

Nonionic/Anionic Mixed Surfactants System for Colorimetric Determination of Metal-Dithizone Complexes

FARID ABU-SHAMMALA

Department of Chemistry

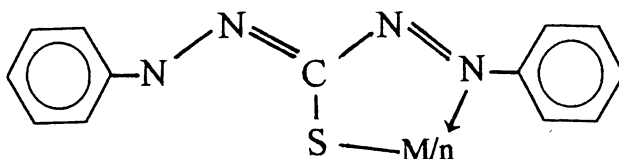
The Islamic University of Gaza

P.O. Box 108, Gaza City (Via Israel), Palestine

Dithizone (diphenyl thiocarbazone, H_2Dz) has been solubilized in a mixed micellar solution of nonionic (poly (oxyethylene) (23) dodecanol) (Brij 35) and anionic (sodium dodecylsulfate) (SDS) surfactants. Increasing the surfactants concentration above the critical micelle concentration produces more micelles that provide local nonpolar microenvironments that enhance the solubility of the nonpolar organic compounds in water. Metal ions bind the mixed micellar-solubilized dithizone to form water-soluble colored chelates. The metal-dithizone colored complexes are extracted to the nonpolar “stationary” micellar phase. Potential application of the method for the determination of different metal ions in water has been evaluated. The detection limit of the method ranged from 3 to 6 ppb. Recoveries from individual metal ion solution ranged from 95 to 100% with RSDs between 4–10%, and from mixed metal ions solution ranged from 93–104% with RSDs between 3.5–12%. The recoveries of metal ions obtained in our method are better than the recoveries obtained with the use of extraction in toxic chlorinated hydrocarbons method.

INTRODUCTION

Dithizone (diphenyl thiocarbazone, H_2Dz) is a weak organic acid that has been found to be colorimetric reagent for the determination of mercury, cadmium, copper, zinc and other metal ions¹. Dithizone complexes with metal ions to form nonpolar colored complexes that are practically insoluble in water; these complexes are called primary dithizonates; they are presented as $M(HDz)_m$, where m is a metal ion charge. Structural investigations of these complexes have shown that the metal ion is bonded to the sulfur atom and coordinately bonded to the nitrogen, as shown in Figure 1.



$M = Hg(II), Cu(II), Pb(II), Cd(II), Zn(II)$.

Fig. 1 Structure of primary metal-dithizonate complex

These complexes are generally extracted into organic solvents such as chlorinated hydrocarbons like carbon tetrachloride and chloroform, and determined spectrophotometrically. Extraction spectrophotometry is a sensitive method for the determination of metal ions but suffers from several disadvantages. It is tedious, needs extensive sample preparation and involves the use of toxic organic solvents.

Surfactants have found a wide range of use in analytical chemistry techniques². Surfactants are classified as anionic, cationic, nonionic, and zwitterionic based on the polar head groups nature³. Surfactants are used at concentration levels at which micelles form. Micelles form in aqueous solutions when the concentration of the surfactant increases above a certain level called the critical micelle concentration. At this point the surfactants begin to aggregate to form a spherical particle whose hydrocarbon tails are in the interior and whose charged end are exposed to the aqueous phase on the outside. Mixed surfactants have been studied by chemists for a long time^{4, 5}. When a nonionic and anionic surfactants are mixed and incorporated into an aqueous solution the following interactions will exist: hydrophobic-hydrophobic interaction, ion-dipole interaction and hydrophilic-hydrophilic interaction^{6, 7}. These interactions are responsible for the formation of mixed micelles in an aqueous solution. These mixed micelles enhance the solubility of organic compounds in aqueous solution by providing a nonpolar pseudo-stationary phase in the interior of the micelles.

The aim of this investigation was to explore the use of mixed micellar in spectrophotometric determination of metals-dithizone complexes in aqueous solution. This method is simple, less tedious, selective, does not involve the use of extraction by toxic chlorinated hydrocarbons.

EXPERIMENTAL

All the UV-Vis spectra were performed in the range from 200 to 900 nm using scanning double beam UV-Vis spectroscopy (Perkin-Elmer, Lambda 20). The instrument was allowed to warm for 30 min prior to use. All spectra were acquired at 2-nm resolution, integration time of 2 s, and the scan speed was fixed at 60 nm/min. The spectrophotometer cell was a standard 1 cm path length cuvette, of UV-grade silica.

Metal Ions Standards: Metal ions stock standard solutions were prepared using analytical reagent grade chloride or nitrate salts. The metal ions salts were dissolved in hydrochloric acid and then diluted in distilled water. The stock solutions were stored in polyethylene bottles.

Buffers: The acetate buffer (pH 5.0) was prepared by mixing 0.20 M solution of sodium acetate and 0.20 M solution of acetic acid. The phosphate buffer (pH 8.6) was prepared by mixing 9.47 g of sodium hydrogen phosphate and 0.0905 g of potassium dihydrogen phosphate and dilution to 1 L with distilled water.

Surfactant Solutions: Sodium dodecyl sulfate (SDS) and (polyoxyethylene) (23) decanol (Brij 35) were purchased from Merck. All surfactants were used as received. The concentration of SDS/Brij 35 mixed surfactants (50:50)

solutions were varied from 5 to 10%. Mixed micellar solution were made by weighing appropriate amount of SDS and Brij 35 (ratio of 1:1) and diluting with the stock buffer solution in a 100 mL volumetric flask to obtain the desired concentrations.

Dithizone-Surfactant Reagents: The reagents were prepared by dissolving a slight excess of reagent grade solid dithizone (Merck) in the surfactant solution of the desired concentration. The solutions were allowed to equilibrate for 10 min, then filtered through a Whatman No. 41 ashless filter paper to remove the undissolved excess of dithizone.

Calibration and Determination of Metal Ions: Calibration plots of individual metal ions were constructed using standard concentrations cover the range 1–10 ppm by transferring appropriate volume of the stock standard solution of the metal ion in volumetric flask, and the pH was adjusted to the required value that form metal-dithizone complex, and a saturated solution of dithizone in mixed surfactants was then added up to the calibration mark. The solutions were allowed to equilibrate for 5 min before recording the absorption spectra. All the solutions prepared were stored in the refrigerator at 4°C.

RESULTS AND DISCUSSION

Stability of Dithizone

Ueno *et al.*⁹ and others⁸ have reported the poor stability of dithizone when stored for prolonged periods of time in the determination of zinc, mercury and copper. Therefore, dithizone should be prepared fresh before each analysis. As a starting point, we tested the stability of dithizone in single surfactant and in mixed surfactants

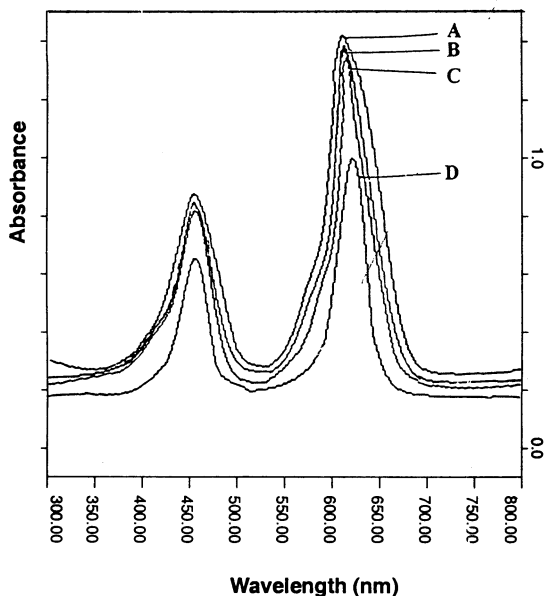


Fig. 2 Change in the absorption spectra of a saturated solution of dithizone in 5% Brij 35 with time (A) 0, (B) 30 min, (C) 60 min, and (D) 120 min.

Mixed surfactants concentrations were in the range 5–10% well above the critical micelle concentration (cmc). We have found that dithizone is relatively stable in single surfactant solution (either nonionic or anionic) for about 1 h after preparation. However, its stability started to decrease markedly after this period of time as shown in Figures 2 and 3.

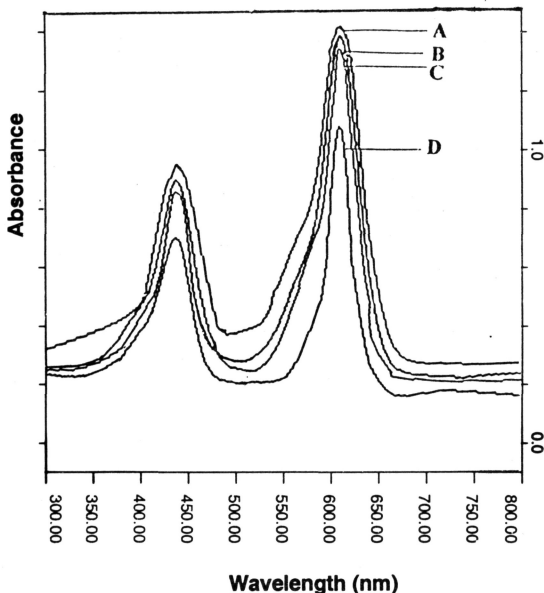


Fig. 3 Change in the absorption spectrum of a saturated solution of dithizone in 5% SDS with time (A) 0, (B) 30 min, (C) 60 min, and (D) 120 min

In an attempt to alleviate the above instability of dithizone, the applicability of mixed micelles solution prepared from nonionic (Brij 35) and anionic (SDS) surfactants was tested. As shown in Figure 4 our investigation revealed that

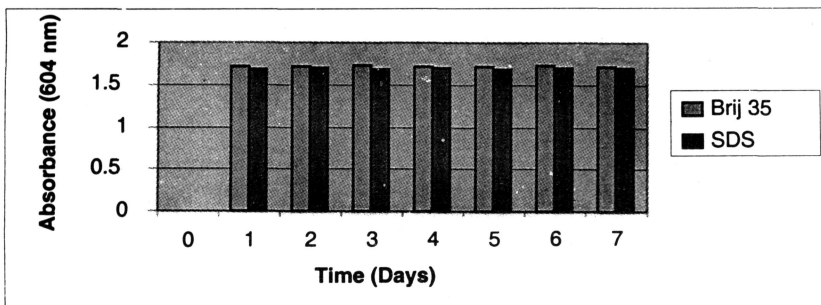


Fig. 4 Test of stability of dithizone in SDS/Brij 35 mixed surfactants solution

mixed micelles of SDS and Brij 35 resulted in dithizone stable for several days. We do not yet have an explanation as to why the SDS/Brij 35 mixed micelle provide more stability to the dithizone than the micelle prepared from single

SDS or Brij 35. Based on the above findings, the remainder of this paper evaluates the utility of dithizone in SDS/Brij 35 mixed micelles for determination of metal ions.

Effect of Surfactants and Dithizone Concentration

Figure 5 shows the effect of the amount of mixed surfactants concentration on the absorption spectra of saturated dithizone solution. The results have shown that absorbance of dithizone in 10% mixed surfactant solution is nearly twice much absorbance of dithizone in 5% mixed surfactants solution. Hence, the solubilization of dithizone is larger in higher mixed surfactants concentration. Figure 6 shows the effect of the amount of dithizone solubilized in 50 mL of 5% mixed surfactant solution. As seen from the absorbance spectra, 5% mixed surfactant solution is saturated after addition of 20 mg of solid dithizone, and an increase in the added amount of dithizone after that does not result in an increase in the absorbance and hence solubility of dithizone. Therefore, the experiment shows that the solubilized amount of dithizone depends on the concentration of surfactants and hence the concentrations of both need to be known and fixed during analysis.

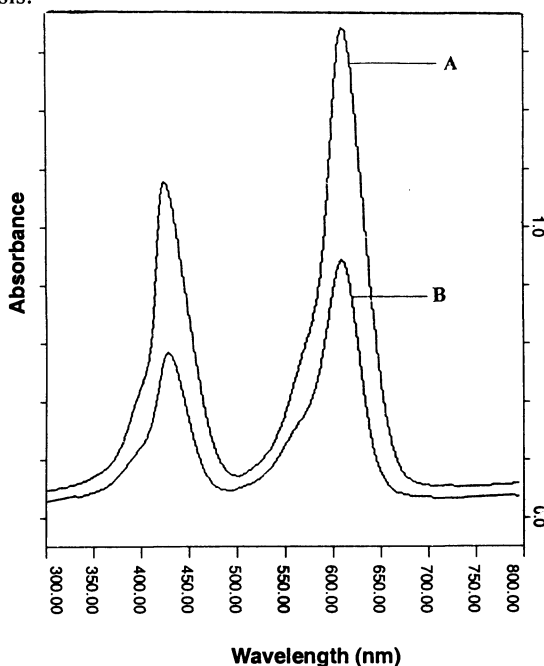


Fig. 5 Saturated solution of dithizone in (A) 5% SDS/Brij 35 mixed surfactants solution, and (B) 10% SDS/Brij 35 mixed surfactants solution

Comparison of the Absorbance Spectra of Metal-Dithizone in Carbon Tetrachloride and in Mixed Surfactant Solution

The absorbance spectra of dithizone in carbon tetrachloride and 5% mixed surfactants are shown in Figures 7 and 8, respectively. The metal-dithizone

complexation conditions are summarized in Table 1. It is important to note that the wavelength of the absorbance maxima for all the metal-dithizone complexes are shifted by exactly 20 nm to higher wavelength in mixed surfactants solutions. This finding may be caused by the residence of the metal complexes in the interior of the nonpolar microenvironment of the SDS/Brij 35 mixed micelles. Lopez *et al.*¹⁰ have reported that the residence time of a solute molecule in the micelles is generally $10^{-3} - 10^{-5}$ s. Thus, the metal-dithizone complexes formation is dynamic and essentially instantaneous.

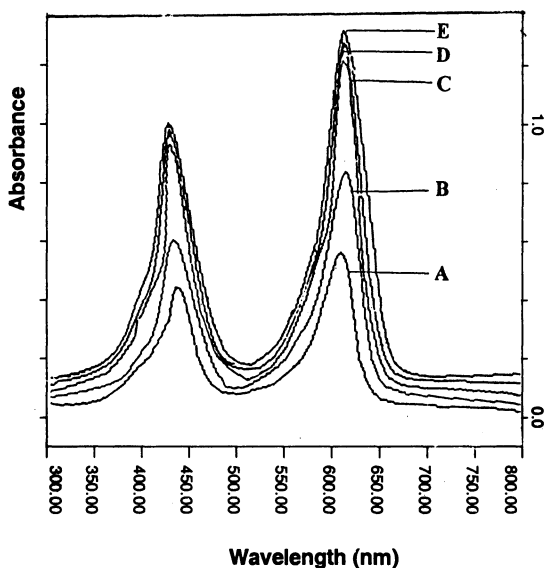


Fig. 6 Absorbance spectra of (A) 5, (B) 10, (C) 15, (D) 20, (E) 25 mg of dithizone in 50 mL of 5% SDS/Brij 35 mixed surfactants solution

TABLE-1
METAL-DITHIZONE COMPLEXES CONDITIONS IN SDS/BRIJ 35 SURFACTANTS SOLUTION AND CARBON TETRACHLORIDE

Metal ion (M^{2+})	pH ^a	λ_{max} (nm)	
		In mixed surfactants	In carbon tetrachloride
Hg	2	470	450
Cd	> 10	535	515
Cu	1	570	550
Pb	7-10	520	500
Zn	5	570	550

^aFrom reference 1, and the pH was adjusted using either NaOH or HCl solutions.

TABLE-2
CALIBRATION DATA FOR METAL-DITHIZONE COMPLEXES IN SDS/BRIJ 35 MIXED SURFACTANTS SOLUTION

Metal ion (M ²⁺)	Regression equation	R ²	Linear range	Detection limit (ppb)
Hg	$y = 0.35432 + 1.4250 \times 10^{-3} x$	0.992	0.5–4	6
Cd	$y = 0.19482 + 7.9563 \times 10^{-2} x$	0.998	0.1–2	5
Pb	$y = 0.60210 + 5.7223 \times 10^{-3} x$	0.993	0.3–2	6
Cu	$y = 0.58902 + 2.2391 \times 10^{-2} x$	0.997	0.1–1	4
Zn	$y = 0.35011 + 6.1021 \times 10^{-2} x$	0.999	0.1–1	3

TABLE-3
RECOVERY DATA FOR METAL IONS BY COMPLEXATION WITH DITHIZONE IN SDS/BRIJ 35 MIXED SURFACTANTS SOLUTIONS

Metal ion (M ²⁺)	Spiked conc. (ppm)	Absorbance	Mean recovery	%RSD
Hg	0.5	0.296	99	5.7
	1.0	0.602	100	9.2
	2.0	1.286	98	4.0
	3.0	1.878	100	8.7
Cd	0.5	0.669	96	5.2
	1.0	1.341	95	10.0
	2.0	2.680	99	5.3
	3.0	4.000	100	4.7
Cu	0.5	0.806	96	6.8
	1.0	1.620	97	7.1
	2.0	3.321	99	8.2
	3.0	4.850	96	10.0
Zn	0.5	0.581	95	8.4
	1.0	1.201	95	6.1
	2.0	2.525	98	7.9
	3.0	3.801	96	9.8
Pb	0.5	0.727	94	4.8
	1.0	1.425	97	10.0
	2.0	2.810	99	9.6
	3.0	4.217	95	7.3

Calibration Data, Recoveries, and Detection Limits

The calibration data for each of the metal ions when complexed with dithizone in mixed surfactants solutions are shown in Table-2. It should be noted that when we constructed the calibration graphs the absorptions for complexes were determined at the absorption maxima. Table-2 shows the linear range (the range over which Beer's law is obeyed), regression equations for each plot and the correlation coefficients over the entire range (R^2). The correlation coefficients were ranging from 0.992 to 0.999 ($n = 5$). Detection limits of the metal ions were obtained by spiking the dithizone in mixed surfactants solution with an analyte such that the resulting concentration of the solution produces an absorbance signal that was equal to twice the peak-to-peak noise. Comparison of the detection limit obtained with the use of mixed surfactants and the detection limit obtains with the use of chlorinated hydrocarbon extraction shows the detection limits improvements range from 10 to 50 x. The recovery data were tested for each metal ion at 4 different concentrations, as shown in Table 3. It was interesting to note that the recovery data (concentrations determined by our method compared to the spiked concentrations) for the various metal ions ranged from 95 to 100% with RSDs ranging from 4.0 to 10%.

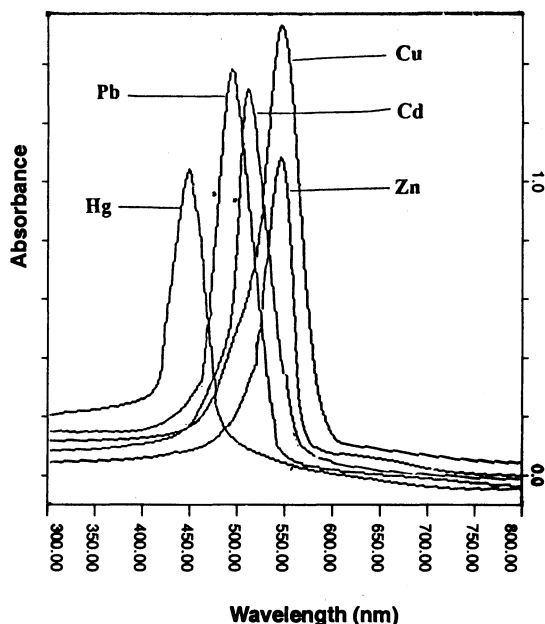


Fig. 7 Absorption spectra of metal-dithizone complexes in carbon tetrachloride

Determination of Metal Ions from Mixed Metal Ions Solution

Based on the above observations, the possibility of applying the method to evaluate metal ions from mixed metal ions solution was studied. In order to

determine the calibration data we spiked a saturated solution of dithizone in 5% mixed surfactants solution with standards from each metal ion.

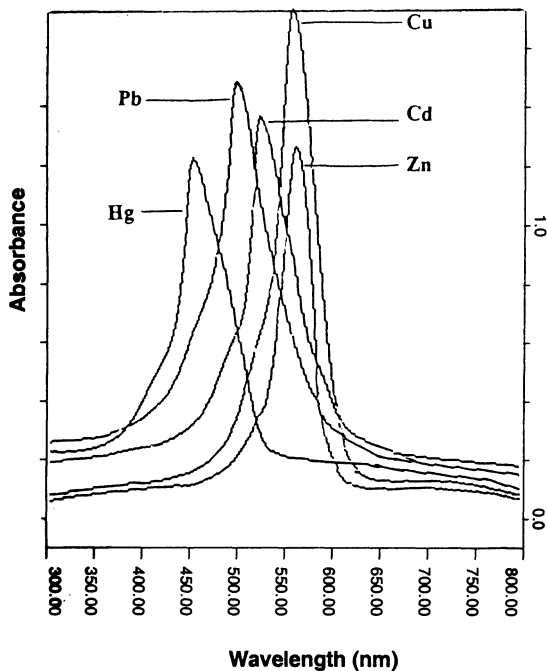


Fig. 8 Absorption spectra of metal-dithizone complexes in 5% SDS/Brij 35 mixed surfactants solution

Table-4 summarizes the calibration data of each of the studied metal ions in a mixed metal ions solution. The quantitative evaluation for each metal ion was calculated at pH at which the metal ion complexes with the dithizone solution as recommended in ref. 1. For example, to evaluate copper the solution was adjusted to pH < 1; a slight excess of a saturated solution of dithizone in 5% mixed surfactants was added. Under this condition copper reacts with dithizone first to form its dithizonate while Hg requires higher pH. The solution was allowed to equilibrate for 5 min before measuring the absorbance of the copper-dithizone complex absorbance at 570 nm. After estimating copper, the solution from the cuvette was transferred back to the original solution, and the pH was adjusted to 2 by addition of 5% NaOH. This resulted in the decomposition of the copper complex and the liberated dithizone combined with mercury to form mercury- dithizone complex. After determination of mercury the other metal ions were determined by adjusting the pH of the solution as reported in Table 4, thus allowing the sequential determination of metal ions. Table-5 summarizes the recovery data for each metal ion from a mixed metal ions solution. The recoveries ranged from 93 to 104% with RSDs between 3.5 and 12% (n = 4). According to these results, our method is thus suitable for the quantitative analysis of metal ions from mixed metal ions solution.

TABLE-4
CALIBRATION DATA FOR METAL IONS IN SDS/BRIJ 35
MIXED SURFACTANTS SOLUTION

Metal ion (M^{2+})	pH	Regression equation	Linear range	R^2
Hg	2	$y = 0.32176 + 2.9607 \times 10^{-2} x$	0.1–1.0	0.993
Cd	>10	$y = 0.15284 + 3.6123 \times 10^{-2} x$	0.1–0.8	0.994
Pb	7–10	$y = 0.42681 + 5.1620 \times 10^{-3} x$	0.4–1.5	0.993
Cu	<1	$y = 0.51570 + 2.0373 \times 10^{-2} x$	0.1–0.8	0.999
Zn	5	$y = 0.34832 + 0.1194 \times 10^{-2} x$	0.1–1.0	0.995

TABLE-5
RECOVERY DATA OF METAL IONS FROM MIXED METAL IONS SOLUTION

Metal ion (M^{2+})	Spiked conc. (ppm)	Absorbance	% Recovery	% RSD
Hg	0.5	0.2875	97	10.0
	1.0	0.5901	102	6.9
Cd	0.5	0.6713	104	7.2
	1.0	1.3957	98	8.6
Pb	0.5	0.7231	94	4.5
	1.0	1.3792	95	10.5
Cu	0.5	0.7810	103	8.6
	1.0	1.6390	95	12.0
Zn	0.5	0.5701	93	5.4
	1.0	1.1587	99	7.8

REFERENCES

1. Z. Marczenko, in C. G. Ramsay (Ed.), *Spectrophotometric Determination of Elements*, John Wiley & Sons, New York, Chapters 2, 12, 19, 28, 31 and 60 (1996).
2. G.L. McIntire, *Crit. Rev. Anal. Chem.*, **21**, 257 (1990).
3. J. Georges, *Spectrochim. Acta Rev.*, **13**, 27 (1990).
4. K. Ogino, H. Uchiyama and M. Abe, in: K. Ogino and M. Abe (Ed.), *Mixed Surfactant Systems*, Marcel-Dekker, New York, p. 206 (1993).

5. L.K. Shao and D.C. Locke, *Anal. Chem.*, **70**, 897 (1998).
6. A. Garcia, M.B. Ghoulm, G. Marion and J. Lachaise, *J. Phys. Chem.*, **93**, 4167 (1989).
7. B. Vaidya and M.D. Porter, *Anal. Chem.*, **69**, 2688 (1997).
8. H. Watanabe and H. Tanaka, *Talanta*, **25**, 585 (1978).
9. K. Ueno, K. Shirashi, T. Togo, T. Yano, L. Yoshida and H. Kobuyashi, *Anal. Chim. Acta*, **105**, 289 (1979).
10. A. Lopez Garcia, E. Blanco Gonzalez, J.I. Garcia Alonso and M. Sanz, *Anal. Chim. Acta*, **264**, 241 (1992).

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