

# Spectrophotometric Determination of Copper(II), Nickel(II), and Cobalt(II) as Complexes with Sodium Diethyldithiocarbamate in the Anionic Micellar Media of Dodecylsulfate Salts\*

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Copper(II), Ni<sup>II</sup> and Co<sup>II</sup> were determined spectrophotometrically as their complexes with diethyldithiocarbamate (DDTC) in the presence of aqueous anionic micellar media of sodium and ammonium dodecylsulfate. The presence of micellar systems allows one to eliminate the previous solvent extraction step that is necessary for the determination of metal-DDTC complexes in the absence of micelles. This reduces the cost and toxicity of the method. The influence of anionic micelles on the analytical characteristics (sensitivity and detection limits) was studied. The proposed method was applied to the determination of Cu<sup>II</sup> in industrial waste water and in nickel covered metallic samples, and the results were compared with those obtained by flame atomic absorption spectrometry.

**Keywords:** Micelles; spectrophotometry; metal ions; diethyldithiocarbamate

## Introduction

One of the main uses of surfactants in analytical chemistry is in the determination of metal ions as their complexes by spectrophotometry and fluorimetry.<sup>1-7</sup> In such metal complex solutions, the addition of a surfactant may cause a decrease in the pH at which the complex is formed, red-shifts in the absorption bands, and/or increases in the molar absorptivity or fluorescence intensity.

Surfactants contain different hydrophobic and hydrophilic regions, and, depending on their chemical structure and the nature of the medium, can give rise to different organized structures, namely normal and reversed micelles, microemulsions, monolayers, bilayers, and vesicles.

Normal micelles are formed when, in aqueous solution the surfactant reaches a certain concentration [the critical micellization concentration (c.m.c.)] and aggregates spontaneously. These systems and other organized structures have been shown to exhibit some interesting properties.<sup>8-12</sup> For example, they can solubilize, concentrate, and compartmentalize ions and molecules, modify acid-base and redox equilibria, and influence reaction rates, chemical pathways, and stereochemistry. In addition, micellar systems are convenient to use because they are optically transparent, stable, and relatively non-toxic.

These advantages illustrate the relevance of surfactant systems in the development of new spectrophotometric and fluorimetric methods for the determination of micro amounts of metal ions, anions, biological compounds, drugs, and pesticides.

Very sensitive methods for metal-ion determination have been developed by using chelating organic reagents (e.g., triphenylmethane, xanthene, and phenoxazone) and cationic or non-ionic surfactants.<sup>13-16</sup> Comparison of the spectral properties of the complexes in the absence and presence of cationic surfactants typically reveals a one- to 10-fold increase in the molar absorptivity (sensitivity), and bathochromic shifts in the wavelength of maximum absorbance in the range 20-100 nm.<sup>17-21</sup>

Although the majority of research in this area concerns cationic surfactants, anionic micelles have also been shown to provide similar analytical benefits.<sup>22-24</sup> Routine use of anionic micelles in the determination of metal ions may be limited due to the occurrence of direct surfactant-metal ion interactions, which can inhibit metal-dye complex formation.

On the other hand, the ability of micelles to solubilize complexes in aqueous solutions can eliminate the need for non-aqueous extraction steps in a given analysis.<sup>4,6,25</sup>

Diethyldithiocarbamate (DDTC) has been used as a chelating agent in the determination of metal ions by ultraviolet-visible spectrophotometry. However, DDTC metal complexes are water insoluble and therefore a solvent-extraction step is necessary. Generally, carbon tetrachloride has been employed as organic solvent, although chloroform has also been used.<sup>26</sup> These solvents can be classified as toxic and as environmental pollutants,<sup>27</sup> and have been listed as carcinogens by the Environmental Protection Agency (EPA).<sup>28</sup>

This paper describes the spectrophotometric determinations of Cu<sup>II</sup>, Co<sup>II</sup>, and Ni<sup>II</sup> as their DDTC complexes in micellar aqueous solutions of sodium and ammonium dodecylsulfate. This method does not require a solvent-extraction step, hence the use of carbon tetrachloride or chloroform is avoided. In place of these organic solvents, less toxic agents<sup>27</sup> in the form of dodecylsulfate salts were used.

## Experimental

### Reagents

All reagents used were of analytical-reagent grade (Merck). Stock solutions of Ni<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup> were prepared from nitrate salts. The sodium diethyldithiocarbamate solutions were freshly prepared in distilled water just before use to avoid acid decomposition. The surfactant ammonium dodecylsulfate (ADS) was synthesized from sodium dodecylsulfate (SDS) using an ion-exchange method with the cationic resin Dowex 50 (20-50 mesh).

### Apparatus

A Hewlett-Packard Model HP8452A diode-array spectrophotometer equipped with 1 cm silica cells was used to record the

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absorption spectra used to measure absorbance data at selected wavelengths for calibration and to determine the c.m.c. of ADS.

Flame atomic absorption spectrometry (FAAS) was conducted using a Perkin-Elmer instrument (Model 2380).

A Metrohm pH meter and combined electrode were used to measure the pH of solutions. Some c.m.c.s were determined using a Crison Model 522 conductimeter.

Ultraviolet-visible (UV/VIS) Spectrophotometric and conductimetric measurements were carried out at  $25 \pm 1^\circ\text{C}$  in a Braun thermostatic bath (Model Thermomix BU).

#### Synthesis of Ammonium Dodecylsulfate

The ion-exchange resin was placed in a column. Prior to its use, several ion-exchange cycles were conducted ( $\text{H}^+/\text{Na}^+$ ) to generate the  $\text{H}^+$  form of the resin. A  $1 \text{ mol l}^{-1}$   $\text{NH}_4\text{Cl}$  solution was passed through the column to generate the ammonium form of the resin, and then a  $0.25 \text{ mol l}^{-1}$  SDS solution was passed slowly through the resin where an ion exchange between the sodium of the SDS and ammonium of the resin occurred. The effluent was collected in a flask. The actual concentration of ADS was determined by titration as follows: a few drops of a formaldehyde solution (20%) were added to 5 ml of ADS; the  $\text{H}^+$  generated in the subsequent reaction was titrated with standardized NaOH; the addition of formaldehyde and the titration were repeated until the reaction appeared to be complete; an additional 2 ml of standardized NaOH were added, and the solution was left in the dark for 15 min; and the excess of NaOH was titrated with HCl which had previously been titrated with sodium carbonate. The concentration of ADS was found to be  $0.24 \text{ mol l}^{-1}$ . The ADS solution was stored in a refrigerator. A second portion of the remaining effluent was precipitated in a freezer and filtered at low temperature to eliminate the solvent. The solid ADS was then dried and kept in a receptacle. The c.m.c. of ADS was determined by both UV spectrophotometric and conductimetric methods.

#### Procedure

##### Determination of surfactant c.m.c.

The c.m.c. value for ADS was determined by spectrophotometry as follows. The absorbance of a Calcon (Merck)-ADS mixture at 219.1 nm was measured at different concentrations of ADS. A change in slope occurred at a point near to the c.m.c. In the absence of Calcon, the absorbance of ADS at 219.1 nm also presents a change in the slope near to the c.m.c. In both cases, the c.m.c. was taken as the intersection of the two straight lines.

The c.m.c. of ADS was determined using conductivity measurements and compared with the value obtained by spectrophotometry, for both the titrated solution and the solid ADS. The cmc of SDS was also determined by this method. The surfactant concentrations ranged from  $10^{-3}$  to  $2.5 \times 10^{-2} \text{ mol l}^{-1}$  for SDS and from  $1.1 \times 10^{-4}$  to  $2.2 \times 10^{-2} \text{ mol l}^{-1}$  for ADS. The occurrence of a sharp inflection point in the plots of specific conductivity versus surfactant concentration indicated the c.m.c.

##### Determination of surfactant c.m.c. in the presence of DDTC

The c.m.c. values in the presence of different concentrations ( $5 \times 10^{-5}$ – $5 \times 10^{-4} \text{ mol l}^{-1}$ ) of DDTC were obtained from conductivity measurements. The surfactant concentration was determined over the same concentration range as in the absence of DDTC, and the c.m.c. was obtained from the sharp inflection point occurring in the plots of specific conductivity versus surfactant concentration.

##### Spectrophotometric determination of metal ion in micellar solutions

Appropriate volumes of stock solutions of metal ion, DDTC, and the selected surfactant were added to a series of 25 ml calibrated flasks, and made up to volume with distilled water. The following concentration ranges of metal ion were used:  $\text{Ni}^{II}$ ,  $2 \times 10^{-6}$ – $3 \times 10^{-5} \text{ mol l}^{-1}$ ;  $\text{Co}^{II}$ ,  $5 \times 10^{-6}$ – $5 \times 10^{-5} \text{ mol l}^{-1}$ ; and  $\text{Cu}^{II}$ ,  $1 \times 10^{-5}$ – $8 \times 10^{-5} \text{ mol l}^{-1}$ . The concentration of DDTC used was  $2 \times 10^{-4} \text{ mol l}^{-1}$  for the nickel and cobalt complexes, and  $4 \times 10^{-4} \text{ mol l}^{-1}$  for the copper complex. The surfactant concentrations, pH values, and analytical wavelengths used are listed in Table 1.

##### Spectrophotometric determination of metal ion after extraction with $\text{CCl}_4$

Appropriate volumes of stock aqueous solutions of metal ion and DDTC were placed in an extractive funnel and 10 ml of  $\text{CCl}_4$  were added. The organic layer was transferred into a 25 ml calibrated flask. In order to obtain complete extraction, the process was repeated twice, the first time with 10 ml of  $\text{CCl}_4$  and the second time with 5 ml. For a total volume of the organic layer of 25 ml, absorbances were measured at the appropriate wavelength for each metal ion (Table 1).

##### Sensitivity and detection limits

The sensitivity of the spectrophotometric method was determined from the slope of the analytical calibration curve and is expressed as the molar absorptivity. The detection limit was

**Table 1** Experimental conditions for metal ion determination with DDTC in anionic micellar medium and in carbon tetrachloride

Surfactant	Surfactant				$\text{CCl}_4$
	SDS ( $0.020 \text{ mol l}^{-1}$ )	SDS ( $0.100 \text{ mol l}^{-1}$ )	ADS ( $0.020 \text{ mol l}^{-1}$ )	ADS ( $0.100 \text{ mol l}^{-1}$ )	
$\text{Co}^{II}$ —					
Wavelength/nm	322	322	322	322	322
pH	9.7	9.0	6.5	6.3	8.0
$\text{Ni}^{II}$ —					
Wavelength/nm	318	326	324	324	328
pH	8.3	7.5	7.1	6.6	6.7
$\text{Cu}^{II}$ —					
Wavelength/nm	446	440	448	434	436
pH	8.1	8.2	6.8	6.8	7.6

defined as the sample solution concentration giving a signal equal to the blank signal,  $y_B$ , plus three times the standard deviation of the blank,  $s_B$ ; hence the probability of either of two types of error (type 1 type 2) occurring was only 5%. A value of  $y_B + 10s_B$  was used to define the determination limit.<sup>29</sup>

A least-squares method was used to calculate the linear relationship between the analytical signal (absorbance) and the concentration. The regression curve thus calculated was used to estimate sensitivity, the detection limit, and the determination limit in accordance with the literature.<sup>29</sup>

#### Determination of $Cu^{II}$ in real samples

The absorbance of a waste water sample obtained from an industrial effluent was measured following sample preparation

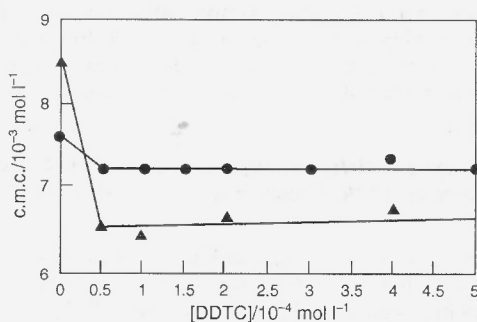


Fig. 1 Variation of critical micellization concentration (c.m.c.) of dodecylsulfate salts ( $\blacktriangle$ , sodium and  $\bullet$ , ammonium) with DDTC concentration.

as follows. Appropriate amounts of ADS and DDTC were added to a 25 ml calibrated flask to obtain final concentrations of  $0.1 \text{ mol l}^{-1}$  in ADS and  $4 \times 10^{-4} \text{ mol l}^{-1}$  in DDTC. Then, 0.05 ml of the sample were added and the absorbance was measured. This absorbance reading was used to calculate the concentration of  $Cu^{II}$  in the diluted sample and hence in the real sample.

For the determination of  $Cu^{II}$  by FAAS, a 0.1 ml aliquot of the sample was diluted with distilled water.

For metallic samples covered with Ni, the solid, metallic matrix was dissolved with nitric acid and subsequently diluted with distilled water to 250 ml. This solution was again diluted to measure the metal ions, the dilution depending on the sample size (samples 1 and 2, 0.02–25 ml; and samples 3 and 4, 0.05–25 ml for the UV/VIS spectrophotometric method as well as for FAAS).

## Results and Discussion

### Surfactant c.m.c.

The c.m.c. of SDS was determined from conductivity measurements. In the case of ADS, the c.m.c. was determined by conductivity and spectrophotometry as described in Experimental.

For SDS, a c.m.c. of  $8.5 \times 10^{-3} \text{ mol l}^{-1}$  was obtained in pure aqueous solution. For ADS, a c.m.c. of  $7.6 \times 10^{-3} \text{ mol l}^{-1}$  was obtained regardless of the method employed. These values are in good agreement with literature values.<sup>30</sup>

### Surfactant c.m.c. versus DDTC Concentration

The c.m.c.s of SDS and ADS were also determined conductimetrically in solutions containing the complexing ligand

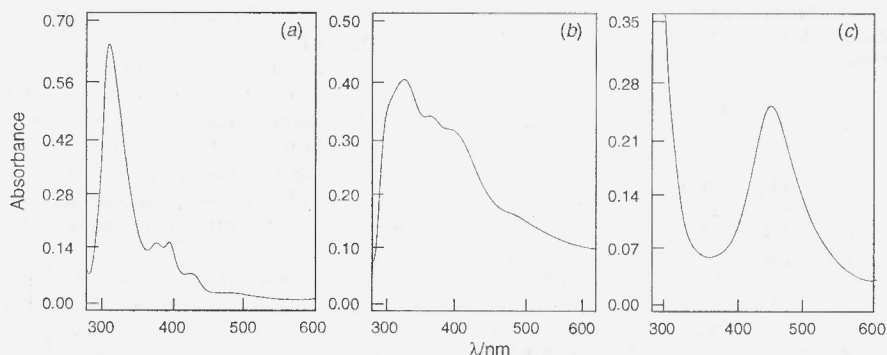


Fig. 2 Absorption spectra of metal ions with DDTC in micellar solutions of  $\text{mol l}^{-1}$  ammonium dodecylsulfate (ADS). Concentrations: (a)  $[Ni^{II}] = 2 \times 10^{-5} \text{ mol l}^{-1}$ ,  $[DDTC] = 2 \times 10^{-4} \text{ mol l}^{-1}$ ; (b)  $[Co^{II}] = 2 \times 10^{-5} \text{ mol l}^{-1}$ ,  $[DDTC] = 2 \times 10^{-4} \text{ mol l}^{-1}$ ; and (c)  $[Cu^{II}] = 2 \times 10^{-5} \text{ mol l}^{-1}$ ,  $[DDTC] = 4 \times 10^{-4} \text{ mol l}^{-1}$ .

Table 2 Detection limits (DLs), determination limits (DTLs), and molar absorptivities ( $\epsilon$ ) for the metal ion determinations with DDTC in anionic micellar medium and in carbon tetrachloride

Surfactant	SDS (0.020 mol l <sup>-1</sup> )	SDS (0.100 mol l <sup>-1</sup> )	ADS (0.020 mol l <sup>-1</sup> )	ADS (0.100 mol l <sup>-1</sup> )	CCl <sub>4</sub>
$Co^{II}$ —					
DL/ $\mu\text{g l}^{-1}$	220.3 $\pm$ 30.2	73.8 $\pm$ 1.0	73.9 $\pm$ 4.3	49.3 $\pm$ 1.8	47.5 $\pm$ 2.4
DTL/ $\mu\text{g l}^{-1}$	724.1 $\pm$ 69.8	226.5 $\pm$ 32.3	246.3 $\pm$ 14.4	164.3 $\pm$ 6.1	159.3 $\pm$ 8.1
$\epsilon/10^{-3} \text{ m}^2 \text{ mol}^{-1}$	22.4	22.1	22.5	22.2	23.3
$Ni^{II}$ —					
DL/ $\mu\text{g l}^{-1}$	101.0 $\pm$ 16.7	24.1 $\pm$ 7.1	25.1 $\pm$ 0.6	9.2 $\pm$ 1.1	24.3 $\pm$ 1.5
DTL/ $\mu\text{g l}^{-1}$	336.7 $\pm$ 35.6	86.9 $\pm$ 28.7	83.6 $\pm$ 2.0	30.5 $\pm$ 3.5	81.0 $\pm$ 5.2
$\epsilon/10^{-3} \text{ m}^2 \text{ mol}^{-1}$	27.4	30.3	26.3	32.3	32.1
$Cu^{II}$ —					
DL/ $\mu\text{g l}^{-1}$	130.9 $\pm$ 13.3	98.7 $\pm$ 28.5	77.6 $\pm$ 5.6	54.4 $\pm$ 1.7	117.3 $\pm$ 3.5
DTL/ $\mu\text{g l}^{-1}$	436.2 $\pm$ 44.0	329.6 $\pm$ 96.2	258.4 $\pm$ 18.5	181.4 $\pm$ 5.7	423.9 $\pm$ 17.2
$\epsilon/10^{-3} \text{ m}^2 \text{ mol}^{-1}$	12.7	13.7	12.0	12.5	14.9

DDTC. Fig. 1 shows the variations of the c.m.c.s of SDS and ADS as functions of the DDTC concentration in solution. Fig. 1 also indicates the c.m.c.s in pure aqueous solution. It is observed that for both surfactants, the presence of DDTC causes a decrease in the c.m.c. value. However, the c.m.c. of SDS and of ADS remains constant in all DDTC-containing solutions regardless of the DDTC concentration. A c.m.c. value of  $6.6 \times 10^{-3} \text{ mol l}^{-1}$  was obtained for SDS and of  $7.2 \times 10^{-3} \text{ mol l}^{-1}$  for ADS. These results indicate that the presence of DDTC improves micelle formation for both anionic surfactants. However, for SDS, the improvement in micellization is greater than that for ADS. This is the opposite of the results obtained for pure aqueous solution in which micelle formation is favoured more for ADS than for SDS.

The reduced values of c.m.c. obtained for SDS and ADS in the presence of DDTC were also obtained for cationic surfactants,<sup>25</sup> and when certain alcohols and salts were added to the micellar solutions.<sup>31,32</sup>

#### Spectrophotometric Characteristics of Ni<sup>II</sup>, Co<sup>II</sup> and Cu<sup>II</sup> Complexes with DDTC

To establish the experimental conditions for the determination of metal ions as DDTC complexes, absorption spectra were recorded for complexes of Cu<sup>II</sup>, Ni<sup>II</sup>, and Co<sup>II</sup> with DDTC. Fig. 2 shows the results obtained in the presence of 0.2 mol l<sup>-1</sup> ADS. Similar spectra were obtained for the three metal ion complexes in the presence of SDS. Fig. 2 shows that, due to the narrow absorption bands obtained for Ni<sup>II</sup> (a) and Cu<sup>II</sup> (c), the latter can be determined in the presence of Ni<sup>II</sup> with no interference. However, the broad absorption band obtained for the Co<sup>II</sup> complex makes it impossible to

determine this element in the presence of Ni<sup>II</sup> and/or Cu<sup>II</sup>. Similarly, neither Ni<sup>II</sup> nor Cu<sup>II</sup> can be determined in the presence of Co<sup>II</sup>. Table 1 lists the analytical wavelength and pH values of the different metal ligand-surfactant systems and metal ligand complexes after solvent extraction of CCl<sub>4</sub>.

Comparison of the analytical wavelengths with the wavelengths after solvent extraction (see Table 1) reveals that the presence of anionic micellar systems produces a displacement of the maximum wavelength ( $\lambda_{\text{max}}$ ) for Ni<sup>II</sup>-DDTC in 0.02 mol l<sup>-1</sup> SDS, Cu<sup>II</sup>-DDTC in 0.2 mol l<sup>-1</sup> SDS and 0.2 mol l<sup>-1</sup> ADS. In contrast, the anionic micelles do not cause any displacement in  $\lambda_{\text{max}}$  for Co<sup>II</sup>-DDTC. The interaction that occurs between metal-DDTC complexes and anionic micelles therefore depends on the nature of the metal ion.

It is of interest to note that for the same metal-DDTC complexes, the presence of cationic micelles (hexadecyltrimethylammonium bromide, chloride, and hydroxide) does not have an effect on  $\lambda_{\text{max}}$ .<sup>25</sup>

It was observed that the pH for the three metal-DDTC complexes in ADS micellar media was always lower than that in SDS micellar media. This behaviour is in accordance with the acidic character of NH<sub>4</sub><sup>+</sup> as a micellar counter ion.

#### Spectrophotometric Determination of Ni<sup>II</sup>, Cu<sup>II</sup>, and Co<sup>II</sup> as DDTC Complexes in the Presence of Anionic Micelles of SDS and ADS

The detection and determination limits and the sensitivity of the method (defined as in Experimental) were determined for each metal ion in each micellar system and in CCl<sub>4</sub>. Six values were obtained for each parameter, the averages of which are listed in Table 2. The standard deviations of the detection and determination limits ( $n = 6$ ) are also given in Table 2.

From the results given in Table 2, it is possible to deduce that the sensitivity of the spectrophotometric method in the presence of SDS and ADS micelles (expressed as molar absorptivity for each of metal ion) is very similar regardless of the nature of the micelle counterion (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>), and the surfactant concentration. According to the molar absorptivities, the sensitivity of the method is highest for Ni<sup>II</sup>: Ni<sup>II</sup> > Co<sup>II</sup> > Cu<sup>II</sup>. The sensitivity of the method in the presence of anionic micelles is similar to that of the metal ion determination with DDTC after extraction with carbon tetrachloride (Table 2).

The detection limits shown in Table 2 indicate that the determination of Ni<sup>II</sup>, Co<sup>II</sup>, and Cu<sup>II</sup> as their DDTC complexes in anionic micellar medium is possible down to  $\mu\text{g l}^{-1}$  levels. The detection limit for Ni<sup>II</sup> is always lower than that for Co<sup>II</sup> or Cu<sup>II</sup>. The lowest detection limit was obtained for Ni<sup>II</sup> in 0.1 mol l<sup>-1</sup> ADS (9.2  $\mu\text{g l}^{-1}$ ) and the highest for Co<sup>II</sup> in 0.02 mol l<sup>-1</sup> SDS (220.3  $\mu\text{g l}^{-1}$ ).

But, to what extent does the nature of the surfactant counterion and the concentration influence the detection limit? It does not appear that the micellar counter ion is a

**Table 3** Detection limits ( $\mu\text{g l}^{-1}$ ) obtained for the anionic surfactants in this work and those obtained for the cationic surfactants (CTAB, CTAC, and CTAOH) in previous work<sup>25</sup>

Surfactant*	Detection limit/ $\mu\text{g l}^{-1}$		
	Co <sup>II</sup>	Ni <sup>II</sup>	Cu <sup>II</sup>
SDS (0.020 mol l <sup>-1</sup> )	220.3 ± 30.2	101.0 ± 16.7	130.9 ± 13.3
SDS (0.100 mol l <sup>-1</sup> )	73.8 ± 1.0	24.1 ± 7.1	98.7 ± 28.5
ADS (0.020 mol l <sup>-1</sup> )	73.9 ± 4.3	25.1 ± 0.6	77.6 ± 5.6
ADS (0.100 mol l <sup>-1</sup> )	49.3 ± 1.8	9.2 ± 1.1	54.4 ± 1.7
CTAB (0.020 mol l <sup>-1</sup> )	37.7 ± 8.2	81.7 ± 7.9	71.9 ± 6.5
CTAB (0.100 mol l <sup>-1</sup> )	136.3 ± 5.9	22.5 ± 5.1	277.6 ± 82.1
CTAC (0.022 mol l <sup>-1</sup> )	53.5 ± 0.4	18.5 ± 0.6	63.1 ± 1.1
CTAC (0.110 mol l <sup>-1</sup> )	46.2 ± 1.4	15.9 ± 0.3	40.6 ± 2.1
CTAOH (0.015 mol l <sup>-1</sup> )	— <sup>†</sup>	— <sup>†</sup>	86.5 ± 2.5
CTAOH (0.060 mol l <sup>-1</sup> )	— <sup>†</sup>	— <sup>†</sup>	55.7 ± 2.1
CCl <sub>4</sub>	47.5 ± 2.4	24.3 ± 1.5	117.3 ± 3.5

\* CTAB = Hexadecyltrimethylammonium bromide (CTA bromide); CTAC = CTA chloride; and CTAOH = CTA hydroxide.

<sup>†</sup> No complex formation.

**Table 4** Results obtained for the determination of copper in four metallic samples by FAAS and by spectrophotometry in a micellar medium of ADS (0.1 mol l<sup>-1</sup>)

Sample	Cu <sup>II</sup> /mg		Ni <sup>II</sup> /mg	Sample mass/g*	Cu <sup>II</sup> (%)
	FAAS	ADS spectrophotometric method			
1	804.2 ± 9.4	782.3 ± 1.6	10.3 ± 0.2	1.5253 ± 4.0 × 10 <sup>-3</sup>	51.3
2	831.4 ± 7.8	836.6 ± 0.9	11.9 ± 0.2	1.5253 ± 4.0 × 10 <sup>-3</sup>	54.8
3	419.4 ± 2.9	417.2 ± 0.6	6.6 ± 0.1	0.7054 ± 1.9 × 10 <sup>-3</sup>	59.1
4	400.4 ± 5.8	409.3 ± 2.9	6.1 ± 0.1	0.7054 ± 1.9 × 10 <sup>-3</sup>	58.0

\* The mean mass of eight samples for samples 1 and 2, and the mean mass of 11 samples for samples 3 and 4.

determining factor, although in the presence of ADS ( $\text{NH}_4^+$  counter ion), the detection limits are generally lower than those in SDS ( $\text{Na}^+$  counterion). Further, the detection limits were observed to decrease, regardless of the surfactant counter ion, as the surfactant concentration increased.

Table 3 lists the detection limits obtained for  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}$  in the anionic micellar media studied in this work and those obtained for the same metal ions in cationic micellar solutions of hexadecyltrimethylammonium bromide, chloride, and hydroxide (CTAB, CTAC, CTAOH) in previous work.<sup>25</sup> Clearly, the best results were obtained for cationic micelles of CTAC  $0.11 \text{ mol l}^{-1}$  and anionic micelles of ADS  $0.10 \text{ mol l}^{-1}$ .

It is interesting to report that detection limits obtained with high concentrations of ADS micelles are the same (determination of  $\text{Co}^{\text{II}}$ -DDTC) or even better (determination of  $\text{Ni}^{\text{II}}$ - and  $\text{Cu}^{\text{II}}$ -DDTC complexes) than those obtained following solvent extraction with  $\text{CCl}_4$ . Furthermore, the ADS method avoids the previous extraction step and eliminates the use of dangerous organic solvents.

#### Determination of $\text{Cu}^{\text{II}}$ in Waste Water

The proposed spectrophotometric method was applied to the determination of  $\text{Cu}^{\text{II}}$  in industrial waste water. As the lowest detection limit for this metal was obtained in  $0.1 \text{ mol l}^{-1}$  ADS, this surfactant was used in the determination. The result of the determination of  $\text{Cu}^{\text{II}}$  in the diluted sample (see Experimental) using the proposed method was compared with the result obtained by FAAS: (four measurements; mean  $\pm$  standard deviation) proposed method,  $924.3 \pm 0.5 \mu\text{g ml}^{-1} \text{ Cu}^{\text{II}}$ ; and FAAS method,  $945.3 \pm 10.9 \mu\text{g ml}^{-1} \text{ Cu}^{\text{II}}$ . Agreement between the two methods was good.

The determination of  $\text{Cu}^{\text{II}}$  in one industrial waste water sample (in quadruplicate) required 90 ml of a  $0.25 \text{ mol l}^{-1}$  ADS solution, whereas the same determination using solvent extraction with  $\text{CCl}_4$  required about 225 ml of the organic solvent.

#### Determination of $\text{Cu}^{\text{II}}$ in Metallic Samples

The proposed method was also applied to the determination of  $\text{Cu}^{\text{II}}$  in  $\text{Cu}^{\text{II}}$  alloys covered with nickel to prevent oxidation and to allow their use as electronic connectors. Copper(II) was determined in four such samples using the proposed method, and  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  were also determined by FAAS. Table 4 shows that the results obtained for  $\text{Cu}^{\text{II}}$  by the two methods agree well, and that  $\text{Cu}^{\text{II}}$  can be determined without interference from  $\text{Ni}^{\text{II}}$ .

The determination of  $\text{Cu}^{\text{II}}$  in the four metallic samples (in quadruplicate) required 200 ml of a  $0.25 \text{ mol l}^{-1}$  ADS solution, whereas 525 ml of  $\text{CCl}_4$  was necessary for the solvent extraction determination.

#### Conclusions

These results for anionic micellar systems and those obtained previously with cationic micellar systems<sup>25</sup> show that  $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Ni}^{\text{II}}$  can be determined as their DTC complexes in aqueous solution. No extraction step is required and hence the use of organic solvents, which are generally toxic pollutants, is avoided.

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