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Cloud point extraction of Cu(II) using a mixture of triton X-100 and dithizone with a salting-out effect and its application to visual determination

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ABSTRACT

A method for the separation and concentration of trace copper(II) ion (Cu(II)) via cloud point extraction (CPE) using a nonionic surfactant with a salting-out effect was developed and applied as a technique for the visual determination of Cu(II). Triton X-100 (TX-100), which has a cloud point at 64–67 °C in aqueous solutions, was used as the nonionic surfactant for the CPE of Cu(II). Although CPE with TX-100 requires heating of the solution to separate the surfactant-rich phase from the aqueous phase, the new method achieves phase separation at 15–30 °C owing to the addition of a large amount of salt to the solution, which lowers the cloud point. The compound 1,5-diphenylthiocarbazone (dithizone) was selected as the chelating agent for complexation and transfer of Cu(II) to the surfactant-rich phase. The extractability of Cu(II) (initial concentration: 10 μM) was 96.6 ± 2.1% when Na_2SO_4 was added to a 20% TX-100/4 μM dithizone solution (pH 2). Using this method, the visual determination of Cu(II) was possible for concentrations ranging from 0.01 to 10 μM. In addition, the extraction system was successfully applied to the visual determination of Cu(II) in a river water sample.

1. Introduction

Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex cytochrome c oxidase [1]. However, long-term exposure to copper leads to health damages of the organisms including human. For example, the Watarase River in Kiryu-city, Gunma Pref., which is located near our laboratory, has a history of being polluted with copper, an event known at the time as the “Ashio Koudoku (Ashio Mine poisoning) ”. Even today, this river water has a higher concentration of copper ion (Cu(II)) compared to other rivers (*ca.* 1.0×10^{-7} M level in the Watarase River *vs.* $< 1.0 \times 10^{-8}$ M level in average river waters of Japan.) [2,3]. The fact has been reported that copper present in the wastewater from mines in the world often pollutes environmental waters, such as river water and ground water [4]. Therefore, the analysis of Cu(II) in environmental waters is very important for environmental preservation and management.

The analysis of Cu(II), as well as other heavy metals, in environmental water samples generally begins with a simplified analytical screening method, which is then followed by an analytical technique designed to provide precise determination. Simplified analytical methods can be broadly divided into two categories: those using small equipment and those based on visual determination. Because visual determination is a simple method that eliminates the need for any specialized equipment, it has become particularly useful in the fields of environmental, food, and medical analysis [5].

For visual determination, a change in color is one parameter used for the estimation of the concentration of a target substance. It can be classified on the basis of three criteria: color phase, brightness, and color saturation [6]. Of these three criteria, changes in color phase are most easily distinguished by human sight.

For visually determining trace constituents in environmental water samples, it is necessary to concentrate the sample to a level at which determination is possible. The measurement of heavy metals in water samples requires the use of preconcentration methods, such as coprecipitation, ion exchange, and extraction [7–15].

In this study, cloud point extraction (CPE) using a nonionic surfactant [16–18] was selected as the preconcentration method for enabling the visual determination of Cu(II). CPE follows the principles of “Green Chemistry” because it uses small amounts of mildly toxic surfactants compared with the more established use of toxic organic solvents. Surfactants are also non-flammable and not particularly volatile, which are qualities that minimize the risk associated with the extraction process [19]. This analytical technique utilizes the clouding behavior observed when a solution containing a polyoxyethylene-type nonionic surfactant is stirred and/or heated before being allowed to settle. Because the surfactant is dehydrated

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Table 1
Characteristics of several nonionic surfactants [20].

	Surfactant (EO mol number)[a]	Cloud point, (°C)	HLB number [b]	CMC, (mM) [c]
Polyoxyethylene nonylphenyl ether	PONPE-7.5 (7.5)	25	–	0.085
Polyoxyethylene octylphenyl ether	Triton X-114 (7–8)	22–25	12.4	0.35
	Triton X-100 (9–10)	64–67	13.5	0.25
Polyoxyethylene sorbitan monooleate	Tween 80 (20)	93	15.0	0.010

[a] EO: ethylene oxide.
[b] HLB: hydrophilic–lipophilic balance.
[c] CMC: critical micelle concentration.

during the settling process, the liquid separates into aqueous and surfactant-rich phases.

The characteristics of the main nonionic surfactants used in the CPE of heavy metals are summarized in Table 1 [20]. Triton X-100 (TX-100) has a cloud point of *ca.* 64–67 °C; phase separation by CPE normally requires heating above the cloud point. Surfactants such as PONPE-7.5 and Triton X-114 (TX-114), which have cloud points near room temperature, might be considered to be alternative options. However, these surfactants are easily affected by changes in temperature during the analysis. Additionally, solutions of these surfactants that contain chelating agents are unstable when exposed to heat and light; phase separation also occurs unpredictably when these solutions are stored in the cold and dark.

Herein, we introduced a salting-out method that enables the room temperature phase separation of surfactants with high cloud points, such as TX-100. When adding an inorganic salt to the nonionic surfactant solution, the cloud point decreases with the concentration of the salt. This is because the water molecules surrounding the nonionic surfactant are more strongly oriented toward the salt anions (*e.g.*, Cl^-, SO_4^{2-}), even at room temperature [21,22].

The 1,5-diphenylthiocarbazone (dithizone) was selected as the chelating agent for the transfer of Cu(II) into the surfactant-rich phase. Dithizone forms water-insoluble complexes with soft metals (*e.g.*, Cu(II), and Cd(II)). This compound has been extensively studied and is commonly used for the spectrometric determination of soft metals [23–25]. Metal-dithizone complexes undergo a significant color change from dark green to red in accordance with the metal ion concentration. Therefore, dithizone is a potentially useful reagent for the CPE-mediated phase separation of Cu(II) and its use as a visual determination method.

Previously, the CPE of Cu(II) with TX-114 and dithizone was reported by Manzoori et al. [26]. Because the cloud point of TX-114 is 22–25 °C, it can separate the surfactant-rich and aqueous phases at these temperatures [20,26]. However, the use of a 40 °C water bath was required to obtain defined phase separation. Scott et al. reported that the cloud point of an aqueous solution containing a nonionic surfactant could be lowered by the addition of a salt [27]. Horvath et al. reported an extraction technique for porphyrins via CPE that depended on the addition of salt to decrease the cloud point and avoid heating the samples [28]. Dilip et al. demonstrated the relationship between the temperature and the salting-out effect for the cloud points of poly(ethylene glycol) and poly(ethylene oxide)-poly(propylene oxide) [29]. However, to our knowledge, the use of the salting-out method for the CPE of Cu(II) at room temperature and its application to the visual determination of such metal have not yet been investigated.

Herein, we report the results of an examination of the effects of salt addition, solution temperature, and settling time on the CPE of Cu(II) introduced into a solution containing dithizone and TX-100. Visual determination of trace Cu(II) was then performed by dropping the surfactant-rich phase obtained following CPE onto a filter paper. This visual detection method was also applied to the determination of the Cu(II) concentration in a sample collected from the Watarase River.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and were purchased from Wako (Osaka, Japan). Water used for the dissolution of reagents and the dilution of sample solutions was obtained from an ultrapure water system (Iwaki, ASK-2DS). Stock solutions of Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) (0.1 M each) were each prepared by diluting aqueous 1% HNO_3 atomic absorption spectrometry standard solutions (1000 mg/L) with appropriate amounts of water. Mixed solutions of dithizone and surfactant were prepared by dissolving an adequate amount of dithizone in 1–30% TX-100 (Sigma-Aldrich) and stirring with a magnetic stirrer (Yazawa KF-22) for 4 h. The prepared TX-100–dithizone solutions were stored in a cool and dark location. Buffer solutions containing metal ions were prepared using HCl ($pH < 2$), CH_3COOH/CH_3COONa (pH 3–5), and NaH_2PO_4/Na_2HPO_4 (pH 6–7) in water.

2.2. Apparatus

Measurement of the pH of the test solutions was performed using pH meter electrodes (Horiba F-22). Heavy metal ion concentrations were determined by flame atomic absorbance spectrophotometry (FAAS: Hitachi Z-5300).

The cloud points of the surfactant solutions were measured in the same manner as reported by Nishi et al. (Fig. S1) [30]. First, a test tube containing a solution cooled to 5 °C was prepared in a beaker that was filled with water at 5 °C. Next, the solution was heated in a thermostat while stirring with a stirring rod. The cloud point of the solution was the temperature at which the solution rapidly became cloudy.

2.3. Cloud point extraction procedure

A buffer solution with a known concentration of heavy metal was mixed with a TX-100/dithizone solution as necessary. The solution was diluted up to 20 mL with water after adjusting the pH with either 0.1 M HCl or 0.1 M NaOH. The prepared solution was then added to a sample bottle, which was followed by the addition of an adequate amount of salt (NaCl, KCl, Na_2SO_4, or K_2SO_4). The solution containing the salt was then stirred at room temperature until it became cloudy. To separate the surfactant-rich phase from the aqueous phase, the clouded solution was allowed to settle for a certain period of time (10–180 min). The heavy metal concentration in the separated aqueous and surfactant-rich phases was measured by FAAS. The extractivity (E, %) was calculated from the concentration of the heavy metal ($[M]_0$) in the solution before the separation and the concentration of the heavy metal ($[M]_a$) that remained in the aqueous phase after phase separation (Eq. (1)):

$$E(\%) = \frac{[M]_0 - [M]_a}{[M]_0} \times 100 \tag{1}$$

For the CPEs of heated solutions of heavy metals, the TX-100/dithizone solutions were prepared according to the procedure as described above, except for the addition of salt. After the clouded solution was added to the sample bottle, it was allowed to settle for 1 h in a 95 °C water bath and then cooled in an ice bath to separate the surfactant and aqueous phases. The experimental procedure after the phase separation was the same as described above. The extractivities of the heavy metal ions into the surfactant-rich phase were calculated using Eq. (1).

2.4. Visual determination

A test solution was prepared according to the procedure described in Section 2.3. The final concentration of Cu(II) in the solution ranged from 0.010 μM to 1.0 μM. The surfactant-rich phase obtained after the CPE procedure was dropped onto a filter paper (high water absorbent qualitative filter paper, 6 mmϕ, Whatman) and then visually inspected.

To prepare the colored samples containing Cu(II), dithizone (50 μL) was first added to a TX-100 solution (2 mL); a Cu(II) solution of 1.0×10^{-4} M, which was adjusted to pH 2 using HCl, was subsequently added to achieve the desired concentrations (0.1–0.5 μM). This solution was diluted to 20 mL with water and stirred for 10 min. After adding Na_2SO_4 (4 g) to the solution, the 20% TX-100/4 μM dithizone mixture was stirred for 15 min and then allowed to settle for 1 h. The separated surfactant-rich phase was subsequently dropped onto a piece of a filter paper.

A river water sample was collected from the Watarase River (Kiryu, Gunma Province, Japan) at a location downstream of the Ashio Copper Mine. The pH was adjusted to *ca.* 2 using 0.1 M HCl, and the sample was stored in a cool, dark place.

For visual determination of Cu(II) in the river water sample, 10 mL of the water sample, which was filtered using a 0.45 μm membrane filter, was mixed with a 20% TX-100/4 μM dithizone solution that was adjusted to pH 2 with 0.1 M HCl. Next, Na_2SO_4 (4 g) was added to the solution, and the same procedure as described above for the preparation of the color samples was followed. The Cu(II) concentration in the real river water sample was determined by comparing the color of the surfactant-rich phase dropped on a filter paper with those of the surfactant-rich phases that were obtained for the samples containing different Cu(II) concentrations.

3. Results and discussion

3.1. Cloud point extraction

3.1.1. Effect of the addition of salt

The effect of the addition of different salts on the extractivity of Cu(II) (1.0×10^{-5} M) from a 20% TX-100/4 μM dithizone solution (pH 5) was investigated. The salts NaCl, KCl, Na_2SO_4, and K_2SO_4, which can effectively decrease the cloud point of nonionic surfactants, were studied [31]. The settling time for the phase separation was 1 h at room temperature.

Clouding was observed for the solutions with NaCl, Na_2SO_4, and K_2SO_4, but not for KCl. The surfactant-rich phase (containing the Cu(II)–dithizone complex) floated to the upper surface after settling for 1 h. Notably, the addition of sulfate salts provided a higher extractivity for Cu(II) than the chloride salt, as observed in Table 2. This behavior follows the order of the Hofmeister series [32]. Additionally, Nishi et al. reported that SO_4^{2-} decreased the cloud point of a nonionic surfactant more competently than Cl^- [31]. Consequently, Na_2SO_4 was selected for subsequent experiments, because it has a higher solubility in water than K_2SO_4 [33].

Table 2
Effect of the addition of different salts on the extractivity of Cu(II)[a].

	Extractivity ± standard deviation (n=3), %
NaCl	57.2 ± 2.0
KCl	15.1 ± 1.5
Na_2SO_4	98.7 ± 1.7
K_2SO_4	98.2 ± 3.5

[a] Conditions: [Cu(II)]: 1.0×10^{-5} M; [TX-100]: 20%; [dithizone]: 4 μM; solution pH: 5; amount of added salt: 4 g to 20 mL of the solution; settling time: 1 h; and liquid temperature: 25 °C.

Next, the effect of the amount of Na_2SO_4 added to the solution was investigated. Fig. 1 shows the results obtained when using Cu(II) as the analyte metal ion. The prepared solution and settling time were the same as described above. Defined phase separation was obtained when 2 g or more of Na_2SO_4 was added (Fig. 1a), and a high extractivity for Cu(II) was achieved using 2–5 g of Na_2SO_4 (Fig. 1b).

3.1.2. Effect of the pH of the solution

The influence of the pH on the extractivities of different heavy metal ions was evaluated. In this case, the experiments were performed by the solutions of heavy metal ions with 20% TX-100/4 μM dithizone adjusted to pH 1–5. Na_2SO_4 (4 g) was added to the solution after mixing the solution.

As can be seen in Fig. 2, the maximum extractivities for Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) occurred at pH 5 and reached 99.1 ± 2.8%, 99.4 ± 2.8%, 97.3 ± 1.4%, 98.4 ± 0.7%, and 97.6 ± 4.8%, respectively. However, in the solution of the pH 5, it is difficult to selectively extract Cu(II) from water sample.

Cu(II) had a high extractivity when compared to the other metals, even at pH 1–3, because dithizone has the highest complexation ability for Cu(II) among the analyte metals [23,25]. At a solution pH of 2, the extractivity of Cu(II) was 96.6 ± 2.1%, while other analyte metals were not detected. This result indicates that the selective determination of Cu(II) should be possible by performing the extraction at *ca.* pH 2.

3.1.3. Effect of surfactant concentration

The effect of the concentration of TX-100 (1%–30%) in the extraction solution on the extractivity of Cu(II) was investigated. A nearly quantitative extraction of Cu(II) was achieved when the TX-100 concentration in solutions at pH 2–6 was 20%. It should be noted that for solutions with a TX-100 concentration $\leq$10%, the dithizone did not completely dissolve, while solutions with a $>$30% surfactant concentration solidified into a paste. Consequently, the TX-100 concentration in the solution was set at 20%.

3.1.4. Effect of temperature

The influence of the liquid temperature on the extractivity of Cu(II) was also investigated. After mixing a 20% TX-100/4 μM dithizone solution with Cu(II) (1.0×10^{-5} M), Na_2SO_4 (4 g) was added. While stirring the solution, the liquid temperature was varied from 0 to 40 °C using either an ice bath or a thermostatic bath. In the temperature range from 15 to 40 °C, Cu(II) was extracted quantitatively, while at temperatures below 15 °C, the extractivities decreased (Fig. S2). This decrease is likely due to the insufficient separation of the surfactant and the aqueous phases resulting from the incomplete dissolution of Na_2SO_4 at 10 °C or below.

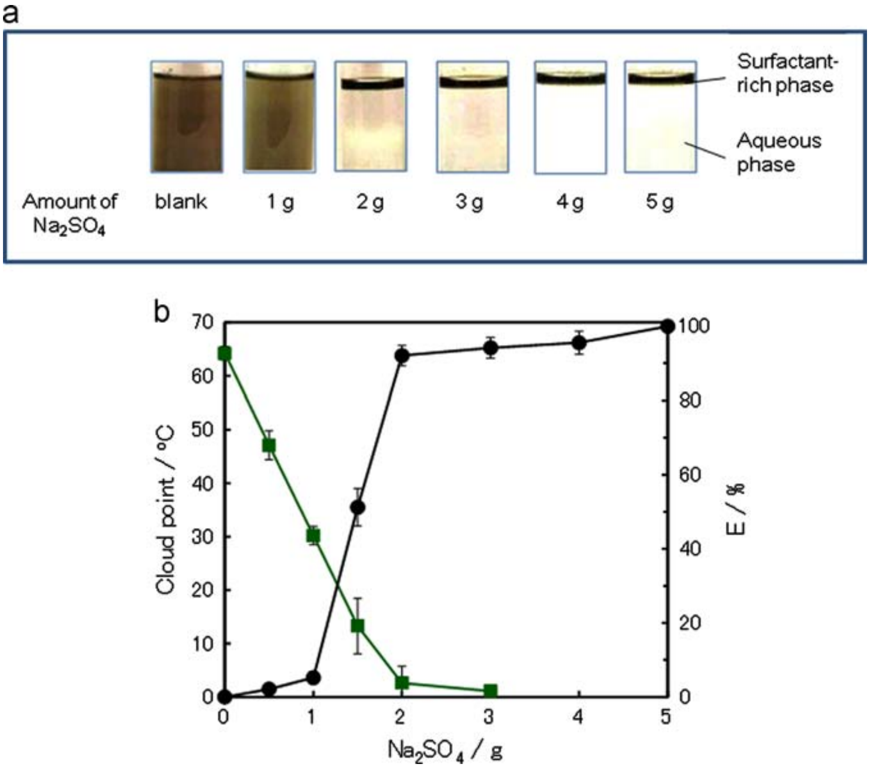

Fig. 1. Influence of the added Na_2SO_4 quantity in the phase separation of a mixture of 20% TX-100 and 4 μM dithizone (pH 5). (a) Photographs of phase separations and (b) (black circle) extractivity of 1.0×10^{-5} M Cu(II) and (green square) the cloud point as a function of the amount of Na_2SO_4 added to 20 mL of the solution. Settling time: 1 h. Liquid temperature: 25 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

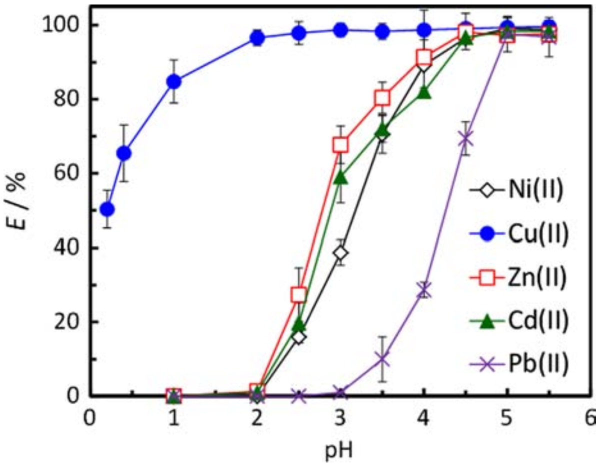

Fig. 2. Extractivities of heavy metals as a function of solution pH. Conditions: metal ion concentration, 1.0×10^{-5} M; [TX-100], 20%; [dithizone], 4 μM; added Na_2SO_4, 4 g to 20 mL of the solution. Other conditions are the same as those in Fig. 1.

Table 3
Extractivity and enrichment factor of Cu(II) using the salting-out and heating methods.

	Salting-out method	Heating method
Extractivity (%)	98.4	90.2
Surfactant-rich phase (mL)	2.0	4.0
Bulk aqueous phase (mL)	50.0	46.0
Enrichment factor	25.0	11.5

3.1.5. Settling time

The influence of the settling time on the extractivity of Cu(II) was also investigated. After adding Na_2SO_4 (4 g) to a 20% TX-100/4 μM dithizone solution containing Cu(II) (1.0×10^{-5} M) and mixing for 10 min, the liquid was left to stand at room temperature (25 °C) for varying lengths of time. Cu(II) was quantitatively extracted into the surfactant-rich phase after settling for 30 min (Fig. S3). However, the surfactant-rich phase obtained after only 30 min was unstable and easily broken; therefore, the settling time was set as 1 h for the subsequent experiments.

3.1.6. Enrichment factor

To determine the enrichment factor for the extraction system, the volumes of the surfactant-rich phases after phase separation using both the present method and the conventional method (heating the TX-100/dithizone solution without added salt) were measured. To ensure that a sufficiently large volume of the surfactant-rich phase was collected after separation, the volume of the extracting solution before phase separation was increased by a factor of 2.5 times compared with that used in the above described experiments. The volumes of the extraction solutions before and after phase separation were measured, and the enrichment efficiencies were calculated on the basis of volumes of the surfactant-rich ($[V]_s$) and aqueous phases $[V]_a$ using Eq. (2):

$$\text{Enrichment factor} = \frac{[V]_s}{[V]_a} \quad (2)$$

As summarized in Table 3, the present method's enrichment efficiency for Cu(II) was at least two times as high as that obtained with heating. In addition, while the aqueous phase was mostly clear for the salt-mediated phase separation, the heated aqueous phase was lightly colored. Although the differences between the separation mechanisms of the salt addition and heating methods are unclear at this stage, the salt addition may facilitate the dehydration of the surfactant molecules.

3.1.7. Interference

Commonly coexisting ions may affect the objective determination of Cu(II) by CPE. To verify this assumption, solutions containing

1.0×10^{-5} M of Cu(II) with added ions (Al(III), Fe(III), Zn(II), Cd(II), and Pb(II)) were prepared and tested according to the optimized procedure. The amounts of interfering ions were determined as Cu(II)-to-interfering ion ratios (w/w), and were found to be 1:100 for Al(III) and Fe(III), and 1:1000 for Zn(II), Cd(II), and Pb(II). The recoveries were 92.7%–107% for Cu(II) at different concentrations of the interfering ions (Table 4). These results indicate that the extraction efficiency for Cu(II) was not perturbed by the presence of foreign ions under the tested conditions.

3.2. Visual determination

The application of this method to the visual determination of Cu(II) by CPE was conducted. The concentration of Cu(II) was varied, and the color changes in the surfactant-rich phases were observed.

The surfactant-rich phases were dropped onto a filter paper; the colors of the samples changed from dark green to yellow, orange, and finally red when the Cu(II) concentration increased (Fig. 3a and b). The limit of quantification (LOQ) for Cu(II) for this visual detection method was also determined, and it was found that Cu(II) concentrations of 0.01, 0.05, and 0.1 μM could be identified.

To expand the visual detection range to even lower Cu(II) concentrations (0.005 μM or lower), the concentration of dithizone in the TX-100 solution should be lowered (1 μM or lower), because dithizone by itself displays a green color in the solution, which makes color identification difficult if the dithizone concentration is very high compared with that of Cu(II). However, the volume of the separated surfactant-rich phase was very small for testing by using the visual inspection method. Therefore, the LOQ for the visual inspection of Cu(II) when using this method was set at 0.01 μM.

Table 4
Effect of interference ions on the recovery of Cu(II) ($n=3$).

Interference	Interference to metal ion ratio	Recovery, %
Al(III)	100	107
Fe(III)	100	96.1
Zn(II)	1000	102
Cd(II)	1000	99.5
Pb(II)	1000	92.7

In this method, because a large amount of Na_2SO_4 was added to each 10 mL of the Triton-X100/dithizone solution, the existence of the impurity in Na_2SO_4 might affect the copper concentration in the surfactant-rich phase, and it must be considered as the blank value. Here, after mixing 4 g Na_2SO_4 in the Triton-X100/dithizone solution without the addition of Cu(II), we measured the cupper impurity in the separated surfactant-rich phase, using an inductively coupled plasma-mass spectrometer (ICP-MS: Perkin Elmer ICP-MS *ELAN* 600). The concentration was 5.40×10^{-4} μM (RSD= 0.8%, $n=3$), and it was much lower than the LOQ in the visual detection (1.00×10^{-2} μM). Accordingly, we concluded that the copper impurity in Na_2SO_4 did not affect the blank value in the visual determination.

3.3. Visual determination of Cu(II) in a river water sample

To demonstrate the applicability of the new method, the visual determination of Cu(II) in a river water sample was attempted.

To visually determine the concentration of Cu(II) in a river water sample, the color results for the samples containing known Cu(II) concentrations ranging from 0 μM to 0.5 μM (Fig. 3b) were used for comparison. By comparing the color of the water sample from the Watarase River (Fig. 3c) with that of the standard samples, the Cu(II) concentration in the Watarase River was determined to range from 0.3 to 0.4 μM. Meanwhile, the Cu(II) concentration in the same river water sample was measured by FAAS and found to be 0.31 ± 0.02 μM, which is in good agreement with the results of the visual determination method.

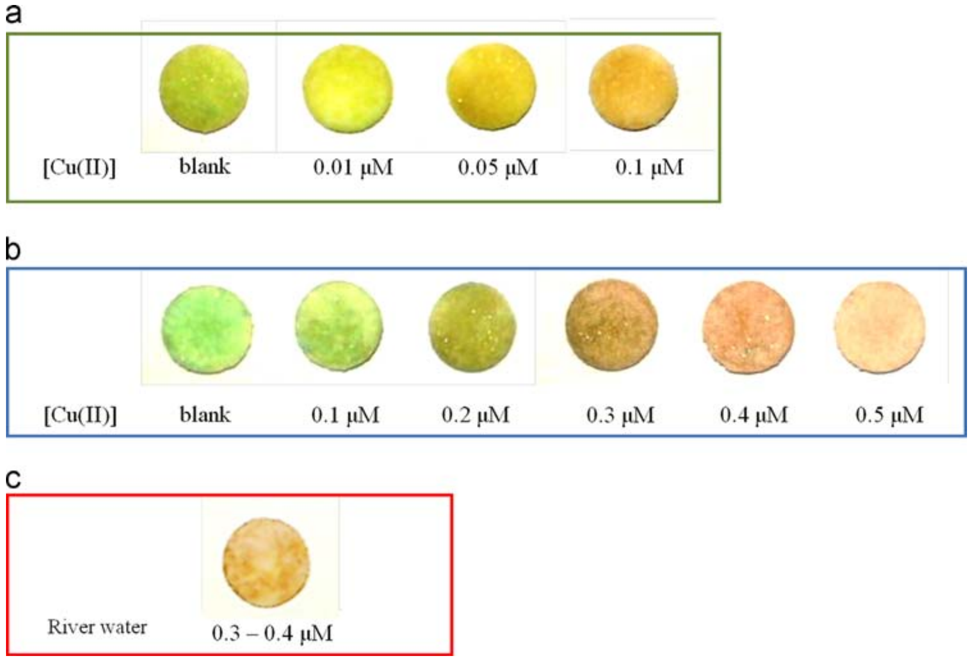

Fig. 3. Color profiles of the surfactant-rich phase for different Cu(II) concentrations and visual detection of Cu(II) in a river sample. Color samples (a and b) [Cu(II)]: (a) 0.01–0.1 μM and (b) 0.1–0.5 μM; [dithizone]: 4 μM; solution pH: 2; added Na_2SO_4: 4 g to 20 mL of the solution. River water sample (c): experimental conditions as described in Section 2.4; visual determination performed using color sample (b).

4. Conclusions

In this study, room temperature phase separation for the CPE of Cu(II) using the nonionic surfactant, TX-100, was achieved by adding salt to the extraction solution, which decreased the cloud point. Color changes for the Cu(II)–dithizone chelate were used for the visual determination of the Cu(II) concentration in the surfactant-rich phase. This extraction system was successfully applied to the visual determination of the Cu(II) concentration in a river water sample. Issues regarding the implementation of the present method involve the simplification of the separation process.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.08.025.

References

[1] M. Bonham, J.M. O'Connor, B.M. Hannigan, J.J. Strain, Br. J. Nutr. 87 (2002) 393–403.

[2] K. Ohmichi, Y. Seno, A. Takahashi, K. Kojima, H. Miyamoto, M. Ohmichi, Y. Matsuki, K. Machida, J. Health Sci. 52 (2006) 465–468.

[3] K. Nakano, M. Sato, A. Tsuda, H. Sekiya, M. Mori, H. Itabashi, Bunseki Kagaku 59(9), 2010, pp. 829–838, Japanese.

[4] A. Medynska-Juraszek, C. Kabala, J. Elem. 17 (2012) 441–451.

[5] E. Kaneko, Anal. Sci. 20 (2004) 247–254.

[6] N. Ohta, A. Robertson, Colorimetry: Fundamentals and Applications, John Wiley & Sons, New Jersey, 2006.

[7] M. Kumano, T. Yabutani, J. Motonaka, Y. Mishima, Int. J. Mod. Phys. B 20 (2006) 25–27.

[8] S.S. Samaratunga, J. Nishimoto, M. Tabata, Anal. Sci. 21 (2005) 1073–1078.

[9] J.E. Silva, A.P. Paiva, D. Soares, A. Labrincha, F. Castro, J. Hazard. Mater. 120 (2005) 113–118.

[10] M. Alkan, D. Kara, Instrum. Sci. Technol. 32 (2004) 291–301.

[11] Y. Murakami, Y. Dobashi, Y. Sasaki, I. Fujiwara, N. Abe, Noritaka, S. Tagashira, Solvent Extr. Res. Dev.Jpn. 15 (2008) 121–126.

[12] G. Monteleone, L. Morroni, B. Robinson, M.R. Tine, M. Venturini, F. Secco, Colloid Surf. A Physicochem. Eng. Aspects 243 (2004) 1–3.

[13] A. Takahashi, Y. Ueki, S. Igarashi, Solvent Extr. Res. Dev.-Jpn. 8 (2008) 235–240.

[14] H.A. Gazzaz, B.H. Robinson, Langmuir 16 (2000) 8685–8691.

[15] Y. Okamoto, Y. Nomura, H. Nakamura, K. Iwamaru, T. Fujiwara, T. Kumamaru, Microchem. J. 65 (2000) 341–346.

[16] D. Citak, M. Tuzen, J. AOAC Int. 95 (2012) 1170–1175.

[17] T. Ingram, S. Storm, P. Glembin, S. Bendt, D. Huber, T. Mehling, I. Smirnova, Chem. Ing. Tech 84 (2012) 840–848.

[18] S. Akita, M. Rovira, A.M. Sastre, H. Takeuchi, Sep. Sci. Technol. 33 (1998) 2159–2177.

[19] C.B. Ojeda, F.S. Rojas, Microchim. Acta 177 (2012) 1–21.

[20] W.L. Hinze, E. Pramauro, Crit. Rev. Anal. Chem. 24 (1993) 133–177.

[21] W.J. Horvath, C.W. Huie, Talanta 39 (1992) 487–492.

[22] T. Shikata, M. Okuzono, N. Sugimoto, Macromolecules 46 (2013) 1956–1961.

[23] D.G. Hicks, Abstr. Pap. Am. Chem. Soc., Mar-A (1971) 67.

[24] Royal Society of Chemistry, Dithizone, John Wright & Sons Ltd., Bristol, UK (1977) 24–25.

[25] J. Lurie, Handbook of Analytical Chemistry, Mir Publishers, Moscow (1975) 336–339.

[26] J.L. Manzoori, G. Karim-Nezhad, Iran J. Chem. Chem. Eng. Int. Engl. Ed 24 (2005) 47–52.

[27] H. Schott, A.E. Royce, J. Pharm. Sci. 73 (1984) 793–799.

[28] W.J. Horvath, C.W. Huie, Talanta 39 (1992) 487–492.

[29] M. Dilip, S.T. Griffin, S.K. Spear, H. Rodrı´guez, C. Rijksen, R.D. Rogers, Int. Eng. Chem. Res. 49 (2010) 2371–2379.

[30] I. Nishi, I. Imai, M. Kasai, Kaimen Kasseizai Binran, Sangyo Tosho, Tokyo (1960) 793(Japanese).

[31] I. Nishi, I. Imai, M. Kasai, Kaimen Kasseizai Binran, Sangyo Tosho, Tokyo (1960) 175(*Japanese*).

[32] F. Hofmeister, Arch. Exp. Pathol. Pharmacol 24 (1988) 247–260.

[33] A. Seidell, W.F. Linke, Solubilities of Inorganic and Metal Organic Compounds: Fourth Editions, D. Van Nostrand Company, Inc., New York, 1965.