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# Determination of Cu(II) and Zn(II) using silica gel loaded with 1-(2-thiasolylazo)-2-naphthol

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## Abstract

The silica gel with 1-(2-thiasolylazo)-2-naphthol adsorbed was obtained. The adsorption of Cu(II) and Zn(II) from an aqueous solution onto loaded silica gel was studied. The capabilities of 1-(2-thiasolylazo)-2-naphthol immobilized for Cu(II) and Zn(II) preconcentration, visual and diffusion reflectance spectroscopic detection was evaluated. The detection limits were 10 and 15 μg·l$^{-1}$, respectively. Visual test scales for metal ions determination in the range 0.65–13 μg per sample were worked out. The developed methods were applied to Cu(II) and Zn(II) determination in natural and tap water. The obtained results agreed well with the reported value. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* 1-(2-Thiasolylazo)-2-naphthol; Loaded silica gel; Cu(II) determination; Zn(II) determination

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## 1. Introduction

Attention has recently been focused on the development of sorption-spectroscopic and visual test methods by using sorbents modified with analytical reagents [1]. A sorption separation of the trace elements prior to analysis serves the dual purpose of increasing their concentrations to levels at which they can be reliably determined and of removing them from the natural water matrix [2]. The using of specific chromophorous reagents as a modifying agent allows for the increase in selectivity and sensitivity of determination. The sorbents can be modified via ion-exchange, impregnation, adsorption or covalent grafting of analytical reagents [3]. The previous studies [4–7] have shown wide use of chelating sorbents for Cu(II) and Zn(II) determination in different types of water. The resins loaded with organic reagent, 1-(2-thiasolylazo)-2-naphthol (TAN) and 1-(2-thiasolylazo)-2-naphthol-3,6-disulfonic acid (TAN-3,6-S), are known to be one of the effective preconcentration substrates [8,9]. However, they show a lack of stability in high ionic strength media [10]. Simultaneously, the reagents immobilization on the silica supports offers some distinct advantages over immobilization on the organic polymer supports: short time for equilibration, excellent swelling resistance in different solvents,

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ease of surface modification with analytical reagent by adsorption. The preparation of modified silicas with a reagent adsorbed is rather simple, and their chemical–analytical properties do not yield to those of the sorbent with covalent grafted reagent [11]. Such solid-phase reagents are promising for analytical practice. As far as we know, no silica with TAN adsorbed has been proposed for heavy metal ion determination.

In the present work, we have studied the adsorption of TAN from organic solvents onto a silica surface, and established the TAN immobilized usefulness in the sorption–spectroscopic and visual test determination of copper and zinc.

## 2. Experimental

### 2.1. Reagents

Water and hexane were purified according to [12] and by flowing over metallic sodium, respectively. TAN was synthesized and purified according to [13]. All other chemicals were of analytical reagent grade. Stock Zn(II) and Cu(II) solutions were prepared by nitrates dissolving in 1 $\text{mmol·l}^{-1}$ nitric acid and standardized by complexometry. Sodium chloride (4.0 $\text{mol·l}^{-1}$), fluoride, hydroxide (0.1 $\text{mol·l}^{-1}$) and thiosulphate (0.5 $\text{mol·l}^{-1}$), potassium iodide (1.0 $\text{mol·l}^{-1}$) and saturated hydrazine sulphate aqueous solutions were prepared by dissolving appropriate substances. The standard solutions of metal salts were acidified with nitric acid and further diluted as required. The aqueous solutions of TAN-3,6-S, 4-(2-pyridylazo)-naphthol (PAN), hexane and acetone solutions of TAN were obtained by dissolving appropriate substances. Silica gel Silpearl UV 250 (SG) for chromatography (Chemapol, Prague, Czech Republic) was digested in hydrochloric acid, washed with purified water and dried at 80°C for 8 h, and then at 200°C for 12 h. Nonporous highly dispersed silica Silics (Kalush, Ukraine, specific surface area $S = 300$ $\text{m}^2\text{·g}^{-1}$) was dried in vacuum at 68°C for 10 h to remove water adsorbed on the sorbent surface [14].

### 2.2. Apparatus

The absorbance spectra of solutions and reflectance spectra of sorbents were registered with a UV/Vis spectrophotometer Specord M-40 (Carl Zeiss Jena, Germany). The IR spectra of sorbents were registered with an automatic IR photometer UR-20 (Carl Zeiss Jena, Germany), samples being prepared as thin films between KBr windows. Atomic absorption measurements were recorded on an atomic absorption spectrometer model Saturn (Severodonetsk, Ukraine) equipped with a standard burner for use with an air–propane–butane flame. Standard hollow-cathode lamps were used as a line source for all elements.

A potentiometer model EV-74 with glass electrode (Gomel, Belarus) was used for pH measurements.

The ultrasound destruction of Cu(II) complexes with organic substances of natural water were realized by using USDN-A (Sumy, Ukraine).

### 2.3. Procedures

The batch technique was used for the research of TAN, Cu(II) and Zn(II) adsorption onto unloaded silicas and metal ions adsorption onto silica gel modified with TAN (TAN-SG). The reagent desorption from TAN-SG surface into aqueous solutions at a different pH was studied by this technique also.

#### 2.3.1. Adsorption of TAN from hexane solution

Silicas (0.01 g) was stirred with 5 ml of 0.05–1.0 $\text{mmol·l}^{-1}$ TAN hexane solution for 1–60 min. The TAN residue in the hexane solution after a sorbent separation was controlled spectrophotometrically by an absorbance at 480 nm. The amount of reagent adsorbed was calculated as: $a = (C_0 - [C])*V/1000*m$, where $C_0$, $[C]$, $\text{mol·l}^{-1}$ were initial and equilibrium TAN concentrations in solution, respectively; $V$ (ml) was volume of solution; and $m$, $g$ was sorbent mass.

#### 2.3.2. Desorption of TAN from TAN-SG surface into aqueous solution at different pH

The aqueous solution (5–100 ml) at the desired pH (2–8) was stirred for 1–60 min with weighed amount (0.01–0.1 g) of sorbents containing a known amount of TAN ($a$, μmol·g$^{-1}$: 1.0, 2.5, 25 or 50). The portion (4.5 ml) of solution after sorbent separation was mixed with 0.5 ml of acetone. The amount of TAN removed from surface into solution was determined spectrophotometrically by the own absorbance in aqueous–acetone (9:1) mixture at 450 nm. The equation of calibration graph was $A_{450} = 0.091 \cdot C$ (μmol·l$^{-1}$).

### *2.3.3. The preparation of silics loaded with TAN for IR spectroscopy measurement*

The silics (0.1 g) were stirred with 10 ml of hexane solutions containing 1.0, 25 or 250 μmol·l$^{-1}$ of TAN for 15 min. Then sorbents were separated and dried in a vacuum at room temperature for 1 h. The amount of reagent adsorbed was $a$, μmol·g$^{-1}$: 0.3, 7.5 and 69.

### *2.3.4. Adsorption of Zn(II) and Cu(II) onto SG and TAN-SG*

Zinc containing an aqueous solution (30 ml) at pH 6.0 was stirred with 0.05 g of SG and TAN-SG with different reagent amounts on the surface ($a$, μmol·g$^{-1}$: 1.0, 2.5, 25 or 50). Copper adsorption was realized from the 0.5 mol·l$^{-1}$ NaCl aqueous solution with pH 3.5. Zn(II) and Cu(II) residue in the solution was controlled spectrophotometrically with PAN [5] and TAN-3,6-S [9], respectively. The amount of metal ions adsorbed onto the silicas surface was determined as before. Sorbents with metal ions adsorbed were separated and dried at 60°C for 1 h.

### *2.3.5. Ultrasound destruction of Cu(II) complexes with organic substances in natural water samples*

The sample of natural water (10 ml) was acidified to pH 1.0 (0.1 mol·l$^{-1}$ $HNO_3$) and exposed to ultrasound at 44 kHz, at an intensity of ≤10 Watts·cm$^{-2}$ for 3 min [15].

## 3. Results and discussion

### *3.1. TAN adsorption onto SG*

The adsorption of TAN onto SG from chloroform, toluene, hexane and their mixtures was studied. It was found that the best TAN adsorption was observed when hexane was used. That is why modification of SG with TAN has been carried out from a hexane solution.

The kinetics experiments shown that the equilibrium of TAN adsorption from a hexane solution onto SG surface was reached in 5 min ($m = 0.01–0.1$ g, $V = 5–10$ ml). TAN adsorption as a function of reagent concentration in solution was studied. The results obtained testify that SG capacity in relation to TAN ($a_{max} = 69$ μmol·l$^{-1}$) was limited by reagent solubility in hexane. The isotherm of TAN adsorption is represented in Fig. 1 (curve 1). Its initial part shows that the reagent adsorbed completely ($a > 0$ at $[C] = 0$) from dilute solutions ($C \leq 5.3$ μmol·l$^{-1}$). This fact is known to indicate strong adsorbate connection with a sorbent [16]. That may be a result of interaction between TAN functional groups and OH-groups of SG surface [17]. The maximum value of TAN full adsorption is 2 μmol·g$^{-1}$. The further reagent adsorption ($a > 2$ μmol·g$^{-1}$) may take place onto new surface (SG with TAN adsorbed) and caused intermolecular interaction. Low affinity of TAN molecules for new surface may explain S-shape of

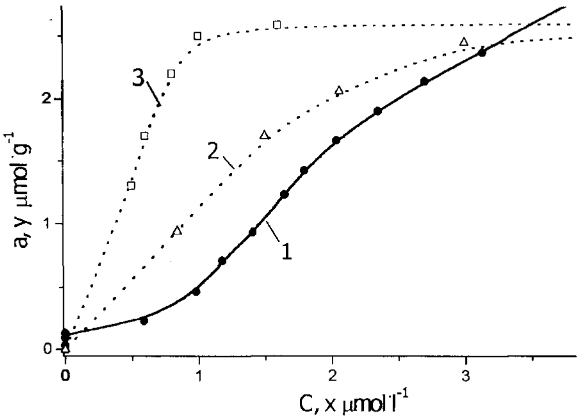

Fig. 1. Isotherms of TAN adsorption onto SG (1) and Zn(II) (2), Cu(II) (3) onto TAN-SG.; $a_{TAN}$, mmol·g$^{-1}$: 25(2), 2.5(3); pH 6.0(2), 3.5(3); $x$: 20(1), 1(2,3); $y$: 20(1), 10(2), 1(3); $C_{NaCl}$ = 0.5 mol·l$^{-1}$ (3); $m = 0.01$ g; $V = 5$ ml; $T = 293.0 \pm 0.5$.

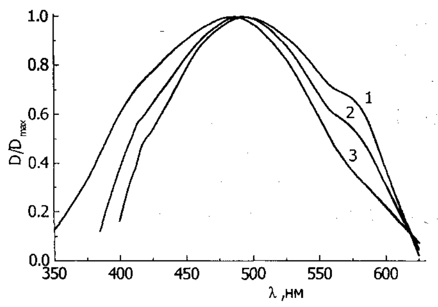

Fig. 2. Stadardized diffusion reflectance spectra of TAN-SG. *a*, μmol·g$^{-1}$: 0.5(1), 1(2), 5(3).

isotherm second part at $C > 5.3$ μmol·l$^{-1}$ [17]. The diffusion-reflectance spectra of TAN-SG with different reagent content on the surface were compared for this supposition examining. Fig. 2 shows that the polarizing effect of SG on TAN molecule is decreased with the increasing of reagent content on the surface. The diffusion-reflectance spectra of TAN-SG with $a > 5.0$ μmol·g$^{-1}$ is similar to absorbance spectra of TAN solution in polar solvent. This fact confirms TAN second layer formation as a result of intermolecular interaction.

The nature of TAN binding with the SG surface has also been investigated using IR-spectroscopy [18]. The IR spectra of silics modified with TAN are shown in Fig. 3. They indicate that the absorbance band at 3749 cm$^{-1}$ belonging to valence vibration of singular surface OH-groups [18] becomes less intensive as TAN surface content increases. Simultaneously, the absorbance band at 3200–3600 cm$^{-1}$ corresponding to valence vibration of hydrogen bonded silanol groups becomes more intensive. This may be the result of hydrogen bonds forming between N or S atoms of reagent molecules and surface OH-groups at TAN fixation.

To establish the possibility of new solid-phase reagent application to analytical practice, reagent desorption from TAN-SG surface as a function of pH of solution was studied. The data obtained show that TAN desorption at pH 3.5–7.0 (sorbent mass ≥ 0.01 g, aqueous solution volume ≤ 100 ml, time of phases contact ≤ 60 min) was not more than 15, 10, 2 and 1% for reagent surface 1.0, 2.5, 25 and 50 μmol·g$^{-1}$, respectively. It is known [9] that the sorbents with maximum capacity in relation to a reagent are useless in determining metal ions because of the strong inter-

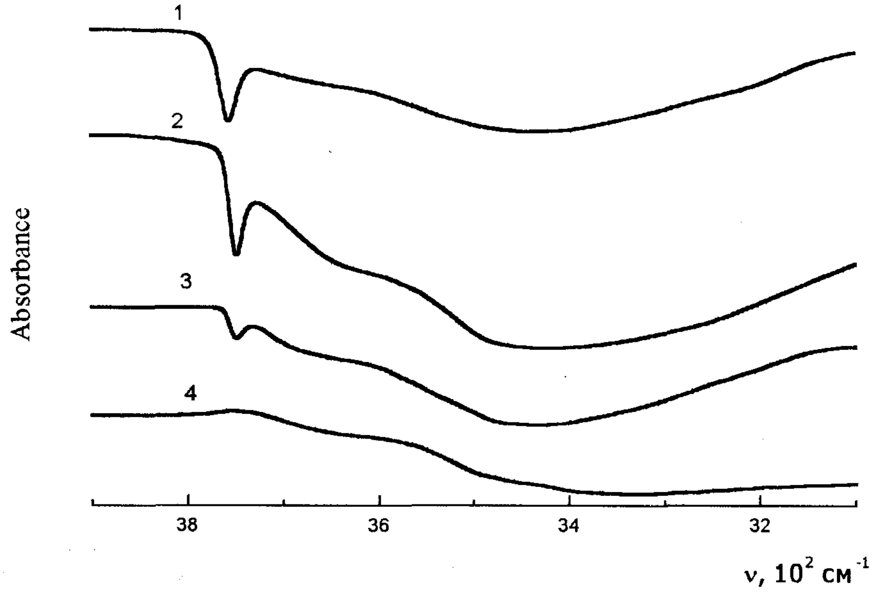

Fig. 3. IR spectra of silica modified with TAN containing on the surface, mmol·g$^{-1}$: 0(1), 1(2), 5(3), 70(4).

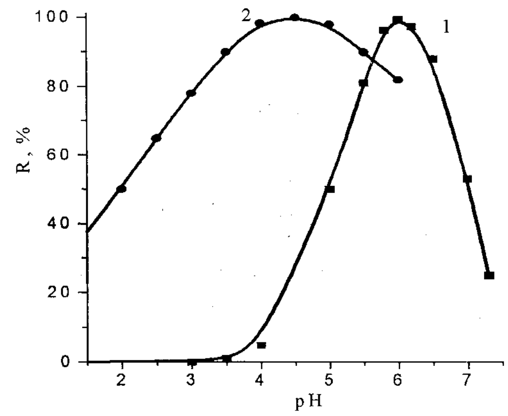

Fig. 4. Adsorption of Zn(II) (1) and Cu(II) (2) onto TAN-SG as function of pH. Initial concentration of metal ions 1 mmol·l$^{-1}$; $a_{TAN}$, mmol·g$^{-1}$: 25(1), 2.5(2); $m = 0.01$ g; $V = 5$ ml.

molecular attraction between molecules of a modifying agent, making complexing centers inactive. Therefore, the silicas with TAN surface content 2.5–25 μmol·g$^{-1}$ were used for the study of Cu(II) and Zn(II) adsorption.

### 3.2. *Zn(II) adsorption onto TAN-SG*

The pH dependence of Zn(II) adsorption by TAN-SG from an aqueous solution ($m \leq 0.05$ g, $V \leq 30$ ml, $a = 25$ μmol·g$^{-1}$) is represented in Fig. 4 (curve 1). The Zn(II) recovery seems to be complete at pH 5.5–6.8. Zinc ions are not adsorbed onto unloaded silica gel under these conditions [19]. The dependence of Zn(II) adsorption as a function of TAN surface content was studied. The data obtained indicates that the maximum recovery was reached at $a \geq 25$ μmol·g$^{-1}$. Therefore, TAN-SG with $a = 25$ μmol·g$^{-1}$ was used to further investigate Zn(II) adsorption.

Kinetic experiments shown that the Zn(II) adsorption equilibrium was reached in 10 min. The sorbent mass and solution volume dependencies of Zn(II) adsorption onto TAN-SG were studied. The maximum concentration factor was found to be 600 ml·g$^{-1}$ at volume of solution 30 ml and mass of sorbent 0.05 g.

The isotherm of Zn(II) adsorption onto TAN-SG is shown in Fig. 1 (curve 2). Its shape (L-type) may testify about chemical interaction between Zn(II) and TAN immobilized. The chelating capacity of TAN-SG was 25 μmol·g$^{-1}$ Zn(II) for 25 μmol·g$^{-1}$ reagent. It was assumed that the complex with the ratio Zn:TAN = 1:1 has been formed on the surface of TAN-SG. Spectra shown in Fig. 5 confirmed such surface complex formation.

### 3.3. *Cu(II) adsorption onto SG and TAN-SG*

The pH dependence of Cu(II) adsorption onto TAN-SG from an aqueous solution was studied. For escaping difficulties, with insoluble hydroxide of Cu(II) conformation at pH > 3, the adsorption from the NaCl aqueous solution was investigated [21]. It was found experimentally, that optimum concentration of sodium chloride was more than 0.5 mol·l$^{-1}$. The pH-dependence is represented in Fig. 4 (curve 2). The optimum pH range of Cu(II) adsorption was 3.3–4.6. For comparison, an attempt to adsorb Cu(II) onto unloaded SG was carried out, but there was no effect under such conditions.

The Cu(II) adsorption as a function of TAN content on the SG surface was studied. It was found that Cu(II), in contrast to Zn(II), Co(II) and Fe(III), was quality recovered by sorbent which contained ≤2.5 μmol·g$^{-1}$ TAN ($m = 0.01$–$0.1$ g, $V = 5$–$100$ ml). This is why the

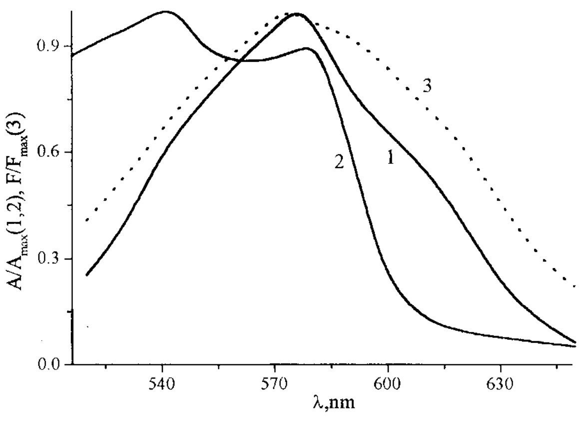

Fig. 5. Stadardized absorbance spectra of ZnTAN aqueous-acetone solution (1); Zn(TAN)$_2$ benzene solution [20] (2); and diffusion reflectance spectra of TAN-SG with Zn(II) adsorbed (3).

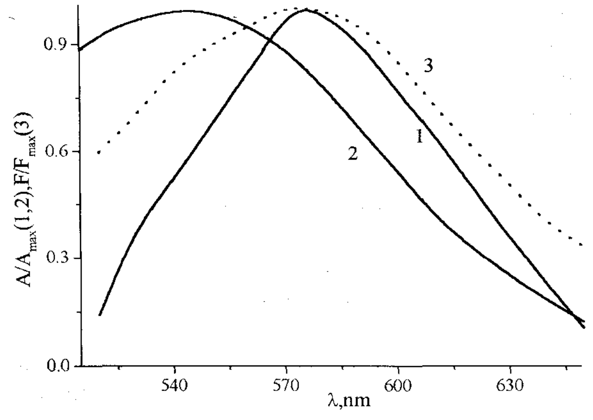

Fig. 6. Stadardized absorbance spectra of CuTAN aqueous-acetone solution (1); Cu(TAN)$_2$ benzene solution [20] (2); and diffusion reflectance spectra of TAN-SG with Cu(II) adsorbed (3).

modified sorbent with $a = 2.5$ μmol·g$^{-1}$ was used for Cu(II) adsorption.

Kinetics experiments show that the time taken for maximum Cu(II) recovery was 15 min. The sorbent mass and solution volume dependencies of Cu(II) adsorption onto TAN-SG were studied. It was found that the maximum concentration factor of Cu(II) was 1000 ml·g$^{-1}$ at volume of solution 100 ml and mass of sorbent 0.1 g.

The isotherm of Cu(II) adsorption onto TAN-SG is shown in Fig. 1 (curve 3). It may be refereed to L-type. The chelating capacity of TAN-SG was 2.6 mmol·g$^{-1}$ Cu(II) for 2.5 mmol·g$^{-1}$ TAN. Therefore, the formation of complex with the ratio immobilized reagent: Cu(II) = 1:1 on the TAN-SG surface may be supposed. The comparison of absorbance spectra of CuTAN and Cu(TAN)$_2$ solutions with a diffusion reflectance spectrum of TAN-SG with Cu(II) adsorbed (Fig. 6) confirmed this fact.

### 3.4. The interference of foreign ions

The maximum adsorption of metal ions can be reached during complex with the ratio metal ion:immobilized reagent = 1:1 formed on a surface [22]. It is known [8], that among natural water components, only Co(II), Cu(II), Zn(II), Fe(III), Hg(II) and Ag(I) form such complexes with TAN in aqueous–acetone solution. Therefore, their influence on zinc and copper determination was studied. It was shown that Hg(II) and Ag(I) do not interact with TAN immobilized at pH 3.0–7.0. Fe(III) ($\leq 10$ mg·l$^{-1}$) in the presence of 0.01 mol·l$^{-1}$ NaF and cobalt ($\leq 0.5$ μg·l$^{-1}$) do not interfere with Zn(II) and Cu(II) determination. Zinc at concentration $\leq 0.1$ mg·l$^{-1}$ does not influence $\geq 10$ μg·l$^{-1}$ Cu(II) determination by using TAN-SG with chelating capacity 2.5 μmol·g$^{-1}$. Copper at concentration $\leq 1$ mg·l$^{-1}$ in the presence of 0.01 mol·l$^{-1}$ $Na_2S_2O_3$ does not interfere with Zn(II) determination.

### 3.5. Application of modified SG to zinc and copper ions determination

The possibility of TAN-SG application to Cu(II) and Zn(II) ions determination in water has been studied.

#### 3.5.1. Zn(II) determination in water by using TAN-SG

The diffusion reflectance spectroscopic (DRS) method for Zn(II) determination was developed. The calibration graph was linear in the range 0.5–25 μg per sample. The calibration equation was: $R_{570} = 0.01 + 0.07 \cdot C$ (μg per sample), $r = 0.99$. The detection limit was 15 μg·l$^{-1}$ (for 30 ml of sample solution). Therefore, TAN-SG can be conveniently used to detect zinc ions in natural water at values as low as 0.15 MAC [23].

The colour scale for zinc visual test determination was prepared by stirring 10 ml of Zn(II) solution containing 0, 0.65, 1.95, 3.25, 6.50, 9.80 and 13.00 μg at pH 6.0 with 0.05 g of TAN-SG ($a = 25$ μmol·g$^{-1}$) for 10 min. The sorbents were separated. The sorbent colour changed from orange to violet with Zn(II) concentration increasing. The scale stored without air access has been stable for more than 4 months. The characteristics of developed and known visual test (VT) methods for Zn(II) determination are compared in Table 1. The data indicate that the test proposed is more sensitive.

Zn(II) is known to form unstable complexes with organic substances of natural water [24]. Therefore, it is possible to determine the Zn(II) concentration in water without mineralization.

The sample of water ($V = 10$ ml) containing $\geq 1$ µg of Zn(II) at pH 6.0 was mixed with 0.1 ml of 1.0 mol·l$^{-1}$ NaF and 0.1 ml of 1.0 mol·l$^{-1}$ $Na_2S_2O_3$ and stirred mechanically with 0.05 g of TAN-SG ($a = 25$ µmol·g$^{-1}$) for 10 min. Sorbent was separated and its colour was compared with the standard scale. The dried sorbent was examined using diffusion reflectance spectroscopy.

### *3.5.2. The Cu(II) determination in water by using TAN-SG*

The DRS method of Cu(II) determination was developed. The calibration graph was linear in the range 1.0–10.4 µg per sample. The calibration equation was: $R_{560} = 0.004 + 0.03 \cdot C$ (µg per sample), $r = 0.98$. The detection limit was 10 µg·l$^{-1}$ (for 100 ml of sample solution and sorbent mass 0.1 g). Therefore, TAN immobilized may be applied to Cu(II) determination in natural water at a content as low as 0.05 MAC level [23].

The colour scale for Cu(II) visual test determination in the range 0.65–13 µg per sample was developed. It was prepared by stirring 10 ml solution containing 0, 0.65, 1.3, 2.6, 5.2, 6.4 and 13 µg of Cu(II) and 0.5 mol·l$^{-1}$ NaCl at pH 3.5 with 0.1 g TAN-SG ($a = 2.5$ µmol·g$^{-1}$) for 15 min. The sorbents were separated. The colour of sorbents changed from light-pink to violet with Cu(II) concentration increasing. The scale stored without air access has been stable for more than 4 months. The comparison of developed and known VT methods for Cu(II) determination represented in the Table 1 shows higher sensitivity of test proposed.

Copper forms the stable complexes with organic substances of natural water [24], so it becomes inactive in reaction with TAN immobilized. Therefore, the natural water was analyzed after the ultrasound mineralization.

The sample ($V = 10$ ml) of mineralized water was neutralized with 1 mol·l$^{-1}$ NaOH up to pH 3.5, mixed with 1.25 ml of 4 mol·l$^{-1}$ NaCl, 1 ml of 0.1 mol·l$^{-1}$ NaF and stirred mechanically with 0.1 g of TAN-SG ($a = 2.5$ µmol·g$^{-1}$) for 10 min. The sorbent was separated and its color was compared with standard scale. Dried sorbent was examined by using diffusion reflectance spectroscopy.

The results of the zinc and copper determination in natural and tap water by using developed and flame atomic absorption spectroscopic (FAAS) [23] methods are represented in Table 2. The data obtained show that the method proposed gives reproducible and reliable results. The comparison of results of copper determination in tap and river water indicate the necessity for prior mineralization in both cases.

The developed DRS and VT methods on the base of silica with TAN adsorbed are simple and rapid in procedure and appear to offer a faster and more effective route to natural water analysis.

Table 1
Comparative description of visual test methods of Cu(II) and Zn(II) determination[a]

| Ion | Sorbent | Detection limit (mg·l$^{-1}$) | Detection range (mg per sample) | Reference |
|---|---|---|---|---|
| Cu(II) | TM-cellulose | 0.05 | 0.05–2* | [25] |
| | DETC-polymer fiber | 0.05 | 0.5–10 | [26] |
| | PAN-Silochrome | 0.1 | 0.5–5.0 | [27] |
| | Copper Test Aquaquant | 0.05 | 0.05–0.5* | [28] |
| | TAN-SG | 0.010 | 0.65–13 | Proposed |
| Zn(II) | Dz-textile with ion exchanger | 0.1 | 1.0–5.0 | [26] |
| | PAN-Silochrome | 0.03 | 5.0–50 | [27] |
| | Zinc test aquaquant | 0.1 | 0.1–5.0* | [28] |
| | TAN-SG | 0.015 | 0.65–13 | Proposed |

* mg·l$^{-1}$.

[a] TM-4,4′-Bis-(dymethylamino-)thiobenzophenone, DETC, Diethylthiocarbazone; PAN-1-(2-Pyridylazo)-2-naphthol, Dz, Diphenylthiocarbazone.

Table 2
Results of Cu(II) and Zn(II) determination using the VT, DRS and FAAS methods ($n = 3$, $P = 0.95$)

| Ion | Sample | Concentration (mg·l$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Added | Founded | | |
| | | | VT | DRS | AAS |
| Cu(II) | Standard solution | 0.55 | $0.52 \pm 0.3$ | $0.55 \pm 0.2$ | $0.55 \pm 0.05$ |
| | Tap water | 0.64 | $0.4 \pm 0.1$ | $0.45 \pm 0.2$ | $0.61 \pm 0.06$ |
| | River water | — | $<0.07$ | $<0.1$ | $0.06 \pm 0.01$ |
| | River water* | — | $0.13 \pm 0.07$ | $0.10 \pm 0.3$ | $0.06 \pm 0.01$ |
| Zn(II) | Standard solution | 0.2 | $0.20 \pm 0.07$ | $0.20 \pm 0.02$ | $0.22 \pm 0.02$ |
| | Tap water | 0.2 | $0.98 \pm 0.15$ | $1.00 \pm 0.05$ | $1.10 \pm 0.07$ |
| | River water | — | $0.13 \pm 0.03$ | $0.12 \pm 0.03$ | $0.09 \pm 0.01$ |

* After ultrasound destruction.

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