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SHORT COMMUNICATION

**Room temperature cloud point extraction: An application to
preconcentration and spectrophotometric determination of
copper(II)**

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Abstract: The novel cloud point extraction procedure for preconcentration of copper(II) was discovered. A simple chemical method for initiating the cloud point extraction (CPE) has been proposed. The formation of surfactant rich phase in a system containing a nonionic surfactant Triton X-100, copper(II), 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride (DHMPb) and ammonium benzoate is observed immediately upon the sulfuric acid addition into solution. Under the optimal conditions (absorption band maximum was 540 nm, concentration 1.5×10^{-4} mol dm⁻³ of DHMPb, 1.0 vol.% of Triton X-100, 2.0 cm³ of 0.75 mol dm⁻³ ammonium benzoate, and 1.0 cm³ of 0.5 mol dm⁻³ sulfuric acid solution for obtaining benzoic–benzoate buffer solution with pH 4.5 and initiation immediate surfactant rich phase formation) the calibration plot for spectrophotometric determination of copper(II) was linear in the range of copper(II) concentration 0.02–0.95 μg cm⁻³. The limit of detection was calculated 0.006 μg cm⁻³. The water samples were analyzed according to a suggested procedure with satisfactory results.

Keywords: cloud point extraction; spectrophotometry; copper(II); water analysis; surfactant rich phase.

INTRODUCTION

The cloud point extraction (CPE) is a modern, environmentally friendly and an effective alternative to classical liquid–liquid extraction (LLE).¹ The CPE is easily combined with various analytical methods, such as spectrophotometry, atomic absorption spectroscopy, atomic emission spectroscopy, ICP-MS and other. The CPE is based on heating a solution that contains an analyte, a complexing agent and a surfactant to the cloud point temperature.^{2–4} Nonionic surf-

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actants are the most commonly used for CPE.^{1,4} For CPE intensification the ultrasonic or microwave irradiation was used.⁵⁻⁸ In most cases, with the help of physical influence on the system, there is only an opportunity to slightly lower the cloud point temperature and shorten the time of the surfactant rich phase generation. Thus, as the main disadvantage of CPE should be considered the duration time of the surfactant rich phase formation. Chemical methods for initiating CPE are more typical when anionic surfactants are used.^{1,9} In the case of non-ionic surfactants, the chemical initiation of CPE has been little studied. A number of studies have described that sodium sulfate introduction leads to immediate formation of the surfactant rich phase.^{10,11} In turn, in many studies was noted that the introduction of sodium sulfate and other electrolytes led to a more or less significant decrease in the cloud point temperature.^{1,11} In this case, the positive effect of salts (salting out effect) does not completely avoid heating the solution to initiate CPE. Thus, one can point out that one of the directions of development of CPE is the search for ways to initiate it. It is known that the cloud point phenomenon occurs due to the destruction of hydrogen bonds and the dehydration of oxygen atoms of surfactant molecules, which leads to the aggregation of micelles when the solution is heated to a cloud point temperature.¹⁻⁴ In our opinion, a similar effect can be achieved by introducing organic substances, for example, certain aromatic carboxylic acids. A high content of benzoic or salicylic acids will make it possible to dehydrate large surfactant molecules and their micelles by more profitable hydration of comparatively small molecules of acids and lead to the generation of a surfactant rich phase. Due to the poor solubility of these acids in water, they are obtained directly in the system by the reaction of their sodium or ammonium salts with mineral acids.

Copper is an essential trace element that performs a number of important physiological functions in living organisms. In other hand, copper is one of the most toxic heavy metals.¹² Therefore, in recent years, special attention has been focused on the control of environmental pollution by heavy metals, including copper. The increase of copper content in water and plants is associated with human industrial activities, namely waste dumping and the excessive use of herbicides. In turn, various methods for copper determination were proposed. Basically, flame atomic absorption spectroscopy¹³, ICP-AES¹⁴ and spectrophotometry¹⁵ were used for copper quantification. Due to the fact that copper in plants, water and food products is in trace level, there is a need for preconcentration regardless of the measurement method used. A various techniques for copper preconcentration, such as LLE¹⁶, solid-phase extraction (SPE)¹⁷ and CPE were proposed.¹⁸⁻²⁰ In order to apply CPE effectively, it is necessary to use analytes with high hydrophobicity. Therefore, it becomes necessary to convert copper into hydrophobic compounds, for example, by complexation with chelating ligands. The most widely used organic chelating ligands for copper are 4-(2-pyridylazo)res-

orcinol, 1-(2-pyridylazo)-2-naphthol, 1-(2-thiazolylazo)-2-naphthol, sodium diethyl-dithiocarbamate, dithizone and eriochrome cyanine R.¹⁵ Effective chelating ligands based on benzopyrilium derivatives should also be noted. Synthesis, acid–base, spectroscopic and complexing properties of some 6,7-dihydroxybenzopyrilium derivatives were described in previous studies.^{21,22}

The aim of this work was to investigate a room temperature CPE (RT-CPE) process for copper(II) preconcentration in form of its complex with 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride (DHMPPhB) prior to Cu(II) spectrophotometric determination.

EXPERIMENTAL

Chemicals

The Cu(II) 1×10^{-2} mol dm⁻³ stock solution was prepared by dissolving CuSO₄·5H₂O in distilled water and standardized by iodimetric titration. The nonionic surfactant Triton X-100 (Merck, Germany) aqueous solution with concentration 10 vol.% was used. The DHMPPhB was synthesized²¹ by condensation of pyrogallol A (TOR, Ukraine) with benzoylacetone (Acros, Belgium) in presence of hydrochloric acid and recrystallized from ethanol.

A 10^{-3} mol dm⁻³ stock solution of DHMPPhB was prepared by dissolving its appropriate weight in ethanol. The ammonium benzoate and sulfuric acid were used for initiate CPE. The pH of mixture was adjusted by benzoic acid/ammonium benzoate buffer solution. Some organic solvents, such as methanol, dimethylsulfoxide (DMSO), acetonitrile, 2-propanol, tetrahydrofurane (THF), acetone and its mixtures were used for dilution of surfactant rich phase. All organic solvents and chemicals used were analytically pure grade.

Instrumentations

An SF-56 spectrophotometer (OKB “Spectr”, Russia) was used for recording absorption spectra and absorbance measurements with 1 cm quartz cells. The pH values were measured using an I-160 potentiometer (ZIP, Belarus) with combined glass electrode. A centrifuge model MPW-340 with conical 15 cm³ tubes was used for phase separation.

General procedure

Various amounts (0.1–1.5 cm³) of Cu(II) solution with a concentration 10^{-4} mol dm⁻³, 0.3 cm³ of 5×10^{-3} mol dm⁻³ DHMPPhB solution, 1 cm³ of Triton X-100 solution (10 vol.%), 2 cm³ of ammonium benzoate (0.75 mol dm⁻³), 1.0 cm³ of sulfuric acid solution (0.5 mol dm⁻³) were placed into 15 cm³ centrifuge test tubes and diluted with double distilled water to a total volume of 10 cm³. The solution immediately became cloudy and a surfactant rich phase was formed. The tubes are centrifuged for 5 minutes at 3000 rpm. The more viscous surfactant rich phase was at the bottom and the upper aqueous layer was removed by just inverting the test tube. The surfactant rich phase was unsuitable for direct absorbance measurement and it was diluted with 1 cm³ of THF to reduce the viscosity.

Sampling and sample pretreatment

A tap water sample was taken from our laboratory. A drinking water sample was taken in one of the Odessa pump rooms (Odessa, Ukraine). The water samples of 100 cm³ volume are evaporated almost to dryness, 3 cm³ of ammonia solution was added for the interfering matrix components removal and the formed precipitate was filtered off. The filtrate was neutralized

to pH 6–7 and diluted in a 10 cm³ volumetric flask with double distilled water. The obtained solutions were used for analysis by the described method.

RESULTS AND DISCUSSION

The absorbance spectra of DHMPPhB and its complex with Cu(II) in aqueous solution and after RT-CPE are shown in Fig. 1.

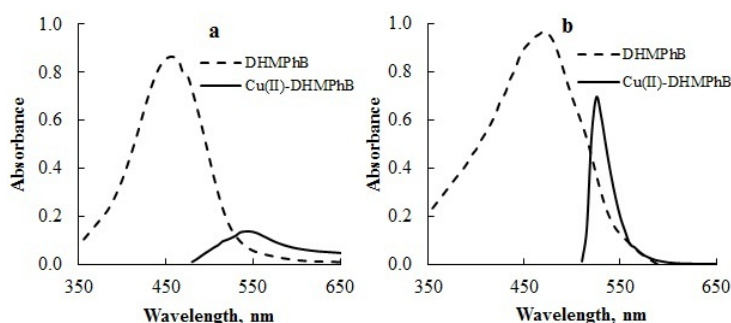


Fig. 1. The absorbance spectra of DHMPPhB and its complex with Cu(II) in: a) aqueous solutions ($c_{\text{Cu(II)}} = 7.0 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{\text{DHMPPhB}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$) and b) after RT-CPE ($c_{\text{Cu(II)}} = 7.0 \times 10^{-6} \text{ mol dm}^{-3}$, $c_{\text{DHMPPhB}} = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$); $l = 1 \text{ cm}$.

As can be seen from Fig. 1a, one absorption band is observed in the absorption spectrum of DHMPPhB with a maximum at 450 nm, and interaction with copper(II) leads to the appearance of an absorption band with a maximum at 540 nm. It is interesting that the replacement of the aqueous medium with the micellar one leads to a narrowing of the absorption band of the complex (Fig. 1b).

To take full advantage of the RT-CPE technique, the DHMPPhB concentration and all reaction conditions must be optimized. It was established that with less than 0.15 mol dm^{-3} of ammonium benzoate (2 cm^3 of 0.75 mol dm^{-3} ammonium benzoate solution) introduction into the system and also with sulfuric acid addition, the clouding phenomenon is not observed. The addition of sulfuric acid to the solution containing Cu(II), DHMPPhB, Triton X-100 and 0.15 mol dm^{-3} of ammonium benzoate leads to an immediate surfactant rich phase formation and the formation of benzoic–benzoate buffer solution, which determines the medium acidity. The pH plays an important role in the formation of chelate complexes of metal ions with organic ligands. The effect of the medium acidity on the formation and the PT-CPE of Cu(II) complex with DHMPPhB is shown in Fig. 2a.

As can be seen from Fig. 2a, the maximum of RT-CPE efficiency was obtained at pH 4.5 and this was selected for the further study. Following the Fig. 2b data optimum concentrations of DHMPPhB and Fig. 2c Triton X-100 were found to be $1.5 \times 10^{-4} \text{ mol dm}^{-3}$ and 1.0 vol.%, respectively.

Because the surfactant-rich phase was viscous and unsuitable for direct absorbance measurement, different solvents were tried, in order to select the one

producing the maximal sensitivity. The maximum of absorbance is observed when using THF as a diluting solvent and the change in absorbance is due to the nature of the solvent: the absorbance increases with decreasing of Dimroth–Reichardt solvatochromic parameter.

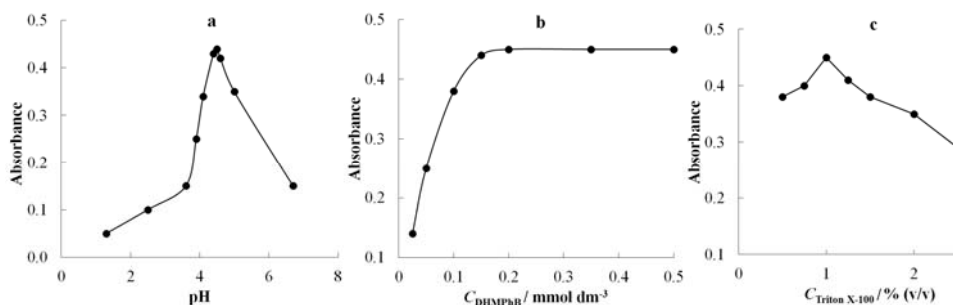


Fig. 2. Effects of chemical variables on the RT-CPE efficiency of Cu(II) complex with DHMPhB: effect of pH (a), DHMPhB concentration (b) and Triton X-100 concentration (c); pH 4.5, $c_{\text{Cu(II)}} = 5.0 \times 10^{-6} \text{ mol dm}^{-3}$, $l = 1 \text{ cm}$.

Under the optimized conditions, a calibration graph for RT-CPE procedure for Cu(II) preconcentration and spectrophotometric determination of Cu(II) was linear in the concentration range of $0.02\text{--}0.95 \mu\text{g cm}^{-3}$ and is described by the equation: $A = 1.3363c_{\text{Cu(II)}} + 0.0092$ ($R^2 = 0.999$). Also, the limit of detection (LOD , $3\sigma_b/m$) and the limit of quantification (LOQ , $10\sigma_b/m$) were calculated to be 0.006 and $0.02 \mu\text{g cm}^{-3}$, respectively. The precision and accuracy of the proposed RT-CPE technique were checked by performing 6 measurements at two concentration levels (0.15 and $0.65 \mu\text{g cm}^{-3}$ Cu(II)), over two consecutive days. The relative standard deviations (RSD , %) and recoveries (R , %) were in the range $3.1\text{--}4.9\%$ and $98.5\text{--}106.7\%$, respectively.

The effect of some interfering ions on the spectrophotometric determination of Cu(II) after its RT-CPE preconcentration was examined. A ratio of Cu(II):interferent, which resulted in an error not exceeding 5% , was taken as the tolerable amount for each ion. It was established that ions of alkaline and alkaline earth metals did not interfere. Some other of the examined ions didn't interfere at the following mole ratios: $1:1000$ (Mg^{2+} , Cd^{2+} , Mn^{2+} , Pb^{2+} , NO_3^-); $1:500$ (SO_4^{2-} , F^- , Br^- , Cl^- , PO_4^{3-}); $1:200$ (Zn^{2+} , Al^{3+}); $1:50$ (Ni^{2+} , Co^{2+}). The determination was hindered by Fe^{2+} and Fe^{3+} which were masked with NaF, or previously removed from the sample.

The proposed method was successfully applied to the determination of Cu(II) ion in water samples (Table I).

The recoveries are close to 100% and indicate that the suggested RT-CPE procedure was helpful for the Cu(II) preconcentration and spectrophotometric determination.

Table II shows a comparison of the RT-CPE technique described in this work with some literature studies. The comparison discovers that the developed RT-CPE method is characterized by a wide linear range and a relatively low limit of detection (*LOD*). In contrast to the more sensitive CPE techniques^{23,24} it does not require heating to initiate a cloud point phenomenon and extraction is fast (>1 min).

TABLE I. Determination of Cu(II) in water samples by the proposed method ($n = 5$, $P = 0.95$)

Sample	Cu(II) concentration, ng cm ⁻³		RSD / %	R / %
	Added	Found		
Tap water	–	22.1±1.04	3.8	–
	10.0	32.2±1.64	4.3	101.0
Drinking water	–	<LOQ	–	–
	10.0	10.05±0.46	3.5	100.5

TABLE II. Comparison of proposed RT-CPE technique with some literature studies; CPE – cloud point extraction; LLE – liquid–liquid extraction; SPE – solid-phase extraction; RT-CPE – room-temperature cloud point extraction; Pb(DDTC)₂ – lead diethyldithiocarbamate; DRS – diffuse reflectance spectroscopy; FAAS – flame atomic absorption spectroscopy; ST – spectrophotometry

Reagent	Preconcentration technique	Detection	Linear range μg cm ⁻³	<i>LOD</i> μg cm ⁻³	Ref.
Dithizone	CPE	ST	0.015–0.25	0.0046	23
Isoleucine	CPE	ST	0.010–1.00	0.005	24
Caproic acid and octylamine	CPE	FAAS	up to 2.0	0.01	20
<i>S,S'</i> -bis(2-minophenyl)-oxalate	LLE	ST	0.4–150	11.5	25
Pb(DDTC) ₂ ^a	SPE	DRS	0.5–50.0 μg	0.3 μg	17
DHMPbB	RT-CPE	ST	0.02–0.95	0.006	This work

^aAbsolute values are given

CONCLUSION

A room temperature cloud point extraction procedure for copper(II) preconcentration as a complex with 6,7-dihydroxy-4-methyl-2-phenylbenzopyrilium chloride has been described. The immediate formation of the surfactant rich phase in the system based on Triton X-100 begins during the benzoic acid generation following the reaction between ammonium benzoate with sulfuric acid. The optimum conditions for copper(II) preconcentration and spectrophotometric determination were found to be: absorption band maximum (540 nm), concentration of reagent (1.5×10^{-4} mol dm⁻³), mass fraction of Triton X-100 (1.0 %), 0.5 cm³ of 0.75 mol dm⁻³ ammonium benzoate, and 0.5 cm³ of 0.5 mol dm⁻³ sulfuric acid solution for obtaining benzoic-benzoate buffer solution with pH 4.5 and initiation surfactant rich phase formation. The effective molar absorptivity, limit of detection, limit of quantification and Beer's low range were 8.5×10^4 dm³ mol⁻¹ cm⁻¹, 0.006 μg cm⁻³, 0.02 μg cm⁻³ and 0.02–0.95 μg cm⁻³ respectively.

ИЗВОД
 ЕКСТРАКЦИЈА У ТАЧКИ ЗАМУЋЕЊА: ПРИМЕНА У ПРЕКОНЦЕНТРАЦИЈИ И
 СПЕКТРОФОТОМЕТРИЈСКОМ ОДРЕЂИВАЊУ Cu(II)

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Описана је новооткривена процедура за прекоцентрацију Cu(II) применом екстракције у тачки замућења (CPE). Одмах по додатку сумпорне киселине примењено је формирање сурфактантом богате фазе у систему који садржи нејонски сурфактант Triton X-100, Cu(II), 6,7-дихидрокси-4-метил-2-фенилбензопирилијум-хлорид (DHMPbV) и амонијум-бензоат. Под оптималним условима (апсорпциони максимум: 540 nm, концентрација DHMPbV $1,5 \times 10^{-4}$ mol dm⁻³, концентрација Triton X-100: 1,0 запр.%, 2,0 cm³ 0,75 mol dm⁻³ амонијум-бензоата и 1,0 cm³ 0,5 mol dm⁻³ сумпорне киселине за добијање пуфера pH 4,5), калибрациона права за спектрофотометријско одређивање Cu(II) је линеарна у опсегу концентрација 0,02–0,95 µg cm⁻³. Граница детекције износи 0,006 µg cm⁻³. Анализа узорака вода према предложеној процедури је дала задовољавајуће резултате.

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