A new Cu(II)- 5-(4-sulphophenylazo)-8-aminoquinoline complex used for copper determination in presence of gold and silver in water and mineral samples

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Abstract

In this work, a characterization of reagent chromophere 5-(4-sulphophenylazo)-8-aminoquinoline [SPA] by IR and ^{1}H RMN was carried out and a pK_a value of 3.55 ± 0.03 was found as well. An 1:2 stoichiometry for the Cu(II)-SPA complex was determined at pH 9 by Job and molar ratio methods. A value of 1.4×10^{14} for the stability constant was also found. Based on the formation of this complex a new method for the copper determination in presence of gold and silver was developed by derivative spectrophotometry using a previous preconcentration on solid phase. In this method, the analytical measures were executed directly in the solid phase containing the complex. The Cu(II) reacts with the reagent chromophere SPA previously retained in the anionic exchange DEAE Sephadex A25. In this determination, the first derivative at 605 nm was used. The quantification range was between $(3.2 \pm 0.3 \times 10^{-1}) \times 10^{-8}$ and $(94.4 \pm 0.9) \times 10^{-8}$ mol L^{-1} $(3.2 \pm 0.3 \times 10^{-1}) \times 10^{-8}$, and $(94.4 \pm 0.9) \times 10^{-8}$ mol L^{-1}. The repeatability expressed as RSD was between 1.1 and 2.0%. The method was applied successfully for the copper determination in mineral residuals and natural water samples. The results were consistent with those provided by ICP-mass spectrometry.

1. Introduction

The copper is extensively examined in environmental studies, industrial, biological applications, etc. However, there are many difficulties to determine traces in this type of samples due to insufficient sensitivity or matrix interferences. For this reason, a different preconcentration process has been employed together with diverse techniques. In this context, it was found that the use of solid phase with the incorporation of different chemical compounds or biological species that contain groups which permit the retention and preconcentration of different analytes, among them, the alga *Pilayella littoralis*, immobilized on silica gel employed as a biosorbent using flow injection system on line, and the amberlite XAD-2 functionalized with 2-aminothiophenol with a short column packed. This permits

the preconcentration of metallic ions being subsequent eluted and detected by inductively coupled plasma–atomic emission spectrophotometry (ICP–AES) [1,2].

On the other hand, chromatographic techniques have also incorporated preconcentration on solid phase or liquid–liquid in its methodologies for the determination of copper and other metallic ions, achieving the increase of the detection limits [3,4]. With the same purpose, in flame atomic absorption spectrometry (FAAS), a preconcentration has been used in batch and continuous [5–7]. All these methodologies incorporate preconcentration for the determination of Cu(II) at trace level. However, in spite of the use of a preconcentration and sophisticated instrumentation, the values of detection limits were found between 0.05 and 0.6 µg L^{-1}. A disadvantage of the procedures that use a preconcentration is in the analyte elution because it diminishes the sensitivity for dilution effect and increases the previous stages of the analytic process, favoring the errors in the determinations.

The UV–vis spectrophotometry is an alternative technique that also allows carrying out the copper determination. Many

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analytic methods are based on this technique, due to the rapidness, simplicity and multiplicity of applications [8–10].

When kinetic reactions are used, it is possible to obtain a method by this technique with similar detection limit. Prasad [11] describes a highly-sensitive and selective catalytic kinetic spectrophotometric method for the determination of Cu(II) as low as $6 \mu g \, L^{-1}$ which is based on the catalytic effect of copper on the oxidation of citric acid by alkaline hexacyanoferrate(III) at 420 nm. A method has also been proposed for the determination of this metallic ion at 560 nm based on the catalytic effect of copper on the reduction of Ponceau S by sodium sulfide in an alkaline media. The method allows determination of copper at $2 \mu g \, L^{-1}$ levels [12]. The simultaneous determination of copper and iron, proposed by Ohno et al. [13], is based on their catalytic effects on the oxidative coupling of *p*-anisidine with *N,N*-dimethylaniline to form a colored compound in the presence of hydrogen peroxide in acid media. The quantification limit for copper was $0.16 \mu g \, L^{-1}$ and the method was successfully applied to the analyses of these ions in tap, well, river, and pond waters.

Nevertheless, when are not considered kinetic reactions, unfortunately, this technique presents a smaller sensitivity and selectivity, which limits its applicability. Some works have shown that it is possible to increase the sensitivity incorporating a preconcentration on solid phase (SPE), compensating the disadvantages of the liquid–liquid extraction [14,15]. Several methods have been described that include a preconcentration process, where the analytes are eluting being evaluated by their analytic signals later on, producing an increase of the previous stages [16]. Other methods require extended preconcentration times in order to obtain the quantitative extraction [17].

In the extraction and preconcentration process on solid phase, several supports have been used: chitosan microspheres [18], *Aspergillus niger* [19], polyestyrene divinylbenzene resins, etc. The resins can be functionalised, as well as loaded with a variety of organic ligands having various functional groups [20–23]. Some resin beads are commercially available as Dowex and Amberlite, which differ in their cross-linkage degree, bead size, pore diameter, etc. The use of these resin types are in concordance when the analytes are eluted and then evaluated for the techniques previously indicated. However, the dilution effect, when the analytes are eluted, is a disadvantage for spectrophotometric determination.

This work proposes to use spectrophotometry in derivative modality to reach detection limits at trace level carrying out a previous preconcentration to the instrumental measure, obtaining the analytical signal directly in the solid phase, in order to increase the sensitivity and to diminish the previous stages, since the preconcentration and the formation of the complex is carried out in a single stage directly in the solid phase that contain to 5-(4-sulphophenylazo)-8-aminoquinoline ligand, previously retained on DEAE Sephadex A25 anionic exchange, since it was found that it is the most promising polymeric support, because it has a greater surface area for immobilizing the ligand. Further, the grains are small and uniform, whereby it is possible to obtain a good repeatability. The interaction is produced by electrostatic attraction between the group [...$OCH_2CH_2NH(CH_2CH_3)_2^+$] of the resin and the sulfonic groups of the ligand. The groups of the ligand $-C_5H_3N$ and $-NH_2$ reach a position in the solid phase that permits to form complex with Cu(II) and to obtain the preconcentration. This process makes it possible to reduce solvents, costs and time of extraction in the preparation of the samples and permits copper determination without highly sophisticated instruments [24,25].

The 5-(4-sulphophenylazo)-8-aminoquinoline (SPA) is a ligand that was synthesized and characterized only using elemental analysis by Zuotao and McCreedy [26]. This ligand only has been used in alkaline aqueous solution in presence of cetyltrimethylammonium bromide for the Au(III) determination by flow injection spectrophotometry.

In this work is presented the characterization and the structure of the Cu(II)-SPA complex in aqueous solution including a deep characterization of the SPA ligand by mean of IR, ^{1}H NMR and elemental analysis. In our work, the result of the last analysis differs with those obtained by Zuotao and McCreedy [26].

Based in this new Cu(II)-SPA complex a method for the copper determination in presence of silver and gold is proposed. The application of the method was realized in mineral residuals and natural water impacted by the mining activity.

2. Experimental

2.1. Apparatus

A Shimadzu UV–vis 1603 absorption spectrophotometer with a 1 mm quartz cell was used for absorbance measurements and derivative absorption spectra in solid phase. A 10 mm quartz cell was also used when the measurements were realized in aqueous solution. The derivative spectra were obtained using a software, Shimadzu kit version 3.7 (P/N 206-60570-04). An Orion Digital Research Ion-Analyzer 701 with glass and saturated calomel electrodes was used for pH determinations. A magnetic stirrer, HI 190 M Hanna Instrument, for the preconcentration step was also used.

An inductively coupled plasma–optical emission spectrometer (ICP–OES) Perkin–Elmer Optima 3300 XL was used to compare the proposed method.

2.2. Chemicals and reagents

All reagents were of analytical grade and the solutions were prepared with high-purity water from a NANO pure Barnstead ultrapure water system device.

Commercial standard solutions of $1000 \, mg \, L^{-1}$ Cu(II), Ag(I) and Au(III) were purchased from Merck®. The pH 9 was adjusted with H_3BO_3 $1 \, mol \, L^{-1}$/H_2BO_3Na $0.6 \, mol \, L^{-1}$ buffer solution. DEAE Sephadex A25 ionic exchanger was purchased from Aldrich®.

The chromogenic reagent SPA was synthesized, according to the procedure proposed by Zuotao and McCreedy [26]. Thus, SPA was prepared by dissolving sulphanilic acid (2.1 g) in 2 mL of ice-cold concentrated hydrochloric acid and 10 mL of ice-cold distilled water and was slowly diazotized with a solution of 0.8 g of sodium nitrite in 8 mL of water. The diazotized solution

was added drop-wise with stirring to an ice-cold solution of 8-aminoquinoline (1.6 g) in 50 mL of 2 mol L^{-1} acetic acid, then mixed during 1.5 h with stirring in the ice-bath, neutralized with NaOH and filtered. The red precipitate was recrystallized and salted out with NaCl several times from the water.

The chromophere synthesized was used to prepare a 1.5×10^{-3} mol L^{-1} SPA solution in water.

In the validation of the method a quality control solution High-Purity Standards® QCS-19 (Charleston, USA) was used. This sample had the following content in 100 g mL^{-1} Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Se, Tl, Ti, V, Zn, and Ni.

2.3. Characterization of SPA

The chromophere synthesized was characterized by elemental analysis, FT–IR and ^{1}H NMR spectroscopy. Elemental analysis (EA) of 5-(4-sulphophenylazo)-8-aminoquinoline dried in vacuo was performed using a CE Instrument EA 1108. The samples were analyzed in potassium bromide disks using an infrared Fourier transform spectrophotometer, Bruker vector 22 FT-IR, in the region from 4000 to 450 cm^{-1}. Nuclear Magnetic Resonance spectra of ^{1}H using d$_6$-DMSO were measured in a Bruker AMX-300 spectrophotometer.

The experimental data of elemental analysis of 5-(4-sulphophenylazo)-8-aminoquinoline (C$_{15}$H$_{11}$N$_4$NaO$_3$S) were 45.88% C, 14.34% N, 3.34% H, and 8.67% S. The IR spectrum shows bands corresponding to ν (S(=O)$_2$) 1193 cm^{-1}, ν (N–H) 3500–3250 cm^{-1}, ν (N=N) 1385 c m^{-1}, ν (C=C) 1621 cm^{-1}, and ν (C=N) 1511 cm^{-1}. The ^{1}H NMR shows signals corresponding to δ (–Ar–H) 6.95 ppm (1H), 9.25 ppm (1H), 7.7–7.9 ppm (4H); δ (C$_5$H$_3$N) 7.65 ppm (1H), 8 ppm (1H), 8.85 ppm (1H) and δ (NH$_2$) 7.1 ppm (2H).

2.4. Extraction procedure

2.4.1. Retention of SPA on DEAE Sephadex A25

The retention of SPA in the solid phase from 200 mL of aqueous solution containing 50 mL of ligand SPA 1.5×10^{-3} mol L^{-1} was carried out using 10 g of DEAE Sephadex A25, stirring during 30 min. The solution was filtered and the solid was obtained with the retained ligand [SPA–DEAE Sephadex A25], finally was dried at 50 °C and used in the determinations.

2.4.2. Procedure for preconcentration and determination of metal ions

The formation of the complexes was generated in the ionic exchange with the previously retained ligand. The preparation of the samples was carried out in a final volume of solution of 200 mL and then were added between 20 to 120 μL of metal of 100 mg L^{-1} and 10 mL of H$_3$BO$_3$ 1 mol L^{-1}/H$_2$BO$_3$Na 0.6 mol L^{-1} buffer solution. To each solution was added 60 mg of SPA–DEAE Sephadex A25 and was stirred for 20 min. The solid phase was packed in 1 mm optical path quartz cells and the absorption spectra were carried out in wavelengths ranges from 250 to 800 nm. By means of graphic method at $\lambda = 605$ nm, the copper quantification was carried out by first derivative spectra. The first order derivative was obtained using a smoothing factor of 40,000 and a scale factor of 10,000.

2.5. ICP–OEC method

The copper determination was carried out by ICP–OES, following the US-EPA 6010 B method [27] in order to be used as comparative method.

3. Results and discussion

3.1. Characterization of SPA

The results of the characterization of chromophere synthesized are summarized in Section 2.3.

The results of elemental analysis are not concordant with theoretical data if the molecule is pure. However, taking account that the ^{1}H NMR spectrum presents a high peak at 3.3 ppm, it is possible to postulate that the SPA ligand contains crys-
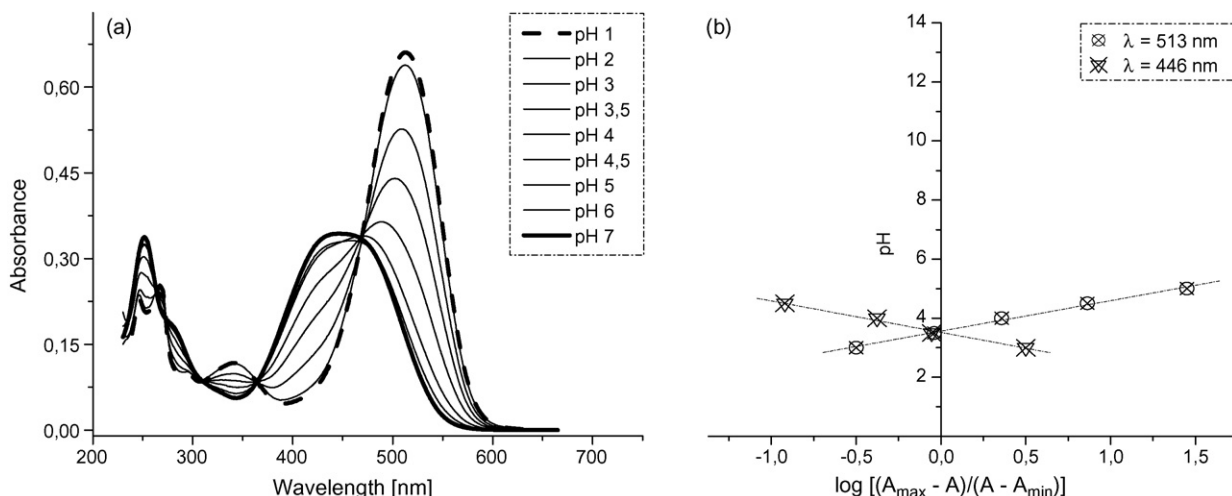

Fig. 1. (a) Abpsortion spectra of 5-(4-sulphophenylazo)-8-aminoquinoline 2×10^{-5} mol L^{-1} in aqueous solution a different pH values and (b) pK_a determination of 5-(4-sulphophenylazo)-8-aminoquinoline by the Henderson–Hasselbach equation.
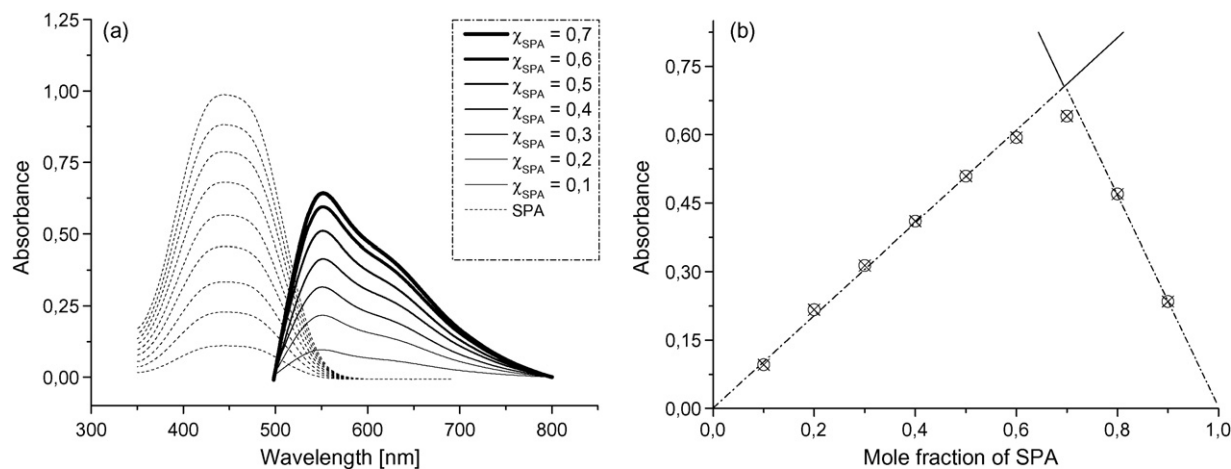
Fig. 2. Job's method of continuous variation of Cu (II)-SPA complex. Cu (II) or SPA 3.3×10^{-4} mol L^{-1}, pH 9 (buffer H$_3$BO$_3$ 1 mol L^{-1}/H$_2$BO$_3$Na 0.6 mol L^{-1}), $\lambda = 550$ nm. (a) Spectra of the Cu(II)-SPA complex and reagent blank in aqueous solution. (b) Job's graphic.

tallization water. The theoretical data 47.2% C, 14.69% N, 2.9% H, 8.4% S has a good correspondence with the experimental data if the molecule has two crystallization water. The 5-(4-sulphophenylazo)-8-aminoquinoline pK_a was determined by spectrophotometric method. The Fig. 1a shows that spectra at 513 nm and 446 nm correspond to the acid and basic form of SPA, respectively. At 470 nm an isosbestic point was found. The quantification of pK_a value was carried out by using the Henderson–Hasselbach linear equation [28]. As can be seen, SPA presents a pK_a 3.55 ± 0.03 value, (Fig. 1b).

3.2. Characterization of Cu(II)-SPA complex

Cu(II) reacts with SPA at room temperature in basic pH and it forms a brown-red complex with molar absorptivity (ε) of 3.4×10^4 L mol^{-1} cm^{-1} at 550 nm. The absorption of this complex is not affected by the buffer addition. The stoichiom-

etry of metal/ligand ratio 1:2 was determined by Job (Fig. 2) and molar ratio methods (Fig. 3) [29]. These determinations were carried out in presence of H$_3$BO$_3$ 1 mol L^{-1}/H$_2$BO$_3$Na 0.6 mol L^{-1} buffer solution in order to reach pH 9 and to maintain constant the ionic strength. In both cases the same stoichiometry was obtained. Mass spectrum of the complex shows the peaks at m/z value of 874.44, 856.11, 818.98, 761.34, and 719.79 corresponding to (C$_{30}$H$_{22}$CuN$_8$Na$_2$O$_6$S$_2 \cdot$ 6H$_2$O)$^+$, (C$_{30}$H$_{22}$CuN$_8$Na$_2$O$_6$S$_2 \cdot$ 5H$_2$O)$^+$, (C$_{30}$H$_{22}$CuN$_8$Na$_2$O$_6$S$_2 \cdot$ 3H$_2$O)$^+$, (C$_{30}$H$_{22}$CuN$_8$Na$_2$O$_6$S$_2$)$^+$, and (C$_{30}$H$_{22}$CuN$_8$O$_6$S$_2$)$^+$, respectively.

Taking into account the relation of the complex and the configuration d^9 of Cu^{2+}, it is possible to propose that Cu(SPAx2H$_2$O)$_2$ bond with 2 molecules of water as axial ligands (long bonds) by mean of the O donor and to form a complex of the octahedral distorted structure, due to the Jahn–Teller effect. When the Cu(SPAx2H$_2$O)$_2$(H$_2$O)$_2$ complex is warmed looses water of coordination to give Cu(SPAx2H$_2$O)$_2$ anhydrous com-
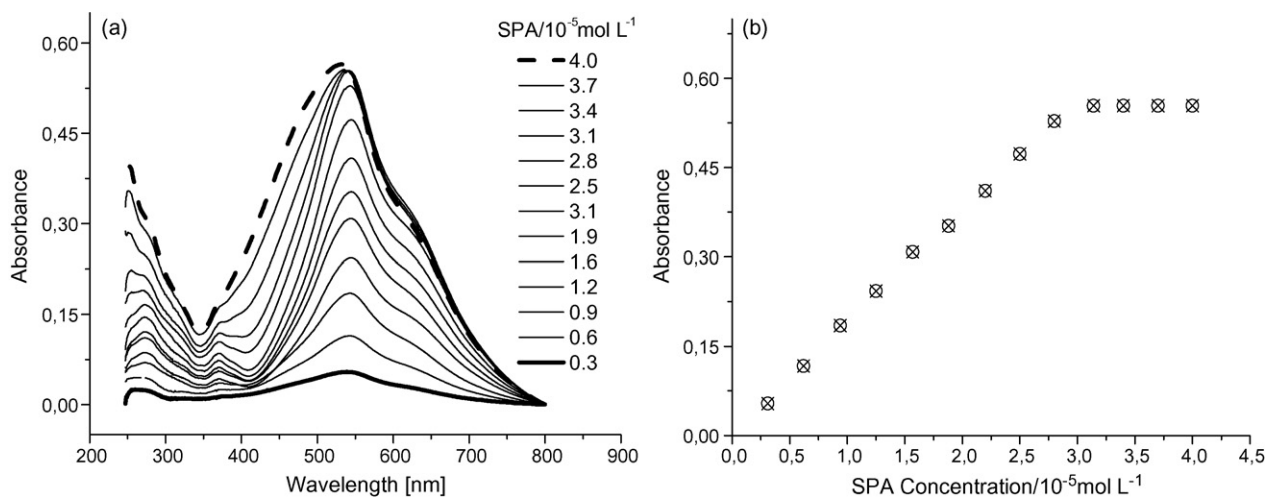

Fig. 3. Method of the molars relationships for the complex Cu(II)-SPA. (a).-Absorption spectra of the complex formed by Cu(II) with different SPA ligand concentrations and (b) Effect of the addition of SPA on the formation of the complex. Cu(II) $1.5 \times c10^{-5}$ mol L^{-1}, buffer H$_3$BO$_3$ 1 mol L^{-1}/H$_2$BO$_3$Na 0.63 mol L^{-1}, pH 9, $\lambda = 550$ nm.
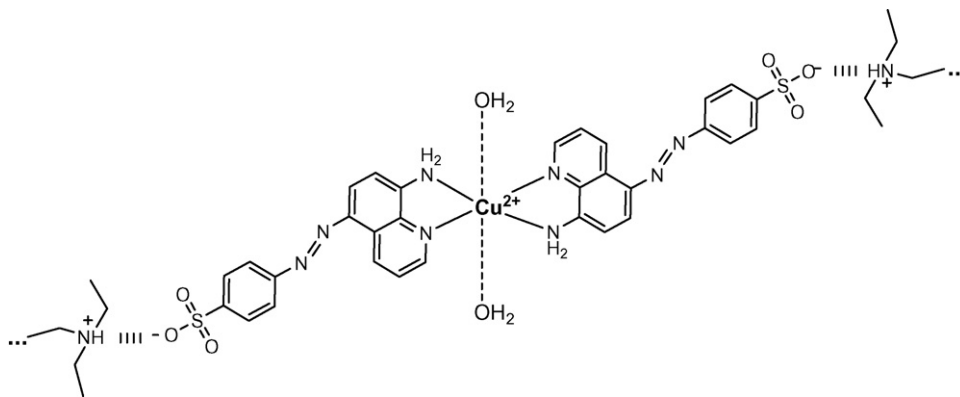
Fig. 4. Interaction Cu^{2+} with SPA–DEAE Sephadex A25. Formation of complex Cu(II)-SPA on solid phase.

plex, where the four molecules of water correspond to the water contained in the SPA ligand.

The stability constant of the complex obtained by Job and Likussar methods was 1.4×10^{14} at $18\,^{\circ}\mathrm{C}$ [30].

3.3. Concentration effect of SPA on DEAE Sephadex A25

The study of the concentration effect of SPA retained in the anionic exchange DEAE Sephadex A25 was carried out. The concentration of SPA in the solution was varied from $1.5 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ to $6.1 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$, being retained successfully in the solid phase. Nevertheless, the spectral signals of SPA retained on Sephadex in the range $3.8 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ to $6.1 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$, present a wide and intense band of absorption, diminishing the zone of absorption of the complex for instrumental limitations. For these reasons $2.3 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ was selected as work concentration.

3.4. Preconcentration of Cu(II) on the SPA–DEAE Sephadex A25

The extraction of the metallic ion from the solution generates the immediate formation of the complex in the solid phase (Fig. 4).

The complex Cu(II)-SPA on the anionic exchange DEAE Sephadex A25 shows a maximum of absorption to 590 nm. Carrying out the absorbance measure of the complex directly in the solid phase appears an increment of the sensitivity, which allows the determination of copper at trace levels. On the other hand, although Ag(I) and Au(III) form complex with SPA–DEAE Sephadex A25, their signals are of low intensity, which does not allow its quantification at low concentrations (Fig. 5).

Nevertheless, the presence of these cations at concentrations of $2.3 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ for Ag(I) and $6.3 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$ for Au(III), produces an increment in the absorbance values near to 10%.

For these reasons a method is developed for the Cu(II) determination in those matrix in that these two ions or at least one of them is present, because the interference caused by Au(III) and Ag(I) can be eliminated with the use of derivative spectropho-

tometry [31], since this technique allows the resolution of the overlapped bands that absorb in common areas of the classic spectrum.

3.5. Optimization of chemical and preconcentration variables

3.5.1. pH Effect
The pH effect on the complex formation in the range 2–11 was studied. The acid medium does not interfere in the SPA retention on the anionic exchange, however, the complex Cu(II)-SPA is formed quantitatively at pH 9.0 reached with H_3BO_3 $1\,\mathrm{mol\,L^{-1}}$/H_2BO_3Na $0.6\,\mathrm{mol\,L^{-1}}$ buffer solution. Further, the effect of buffer concentration was studied on the complex formation selecting 10 mL of this buffer as optimum.

3.5.2. Mass of SPA–DEAE Sephadex A25 Effect
The effect of the mass on the analytical signal was optimized using different mass of solid phase. The signals exponentially decrease with the mass increment of the SPA–DEAE
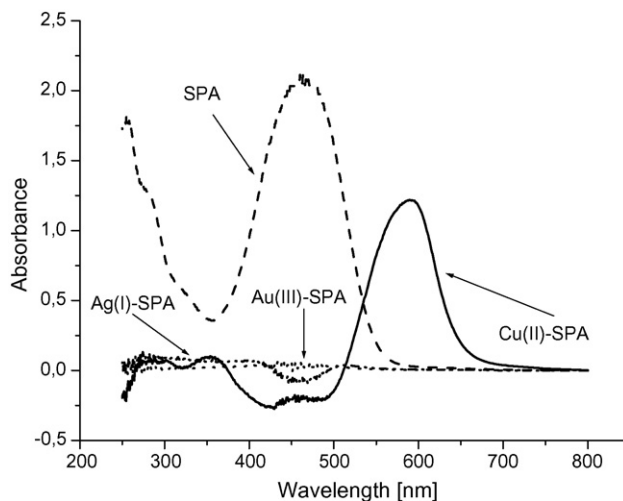

Fig. 5. Zero order spectra of the complexes retained on SPA–DEAE Sephadex A25, against reagent blank. Concentration Cu(II) $7.8 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$, Ag(I) $2.3 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$, Au(III) $6.3 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$. Ten milliliter of buffer H_3BO_3 $1\,\mathrm{mol\,L^{-1}}$/H_2BO_3Na $0.63\,\mathrm{mol\,L^{-1}}$, 60 mg SPA–DEAE Sephadex A25.

Sephadex A25. In order to increase the sensibility a mass of 60 mg ± 0.01 mg was selected.

3.5.3. Stirring time effect

The stirring time effect on the retention of the metal ion in the range 5–30 min was also studied. The stirring time for maximum copper retention was 15 min. However, 20 min was select to assure a quantitative retention.

3.6. Selection of spectral variables

3.6.1. Selection of the derivative order and λ analytical

Two modes of digital derivative spectrophotometry can be used: in the first mode, the derivatives correspond to $\Delta A/\Delta\lambda$ where the derivation process is obtained by a program using a two-column table. In this derivative type the $\Delta\lambda$ values can be varied, this mode is very useful when the spectra are strongly overlapped. In the second mode proposed by Savitzky and Golay [31], the derivative corresponds to $A/\Delta\lambda$, where A is absorbance, which must be measured in fixed points and $\Delta\lambda$ is the wavelength range used in the scanned spectral. In this type of digital derivative spectrophotometry, the minimum squares procedure to smooth and differentiate the spectra numerical data is carried out also by computer processing. The last alternative was adopted in this work, because with this mode it is possible to resolve the spectral bands and to obtain a control of the noise of the baseline and the analytical signal. Under this condition the higher signal/noise ratio was found.

Derivative spectra of different orders were obtained from stored zero order spectra using digital differentiation. The first derivative spectral allows the determination of Cu(II) in a sample that also contains Au(III) and Ag(I), since the first derivative spectra of these analytes are zero between 590 and 680 nm, allowing the Cu(II) determination by means of graphic method at analytical wavelength of 605 nm (Fig. 6). This value does
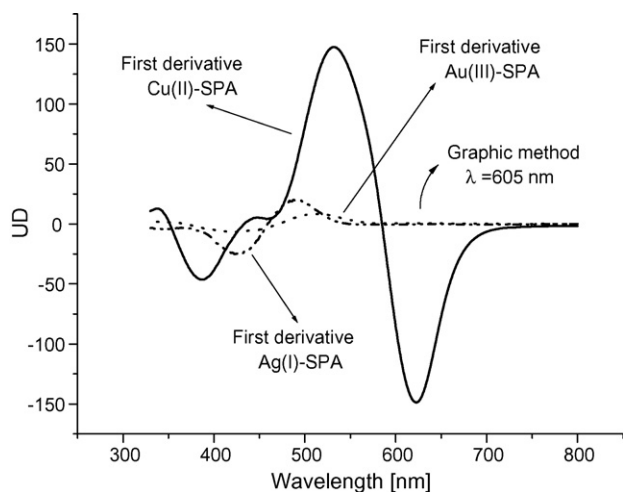

Fig. 6. Derivative spectra of the Cu(II), Au(III) y Ag(I) complexes on SPA–DEAE Sephadex A25. Concentration Cu(II) 7.8×10^{-7} mol L^{-1}, Ag(I) 2.3×10^{-7} mol L^{-1}, Au(III) 6.3×10^{-8} mol L^{-1}. 10 mL of buffer H$_3$BO$_3$ 1 mol L^{-1}/H$_2$BO$_3$Na 0.6 mol L^{-1}, 60 mg de SPA–DEAE Sephadex A25. First derivative, smoothing factor 40,000, scale factor 10,000.

not correspond to the maximum analytical signal of copper, however it was selected in order to increase the selectivity, because in this conditions, the interference of other ions is decreased.

3.6.2. Selection of the smoothing factor

The smoothing factor correspond to the points number used for the derivation zero order spectra together with to smooth the analytical signal. For the first derivative, the following values were used: 5000; 10,000; 20,000 and 40,000, these values are defined by default for the software, which are in relation with the wavelength range where the spectra were scanned. The $\Delta\lambda$ value is constant and correspond to 550 nm. Under these conditions a value of 40,000 points was selected. When the smoothing factor is increased the heights of the derivative signal decrease, but the noise decrease faster, increasing the signal/noise ratio.

3.6.3. Selection of the scale factor

The scale factor permits the amplification and improvement of the analytical signal in order to obtain a better lecture. This factor must be studied in order to observe if the system presents a distortion effect. Considering this fact, a scale factor of 10^4 was selected. It is important to state that this factor does not improve the analytical parameter because the signal of the analytes and the reagents blank increase in the same proportion.

3.7. Analytical features

The determination of the analytical features, for the determination of copper in presence of gold and silver was carried out by first order derivative spectrophotometry to 605 nm using a smoothing factor of 40,000 and an amplification factor of 10,000 in a total solution volume of 200 mL. The equation for the copper determination obtained by the method of least squares is DU $= (15.6 \pm 0.1) \times 10^6$ C (mol L^{-1}) $+ (1.2 \times 10^{-1} \pm 2.0 \times 10^{-3})$ with $r = 0.999$.

For a total volume of 200 mL the quantification range was between $(3.2 \pm 0.3 \times 10^{-1}) \times 10^{-8}$ to $(94.4 \pm 0.9) \times 10^{-8}$ mol L^{-1}. The detection limit (calculated by using the 3σ criterion) was found to be $(0.96 \pm 0.01) \times 10^{-8}$ mol L^{-1}.

The repeatability of the method expressed as relative standard deviation (RSD) for 10 samples containing 7.8×10^{-7} mol L^{-1}, 2.3×10^{-7} mol L^{-1} and 6.3×10^{-8} mol L^{-1} of copper, silver, and gold, respectively, was between 1.1 and 2.0%.

The features of the proposed method are similar to those obtained using methods that require sophisticated instrumental.

3.8. Adsorption isotherm

For the determination of the adsorption behavior of the solid phase, the amount of adsorbed copper was studied as a function of copper concentration (Fig. 7a). The models proposed by Langmuir and Freundlich were analyzed. The linearization of Langmuir isotherm can be obtained by plotting C_e/q as a
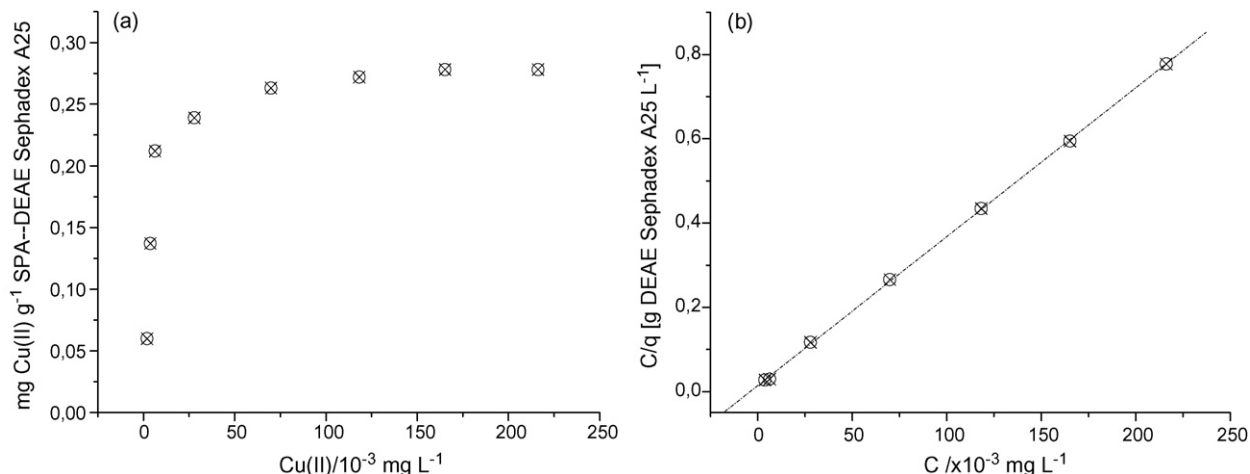
Fig. 7. (a) Adsorption isotherm of SPA–DEAE Sephadex A25 for copper. 60 mg of SPA–DEAE Sephadex A25, 10 mL of buffer H_3BO_3 1 mol L^{-1}/H_2BO_3Na 0.63 mol L^{-1}. $\lambda = 590$ nm. and (b) Dependence of surface coverage SPA–DEAE Sephadex A25 on Cu(II) ion concentration determined from Fig. 7(a) data. The solid line represents the fit according to the Langmuir adsorption model.

function of C_e. The slope of the plot yields the maximum capacity (q_m) whereas its linear coefficient represents the Langmuir constant (K). The Freundlich equation can be linearized using logarithms to determine K_F and n from the slope and linear coefficient of the plot of log q versus log C_e, respectively [32]. The correlation coefficients of the linear equations obtained in this study were 0.999 (Langmuir) and 0.847 (Freundlich). An analysis of the adsorption behavior comparing both models revealed that Langmuir equation yielded the best fit. Thus, the adsorption isotherm of copper is according to the Langmuir equation (Fig. 7b) [33] and the graphical treatment of the data yielded 1.71×10^{-2} mg of Cu(II) per gram of SPA–DEAE Sephadex A25 as maximum saturation capacity and equilibrium binding constant K 1.3×10^7 mol^{-1} L. The Langmuir treatment demonstrated that the surface is nearly fully covered with monomolecular layer of copper at high concentrations. Therefore, at high concentrations adsorption does not increase linearly. The main adsorption sites of the SPA—EAE Sephadex A25 were the – H_2N: and –N: groups forming a solid phase chelate.

3.9. Study of interferences

Potential interferences caused by several cations in the form of chlorides, nitrates or sulphates and anions as potassium, sodium or ammonium salts were studied. The interferences due to several cations and anions were studied thoroughly. In this study, different amounts of the ionic species were added together with Cu(II), Ag(I) and Au(III) containing 7.8×10^{-7} mol L^{-1}, 2.3×10^{-7} mol L^{-1} and 6.3×10^{-8} mol L^{-1}, respectively. The concentration of each interferent was progressively reduced until the ceasing of the interference.

Several cations interfered (variation of signal higher than 8%) at higher (K^+, Mg^{2+}, Ca^{2+}) similar (Ni^{2+}, Co^{2+}, Hg^{2+}) or even lower (Fe^{3+}) molar concentration than copper concentration.

Although in many real samples, most of the interfering species appear at lower concentration than copper. However, in mineral residuals and natural water polluted, the concentration of Fe^{3+} is similar to that of Cu(II), whereby the interference of this cation was eliminated by means of the addition of NaOH 1 mol L^{-1} until reaching pH 5, since to this pH value, it is pos-

Table 1
Tolerance limits for cations and anions in copper determination

Cation	Interferent mol L^{-1}	Molar ratio I/Cu(II)	Anion	Interferent mol L^{-1}	Molar ratio I/Cu(II)
K^+	5.1×10^{-3}	6.5×10^3	SCN^-	3.3×10^{-3}	4.2×10^3
Ca^{2+}, Mg^{2+}	4.2×10^{-3}	5.4×10^3	Br^-	2.0×10^{-3}	2.5×10^3
Na^+	2.1×10^{-3}	2.7×10^3	I^-	1.0×10^{-3}	1.3×10^3
Al^{3+}	8.6×10^{-6}	10.9	Cl^-	3.0×10^{-3}	3.8×10^3
Cd^{2+}	6.2×10^{-6}	7.9	F^-	2.6×10^{-3}	3.3×10^3
Zn^{2+}	3.5×10^{-6}	4.5	O × alate	3.5×10^{-6}	4.5
Bi^{3+}	3.4×10^{-6}	4.3	Tartrate	7.4×10^{-7}	0.95
Cr^{3+}	1.9×10^{-6}	2.5	EDTA	1.4×10^{-7}	0.18
Mn^{2+}	1.8×10^{-6}	2.3	Citrate	1.1×10^{-7}	0.14
Co^{2+}, Ni^{2+}, Pb^{2+}	1.7×10^{-6}	2.2			
Hg^{2+}	1.2×10^{-6}	1.5			
Fe^{3+}	3.6×10^{-7}	0.5			

Table 2
Determination of copper in real samples (comparison of the analytical methods)

Samples	ICP–MS spectrometry[a] Cu (mg L^{-1})*	Proposed method	
		Cu (mg L^{-1})**	Recovery (%)
Natural water[b]	0.424 ± 0.003	0.421 ± 0.008	99.3 ± 1.9
Industrial residuals	78.0 ± 0.6	79.2 ± 1.5	101.5 ± 1.9

ICP–MS spectrometry (USA-EPA 6020), * Three replicates. ** Seven replicates.

[a] Provided by CEPEDEQ, Faculty of Sciences Chemical and Pharmaceutical University of Chile.

[b] Coya river, VI Region of Chile.

sible to eliminate the interference of this cation by precipitation as $Fe(OH)_3$.

The tolerance limits for the different cations and studied anions are shown in the Table 1.

3.10. Validation and application of the method

The validation of the method was carried out using a control solution High-Purity Standards® enriched with gold $1.3 \times ^{-4}$ mol L^{-1} and silver 4.6×10^{-4} mol L^{-1}. An aliquot of 0.1 mL of this sample was measured and diluted to 200 mL solution. The copper recovery was of 98.2%. The relative standard deviation was minor to 2%.

The method was applied on mineral residuals obtained from a confidential source and river water samples. The water samples were collected in the Coya river, VI Region of Chile, this aquatic system has been polluted by copper smelter processes for many years [34].

The results are shown in Table 2 and they are in agreement with ICP-mass spectrometry.

To compare both methods the *t* Student with a 95% threshold level was used. For ICP–MS method three replicates were used, obtaining an average of 0.424 mg L^{-1} with a standard deviation of 3.1×10^{-3}. For the proposed method seven replicates were carried out obtaining an average of 0.421 mg L^{-1} with a standard deviation of 7.5×10^{-3}. The calculated *t* (t_c) was 0.9 taking into account ten degrees of freedom and 95% confidence, the t_c is smaller than the tabulated *t* (2.228), which would be indicating that the methods are not significantly different and the results agree inside the experimental error.

4. Conclusions

In this work, it was found that the SPA ligand presents a pK_a value of 3.6. According to IR, elemental analysis and ^{1}H RMN data it is possible to establish that this ligand crystallized with 2 H_2O molecules. On the other hand, it was also found that Cu(II) reacts with two molecules of SPA, whereby it was proposed that the Cu(II)-SPA complex have an octahedral distorted structure.

Using the synthesized ligand, a method for the determination of copper in the range 3.2×10^{-8} to 94.4×10^{-8} mol L^{-1} was developed. In this determination both the extraction of Cu(II) from aqueous solution and the formation of complex can be executed in only one step, under these conditions it is possible the copper determination in presence of silver and gold. Another feature of this method is that the consumption of organic

solvent is lower than in liquid–liquid extraction methods. This method offers diverse advantages such as simplicity, rapidity, low cost and sensitivity, reaching similar detection limits to those obtained by sophisticated techniques. This method requires good experimental strategies to achieve an appropriate sampling frequency, which could be a disadvantage. The method was applied successfully for the copper determination in industrial residuals and natural water samples.

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