note that the great pH value in the CTAOH is not a drawback in the determination of Cu(II).

The results in Table 3 confirm the utility of this spectrophotometric method for the Cu(II) determination as DDTC complex in CTAOH medium in presence of Ni(II) and Co(II).

Table 4. Foreign ion quantities below which interferences are not produced in the Cu(II) determination in a concentration of 2.5 ppm in cationic micelles of CTAX ($X = Br^-, Cl^-$) and CTAOH

Metal ion	CTAX ($X = Br^-$ or Cl^-)	CTAOH
Al(III)	> 1000 ppm	> 1000 ppm
Cd(II)	2.25 ppm	Precipitate
Co(II)	0.3 ppm	25 ppm
Cr(III)	50 ppm	Precipitate
Cr(VI)	8 ppm	8 ppm
Fe(III)	0.8 ppm	10 ppm
Mn(II)	> 1000 ppm	2 ppm
Ni(II)	0.3 ppm	25 ppm
Pb(II)	3 ppm	Precipitate
Zn(II)	100 ppm	50 ppm

Study of interferences by foreign ions

Interferences of foreign ions in the Cu(II) determination with DDTC in presence of CTAB, CTAC and CTAOH were studied. The results obtained in both media are shown in Table 4. The quantities that appear in this table for each metal ion are the maximum quantities of each metal ion that it is possible to add before an interference is obtained. Some metal ions like Cd(II), Cr(III) and Pb(II) precipitate in CTAOH due to the high pH value of the solution interfering with the determination. The Mn(II) ion which does not interfere in CTAB and CTAC (1000 ppm), interferes in CTAOH at concentrations higher than 2 ppm due to the precipitation of MnO_2. In the case of Cr(VI) ion, the interference is produced by the molecular absorption of $Cr_2O_7^{2-}$ ion in the visible range. Ni(II) and Co(II) interfere in CTAB and CTAC due to the spectral interferences for the complex formation by both metal ions in this medium as seen in Fig. 2, but in CTAOH, these metal ions only interfere at concentrations that begin to precipitate because their complexes have not been formed in this medium, and spectral interferences are not observed.

These interferences can be avoided in general by the addition of a complexing agent, like EDTA, which forms stable complexes with many metal ions, so that, in this medium the Cu(II) reaction with DDTC is highly selective with NH_4^+/NH_3 buffer at $pH = 9$, using the surfactant Triton X-100.[18]

CONCLUSIONS

One of the most important aspects of this paper is the possibility of Cu(II), Ni(II) and

Co(II) determination as DDTC complexes in an aqueous solution produced by the presence of the cationic micelles of CTAX ($X = Br^-, Cl^-, OH^-$) with very acceptable sensitivity and detection limit values. This fact makes easy the metal ion determination, because a tedious and expensive process of a prior step of solvent extraction, using generally toxic organic solvents is not required.

Acknowledgement—The authors are grateful to University of Alcalá de Henares (Spain) (ref. 91B/14 and 92/27) for the financial support provided for the realization of this study.

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