Functional Materials 10, No.4 (2003)

Solid phase spectrophotometric determination of copper (II) using SPADNS

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Received July 23, 2002

Anion-exchange resin modified with 2-(4'-sulfobenzeneazo)chromotropic acid was used for concentration and subsequent determination of copper (II) microscale amounts in large-volume samples of drinking water. The chemistry of copper complexing with 2-(4'-sulfobenzeneazo)chromotropic acid in solid phase has been considered. Quantitative characteristics of the compound composition and stability have been obtained.

Анионит, модифицированный 2-(4-сульфобензолазо) хромотроповой кислотой, использован для концентрирования и последующего определения микроколичества меди (II) в больших объемах проб питьевой воды. Рассмотрен химизм комплексообразования меди с 2-(4-сульфобензолазо) хромотроповой кислотой в твердой фазе. Получены количественные характеристики состава и прочности образующегося соединения.

The use of ion-exchanging functional materials makes it possible to solve various problems associated with industrial applications of closed technologic circuits and complex use of raw materials.

In recent time, the information on applications of ion-exchanging materials modified with various organic reagents became very abundant. These reagents made it possible to develop novel high-sensitive procedures to determine trace amounts of heavy metals in numerous objects. A plentiful information on photometric Cu(II) determination procedures in solutions is presented in [1]. However, all these procedures provide for preliminary concentration of Cu(II) micro-amounts using toxic organic extracting agents. Moreover, most of those procedures are low-selective.

On the other hand, to determine the micro-amounts of Cu(II) in water, evaporation or extraction of large-volume samples is used [2, 3], thus complicating the analysis significantly. Therefore, a method combining sorption of traces of the elements to be determined from large volumes of solutions followed by their simple photometric determination directly in solid phase is highly urgent. There are data [4] on solid-phase spectrophotometric (TPS) determination of copper; those data are presented in Table 1.

The copper detection thresholds using the above-mentioned procedures are not low enough. The 2-(4'-sulfobenzeneazo)chromotropic acid (SPADNS) did not used to date as a modifier for the AV-17-8 anion-exchange resin.

The stock 0.1 M solution of $Cu(NO_3)_2$ was prepared by dissolving a precise weight of the salt in 1 M HNO_3. The solution was standardized using iodometry. The working solution ($1.6 \cdot 10^{-3}$ M) was prepared by diluting the above stock solution.

The AV-17-8 with linear grain dimensions of 0.25 to 0.50 mm was used that was pre-treated as described in [5]. 10 g of AV-17-8 were soaked in water for 1 day. Then the water was decanted, the sorbent was placed in a column, washed with 150 ml of 0.1 M NaOH during 6 h and then washed with water until neutral. Then the sorbent was transferred into a beaker, 200 ml 0f

Table 1. Characteristics of Cu(II) complexes with organic reagents-modifiers for SPS copper determination

No.	Sorbent	Reagent	V/m, ml/g	τ, min	Analyt. signal (λ, nm)
Amberlite A-27-Cl	Batocuproin-disulfonic acid	50/1	5	F(R)485	~10 [4]
Amberlite A-27-Cl	Ammonium pyrrolidine-dithiocarbaminate	50/1	5	F(R)436	~44 [4]
PAN fiber with KU-2	1-(2-pyridylazo)-naphtol	100/0.01	10	F(R)610	~32 [4]
AV-17	1-(2-thiazolylazo)-2-naphtol	25/1	15	(600)	64 [4]
AV-17	SPADNS	25/0.3		A(580)	6.4 (this work)

$8.76 \cdot 10^{-4}$ M SPADNS solution were added (prepared using 0.1 M NaCl), mixed for 30 min using a magnetic agitator, filtered off, washed with water, and dried till air-dry state. The resin capacity for SPADNS has been determined to be of 0.01 g indicator per gram of the sorbent. The modified sorbent looks as transparent crimson-red grains transmitting light well enough.

The SPADNS sorption by the standard anion-exchange resin and by the Cu(II) modified one was studied in static conditions using 0.3 g weights. The SPADNS content in the sorbents was determined using photometry by measuring the optical density decrease of liquid phase at 520 nm wavelength. The post-sorption Cu(II) concentration in solutions was determined using photometry with arsenazo III [6].

The optical density of solid concentrates was measured using a KFK-3 instrument (l = 0.1 cm) at optimum wavelength relative to AV-17-8-OH using a lavsan (Dacron) film similar to [7]. The sample preparation for the photometric analysis was r educed to preparation of a light absorbing layer filled homogeneously with the ion-exchanger. As in the case of solution photometry, parallel-wall quartz cells were used that were filled with water and then the concentrate was transferred to the cell using a pipette; the second cell was filled with soaked modified or standard ion-exchanger of the same grain size (0.1 to 0.5 mm). The light absorption of the sample was measured as the closest packing of the grains in the cells was attained. To reduce the light scattering by the sorbent matrix, the cell was placed as close to the detector window as possible and a lavsan film was placed between the sample and detector. The optical density of solutions was measured at l = 1 cm. The acidity was controlled using an I-160 ionometer. Copper content in the samples was determined by means of a PU-01 polarograph.

The study of analytical applications of Cu(II)-SPADNS complex in solution has shown that it is o very good prospects in development of a novel procedure for TPS determination of Cu(II) in micro-amounts that is improved as compared to the initial one.

First, the SPADNS sorption conditions were studied. The SPADNS molecule contains three sulfonic groups allowing it to be sorbed as an anion similar to arsenazo III [8]. The dye is sorbed within a wide pH range (3 to 10) during 25 to 30 min. The best results have been obtained with AV-17-8-OH modified using 0.1 M NaCl solutions. From solutions of other electrolytes (KNO_3, Na_2SO_4, H_2SO_4, HNO_3, HCl), the sorption proceeds more slowly as it was noted in [8]. SPADNS is not sorbed at all or sorbed very slowly from ethanol, acetone, and dimethyl formamide media. The maximum indicator amount that may be sorbed with 1 g of ion-exchanger is 0.01 g. The ion-exchanging character of SPADNS sorption is confirmed by potentiometric monitoring of liquid phase: pH value increases, thus evidencing the OH-ion displacement in the course of sorption. The modifier can be desorbed with HNO_3, HCl, H_2SO_4, and alkali solutions, all being about 6 M concentration [8].

The optimum conditions of Cu(II) complexing with the modified sorbent are as follows (see Fig. 1): pH 5 to 10, λ_{opt} = 580 nm, the equilibration time 2 h, the complex is stable during 2 days when being concentrated out of 50 ml of solution. The quantitative concentrating out of 500 ml of

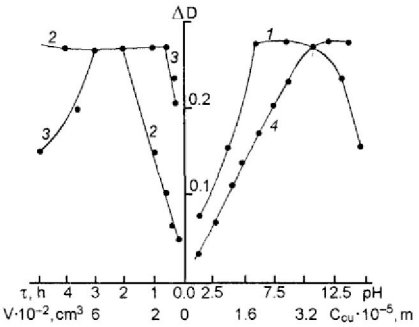

Fig. 1. Dependences of optical density of SPADNS-copper complex in sorbent phase on pH (*1*), phase contact time (*2*), liquid phase volume (*3*), and copper concentration (*4*): $C_{\text{SPADNS-AV-17-8}} = 1.75 \cdot 10^{-4}$ M/g, λ = 580 nm, $l = 0.1$ cm, reference system SPADNS-AV-17-8, $m_{sorb} = 0.3$ g.

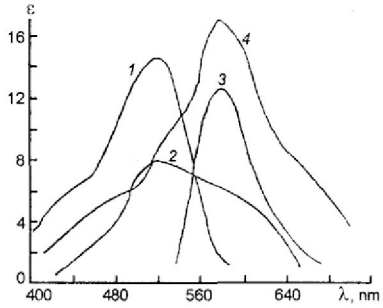

Fig. 2. Absorption spectra of SPADNS and its copper complex in solution (*1*, *3*) and solid phase (*2*, *4*); $\varepsilon \times 10^8$ (*1–3*), $\varepsilon \times 10^5$ (*4*). In solution, pH 5 to 7; $C_{\text{SPADNS}} = 4.0 \cdot 10^{-6}$ M, $l = 1$ cm, reference system H_2O; on sorbent, $C_{\text{SPADNS-AV-17-8}} = 1.75 \cdot 10^{-4}$ M/g, $C_{Cu} = 5.3 \cdot 10^{-6}$ M/g. V = 25 ml, τ = 20 min, $l = 0.1$ cm, reference system AV-17-8, $m_{sorb} = 0.3$ g.

solution is possible in the same conditions. The Beer law is met within a wide Cu(II) concentration range of $0.1 \cdot 10^{-6}$ to $3.2 \cdot 10^{-5}$ mol/l. The detection threshold is 6.4 μg/l. If one liter or more of a solution containing less than 6.4 μg/l is to be analyzed, then it can be concentrated stepwise, the initial sample being subdivided into portions of 500 ml volume each. In this case, thesorbent weight (0.3 g) is reacted successively with each sample portion.

Study on effect of foreign ions on the analytical signal intensity of the colored Cu-SPADNS complex in solution has shown that the reaction is selective enough. Zn(II), Fe(III), Cd(II), Hg(II), Sn(IV), As(III) do not form any complexes with SPADNS. To avoid the Fe(III) hydrolysis, it is reduced with hydroxyl amine purified with dithizone as described in [9]. If Hg(II) and Sn(IV) are present, citrate ion is added after hydroxyl amine is used. Lead forms an unstable complex [10], that does not hinder in essence the determination in the presence of more potent complexing agents. Ca(II), Mg(II) hinder at the ratio 1:500; Cl^-, SO_4^{2-}, NO_3^- do not interfere with the determination.

Study of foreign ions effect on copper determination in solid phase has shown that the selectivity of SPS analysis is as high as in solution. If Pb(II), Fe(III), Cd(II), Hg(II), Sn(IV) are present in solution at 100-times excess or more relative to copper, then the precipitated hydroxides of those metals can be filtered off by washing the sorbent grains on a sieve of <0.25 mm mesh size that would be impossible when the experiment would be made in solution.

Identical absorption spectra of Cu(II)-SPADNS complexes in solution and in sorbent phase (Fig. 2) evidences the same complex composition (1:1) [11, 12].

Thus, the interaction in this system can be presented as $Cu(OH)_i^{+2-i} + H_2R = Cu(OH)_i^{+2-i}H_{2-n}R + nH^+$

Since at pH 5, 99.9 % of copper ions are present in solution in non-hydrolysed state and concentrations of $CuOH^+$ and $Cu(OH)_2$ are negligible, it is just the Cu^{2+} ion that is the coordinating one.

The conditional stability constant of the formed complex was calculated proceeding from the sorption isotherm using the scheme [13, 14].

$$\beta_{cond} = \frac{[CuR\text{–}A\,B\text{-}17\text{–}8]}{[Cu^{2+}] \cdot [H_2R\text{–}A\,B\text{-}17\text{–}8]}. \quad (1)$$

Its value has been found to be $\beta_{cond} = (1.61 \pm 0.20) \cdot 10^4$.

The study results formed the base of the procedure for Cu(II) determination in drinking water using addition method. The procedure is as follows.

Two samples of drinking water are taken of 1.5 l volume each. To one sample, a known amount of Cu(II) is added. Then each sample is subdivided into three portions of 500 ml each. 0.3 g of freshly prepared

modified AV-17-8-SPADNS is added to the first portion of water to be analyzed (the sample acidity should be within the optimum range for this procedure). The samples are agitated with a magnetic mixed for 15–20 min, then the grains are separated by a pipette and transferred into the next portion of water to repeat the above operations.

The experiment is repeated twice. Then the preceding two portions of water are combined with the last one containing the solid concentrate and left for 2 h. Then the grains are separated, transferred into a cell of 0.1 cm optical length and optical density is measured at $\lambda = 640$ nm against AV-17-8-SPADNS. If multiple analyses are to be carried out, the optical density values for a series of samples can be measured next day.

The results of Cu(II) determinations in drinking water are compared in Table 2.

To conclude, a modified ion-exchanger AV-17-8-SPADNS has been proposed. The complexing in the Cu-SPADNS-AV-17-8 has been studied. A low stability complex ($\beta_{cond} = (1.61\pm0.20)\cdot10^4$) with component ratio 1:1 has been found to be formed. The theoretical data obtained allowed to elaborate a procedure for SPS determination of microamounts of Cu(II) in drinking water. Comparison of results obtained for Cu-SPADNS system in solution and in sorbent shows advantages of the SPS version. Novel possibilities are offered to improve the determination selectivity and sensitivity. The range of optimum pH values is enlarged. The determination becomes more rapid because the sample preparation by evaporation is avoided. The work can be organized better in the case of routine mass analyses.

Table 2. Copper determination results in tap water (Kiev)*

Sample No.	Introduced, μg	Found, μg/l	
		By proposed method	By polarography**
1	–	6.00±0.50	6.10±0.40
2	6.40	12.50±0.10	12.60±0.20
3	10.00	16.20±0.20	16.05±0.05
4	20.00	26.00±0.05	26.10±0.03

*$P = 0.95$, $n = 3$, $\lambda_{opt} = 640$ nm
**After solution evaporation

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