Article

An Anionic Resin Modified by di-2-Pyridyl Ketone Salicyloylhydrazone as a New Solid Preconcentration Phase for Copper Determination in Ethanol Fuel Samples

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A adsorção do DPKSH em resina aniônica foi investigada a 25 ± 1 °C e em pH 12 com base em três modelos cinéticos pseudo-primeira ordem, pseudo-segunda ordem e difusão intra-partícula. Os dados experimentais foram aplicados com sucesso aos modelos das isotermas de Langmuir, Freundlich e Dubinin-Radushkevich (D-R). A resina aniônica modificada com DPKSH foi usada na determinação espectrofotométrica do cobre após pré-concentração em linha. Nas melhores condições, foi observada uma resposta linear entre 20 e 80 μg L^{-1}, limites de detecção e quantificação estimados em 0,5 e 1,8 μg L^{-1}, respectivamente, com um nível de confiança de 95%, e um fator de pré-concentração igual a 11. O desvio padrão relativo foi estimado em 2,6% para a concentração de 32 μg L^{-1} Cu(II) (n = 20). Os resultados obtidos na determinação de cobre em amostras de etanol combustível apresentaram concordância, com um nível de confiança de 99%, aos obtidos por espectrometria de absorção atômica com chama (F AAS).

The adsorption of DPKSH onto anionic resin was investigated at 25 ± 1 °C and pH 12 on the basis of three kinetic models including pseudo-first order, pseudo-second order and intraparticle diffusion. Isotherm equations including Langmuir, Freundlich and Dubinin-Radushkevich (D-R) were successfully applied to model the experimental data. An anionic resin loaded with DPKSH was used in a flow system for the in-line concentration of copper prior to spectrophotometric determination. Under optimized conditions, a linear response was observed between 20 and 80 μg L^{-1}, with limits of detection and quantification estimated at 0.5 and 1.8 μg L^{-1}, respectively, at the 95% confidence level with an enrichment factor of 11. The relative standard deviation was estimated to be 2.6% for 32 μg L^{-1} Cu(II) (n = 20). The results obtained for copper determination in ethanol fuel samples agreed with those achieved by flame atomic absorption spectrometry (F AAS) at the 99% confidence level.

Keywords: preconcentration, DPKSH, flow analysis, molecular spectrophotometry, ethanol fuel sample

Introduction

In spite of the recent advances in instrumentation and improvements in selectivity and sensitivity, there is a need for preconcentration and separation of trace elements prior to analyses to achieve low limits of detection and to remove constituents that interfere with the matrix.[1-4]

Several strategies are used for separation and preconcentration, such as liquid-liquid, solid-liquid and cloud point extraction.[4-7] In comparison to other strategies, solid-liquid extraction provides simplicity, lower
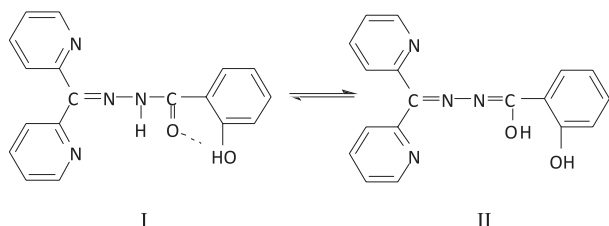
sample contamination and higher enrichment factors, in addition to simple coupling to flow systems, improved sampling throughput and minimal sample and reagent consumption.[8-11]

Recently a number of sorbents have been used for the in-line preconcentration and determination of metal ions including polymeric resins.[1,10,12] The Amberlite XAD-4 resin was modified with β-nitroso-α-naphthol and applied to copper preconcentration and determination in food samples. Modifications included the resin functionalization or impregnation of copolymer with a solution containing β-nitroso-α-naphthol. Both modifications resulted in resins with similar analytical characteristics.[12]

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Di-2-Pyridyl ketone salicyloylhydrazone (DPKSH) is a complexing reagent that is presently used in spectrophotometric method development. DPKSH was adsorbed onto silica gel and Amberlite resins (XAD-2 and XAD-7), and the adsorption was investigated using kinetic and isotherm models.[13-15]

In ethanolic/aqueous solution, DPKSH is in tautomeric equilibrium with the (I) ketonic and (II) enolic form, Scheme 1.

Scheme 1. DPKSH tautomeric equilibrium.

DPKSH may be present in solution as different species and is dependent on the pH of the solution. At a pH between 3.6 and 6.7, neutral species represented by RN are predominant. At pH $\leq$ 3.5, protonation of the pyridine nitrogen occurs (K_1 3.16×10^{-4} mol L^{-1}) and the protonated species is predominant and is represented by RNH$^+$. At pH $\geq$ 6.7, anionic species represented by RO$^-$ are predominant (K_2 1.41×10^{-7} mol L^{-1}). Deprotonation of the enolic form of DPKSH is represented by ROH.[16]

This study focused on the evaluation of an anionic resin modified with DPKSH and the utilization of the modified resin as a solid phase for in-line copper separation and preconcentration. The mechanism of adsorption was obtained through kinetic and isotherm models. A flow system with in-line preconcentration on a mini-column packed with an anionic resin modified by DPKSH was developed. Chemical and hydrodynamic parameters were investigated and the procedure was applied to copper spectrophotometric determination in ethanol fuel samples.

Experimental

Instrumentation

An UV-Vis Cary 50 spectrophotometer (Varian, Palo Alto, CA, USA) equipped with a 1.00 cm quartz cell (Hellma, Müllheim, Germany) was used to determine the absorbance of DPKSH solutions and Cu (II)/DKPSH complexes.

Solutions were mixed (DPKSH and IRA 402) with a MA-140 Marconi shaker (Piracicaba, SP, Brazil) at a controlled speed. The mixtures were centrifuged with a QM222TM centrifuge (Quimis, São Paulo, Brazil).

The measurement of pH was performed with a Metrohm 654 pHmeter (Herisau, Switzerland) equipped with a Metrohm combined glass electrode. The Ag/AgCl reference electrode was filled with 3 mol L^{-1} NaCl.

The flow system was designed with a Gilson Minipuls Evolution peristaltic pump (Paris, France) equipped with 0.7 mm Tygon® tubes for the propulsion of fluid.

An Analyst 200 flame atomic absorption spectrometer (PerkinElmer, Norwalk, CT, USA) equipped with deuterium background correction and copper hollow-cathode lamps as radiation sources was used for the determination of copper in ethanol fuel samples. The instrumental parameters were adjusted according to the manufacturer's recommendations.

Reagents and solutions

All solutions were prepared with analytical grade reagents and deionized water, obtained from Milli-Q system (Millipore, Billerica, MA, USA). Copper reference solutions were prepared by diluting 1.0 g L^{-1} stock solutions Titrisol (Merck, Darmstadt, Germany). Solutions, such as those used to evaluate the proposed method selectivity, were prepared by dissolving their salts into deionized water.

Buffer solutions containing CH$_3$COOH/CH$_3$COONa at pH 4.0 (1.0/0.20 mol L^{-1}), pH 4.7 (0.10/0.10 mol L^{-1}), pH 5.0 (0.50/1.0 mol L^{-1}), pH 5.5 (0.20/1.3 mol L^{-1}) and pH 6.0 (0.10/2.0 mol L^{-1}) and CH$_3$COONH$_4$ at pH 7.0 (1.0 mol L^{-1}) were used for the adjustment of the pH.

DPKSH was synthesized according to a procedure reported in previous paper.[7] The solutions of DPKSH were prepared by dissolving the reagent in ethanol absolute from Merck and diluted in different ethanol concentrations when needed.

Adsorption experiments

DPKSH adsorption kinetics and isotherms were determined using the solution depletion method. In stoppered plastic tubes, 0.200 g of the anionic resin was shaken with 10 mL of a solution comprised of DPKSH and 3% v/v ethanol at pHs 1, 4.7 and 12. In the kinetics study, the mixture was maintained under agitation and an aliquot of supernatant was collected every 20 min up to 240 min, while in the adsorption isotherm study the resulting mixture was then kept in contact for 2 h.

The concentration of DPKSH, at the supernatant aliquots, was determined from the absorption with parameters from the following analytical curves:

pH 1:　$A_{332nm} = 0.010 + 2.21 \times 10^4 \times C_{DPKSH}$,　$r = 0.9983$　(1)

pH 4.7:　$A_{319nm} = -0.017 + 1.91 \times 10^4 \times C_{DPKSH}$,　$r = 0.9989$　(2)

pH 12:　$A_{315nm} = -0.011 + 1.37 \times 10^4 \times C_{DPKSH}$,　$r = 0.9989$　(3)

Preparation of the solid adsorbent and mini-column

Amberlite® IRA 402 (Aldrich Chemical, Saint Louis, MO, USA), an anion exchanger with a particle size of 0.60-0.75 mm and an exchange capacity of 1.2 equiv. L^{-1}, was used in this work. The chloride form of the resin was treated with a 1:1:2 v/v/v HCl:ethanol:H_2O solution in a bath for 3 h. The resin was collected on a Büchner funnel with filter paper and repeatedly washed with deionized water until the filtrate was near neutral (pH *ca.* 6). The washed resin was dried in a desiccator for 2 days to remove any adsorbed water.

After the treatment as stated above, resin IRA 402 was modified by adding 1 g of such in contact with 10 mL of DPKSH 2.2×10^{-4} mol L^{-1} prepared in medium of NaOH (pH 12) and 3% v/v ethanol. The resulting mixture was under agitation at constant both speed and temperature for 24 h. Finally, the modified resin was then washed with deionized water.

A mini-column was packed with 95 mg of modified anionic resin. The ends of the mini-column were fitted with glass wool to prevent changes in height bend.

Flow system

In the flow system (Figure 1a), a sample (S) of a Cu(II) solution was pumped at 6.3 mL min^{-1} and merged with a buffer solution (B, CH_3COOH/CH_3COONa) at pH 5.5 and also pumped at 4.8 mL min^{-1}. The resulting sample was then pumped through a mini-column (C) packed with anionic resin modified by the addition of DPKSH, for 60 s loading time. The injector-commutator valve (IC) was commutated to injection (Figure 1b) and copper was eluted with 100 μL (EV) of a 0.05 mol L^{-1} HNO_3 solution (E) at 6.3 mL min^{-1}. The resulting solution was then merged with 4.8 mL min^{-1} of reagent (R, 1.5×10^{-4} mol L^{-1} DPKSH and 7.5% v/v ethanol, pH 5.5). After the solution passed through a 10 cm reaction coil (RC), the Cu(II)/DPKSH complex was detected (D) at 378 nm. Signals were measured as peak heights using the instrument software. Although the proposed system is manually operated, it can be easily automated by modern methods, such as multicommutation.[10]
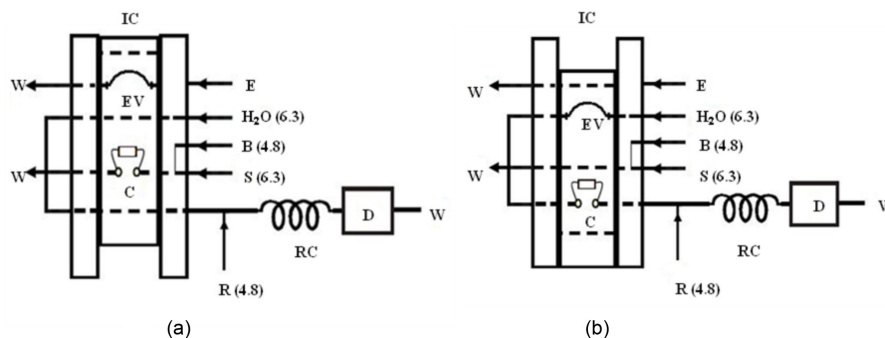
Samples

Commercial ethanol fuel samples were acquired from a local gas station and Cu(II) determination was carried out in triplicate by the standard additions method. Volumes of 75 mL of samples were transferred to volumetric flasks and standard Cu(II), NaF (to avoid Fe(III) interference) and Na_2SO_4 (to recover copper from complexes with organic species)[17] solutions were added. Lastly, deionized water was added so that the final volume of the solution was 100 mL.
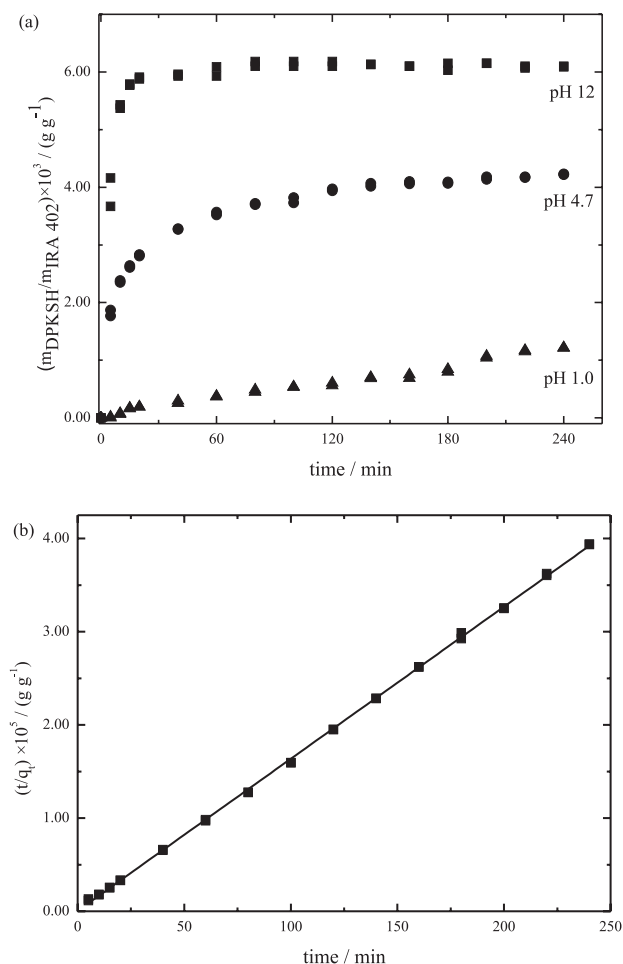
Results and Discussion

Adsorption kinetics

The DPKSH (4.0×10^{-5} mol L^{-1}) mass variation retained *per* gram of resin as a time function is shown in Figure 2a for solutions with pHs 1, 4.7 and 12. The maximum exchange with DPKSH is achieved after 200 min at pH 4.7 and in 60 min at pH 12. At pH 1, the maximum exchange was not observed until 240 min.

Considering the superior capacity for adsorption of DPKSH onto an IRA 402 resin at pH 12, kinetic and isotherm studies were perfgormed at this pH. To investigate the mechanism of ion exchange, a simple kinetic model was used to test the experimental data. This was achieved by applying the Lagergren expression,[13,18,19] which is the

(a)　　　　　　　　　　　　　　　(b)

Figure 1. Flow diagram system for copper (II) determination. IC: injector-commutator valve, RC: 10 cm reaction coil, C: mini-column packed with resin modified by the addition of DPKSH, E: eluent (HNO_3, 0.05 mol L^{-1}), EV: eluent volume, S: Cu(II) sample, B: buffer solution (CH_3COOH/CH_3COONa), R: DPKSH and buffer solution (CH_3COOH/CH_3COONa),W: waste and D: UV-Vis spectrophotometer at 378 nm.

(a)

(b)

Figure 2. (a) Dependence of adsorbed mass of DPKSH *per* unit mass of IRA 402 on time at pHs 1, 4.7 and 12 (b) test of pseudo-second order adsorption of DPKSH onto IRA 402 at pH 12.

first equation developed for the description of adsorption in liquid-solid systems based on solid capacity.

$$\frac{dq_t}{dt} = k_1 \ (q_{max} - q_t) \tag{4}$$

where k_1 is the rate constant of a pseudo-first order process, q_{max} denotes the maximum amount of exchange (g DPKSH g^{-1} IRA 402) and indicates the adsorption capacity corresponding to monolayer coverage, q_t is the amount of DPKSH retained on IRA 402 (g g^{-1}) when $t \neq 0$ and t_{max}. After integration and application of the initial conditions where $q_t = 0$ at $t = 0$ and the conditions at equilibrium where $q_{ads} = q_t$ for each time, t, equation 4 becomes:

$$\log (q_{max} - q_t) = \log q_{max,calc} - \frac{k_1}{2.303} t \tag{4a}$$

The correlation coefficient obtained from the pseudo-first order model at pH 12 was not satisfactory and the calculated value of $q_{max,cal}$ was quite different from the value

of q_{max} observed in the experimental kinetic study, Figure 2a. These results suggest that adsorption of DPKSH on the anionic resin does not follow a pseudo-first order model.

The exchange kinetics may be described by a pseudo-second order equation.[13,18-21] The differential equation may be expressed by:

$$\frac{dq_t}{dt} = k_2 \ (q_{max,calc} - q_t)^2 \tag{5}$$

where k_2 is the rate constant of the pseudo-second order process and q_t and $q_{max,calc}$ are as indicated in equation 4.

Integrating equation 5 and applying boundary conditions gives:

$$\frac{t}{q_t} = \frac{1}{k_2 \ q^2_{max,calc}} + \frac{1}{q_{max,calc}} t \tag{5a}$$

The second-order constant (k_2) and the maximum amount of DPKSH retained $(q_{max,calc})$ may be calculated from the intercept and the slope of equation 5a between t/q_t and t. Figure 2b shows (t/q_t) *vs.* t and the values of k_2, $q_{max,calc}$ and r^2 which are $(6.07 \pm 1.22) \times 10^3$ min^{-1} g resin g^{-1} DPKSH, $(6.13 \pm 0.01) \times 10^{-4}$ g DPKSH g^{-1} resin and 0.9999, respectively. The $q_{max,calc}$ agrees with the q_{max} obtained from kinetic experimental data $(6.10 \times 10^{-4}$ g DPKSH g^{-1} resin) and the value of r^2 is excellent. Thus, the adsorption of DPKSH at pH 12 proceeds according to the pseudo-second order model.

Considering the fact that pseudo-first order equation 4a and pseudo-second order equation 5a models cannot identify a mechanism involving diffusion, the intraparticle diffusion model[14,20,21] was tested using the following equation:

$$q_t = k_p \ t^{1/2} + C \tag{6}$$

k_p is the rate constant for intraparticle diffusion and C is the intercept.

According to this model, if a straight line that passes through the origin is obtained from a plot of q_t *vs.* $t^{1/2}$, the mechanism of adsorption involves diffusion and the slope of the linear curve is the rate constant of intraparticle transport (k_p). Experimental data $(q_t, t^{1/2})$ at pH 12 were applied to equation 6 and a diffusion mechanism did not fit the results.

Adsorption isotherms

To describe the adsorption equilibria, three commonly used mathematical expressions were applied to the experimental data. These equations correspond to the Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherms models.[14,15,18,19]

The Langmuir model[22] was originally developed to represent chemisorption on well-defined localized adsorption sites with identical adsorption energies. The Langmuir model also assumes that adsorption is independent of the surface coverage and interaction between adsorbed molecules does not occur. Maximum adsorption is achieved when the surface of the adsorbent is covered with a monolayer of adsorbate. The linearized form of Langmuir isotherm is expressed as follows:

$$\frac{1}{m_{ads}} = \frac{1}{m_{ads}^{max} \, K_L \, C_{eq}} + \frac{1}{m_{ads}^{max}} \tag{7}$$

where m_{ads} represents the amount of DPKSH adsorbed *per* unit of resin (g g$^{-1}_{IRA\ 402}$), m_{ads}^{max} is the maximum amount of solute retained (g) *per* gram of IRA 402 (the adsorption capacity), C_{eq} is the equilibrium concentration of DPKSH in solution (g L^{-1}) and K_L is the Langmuir constant which is related to the equilibrium constant of adsorption.

Figure 3a shows the experimental data for $1/m_{ads}$ *vs.* $1/C_{eq}$ for IRA 402/DPKSH at pH 12. The curve was fitted using Origin 7.5 software by adjusting the experimental data to equation 7. The parameters K_L and m_{ads}^{max} are (95.5 ± 0.7) L g^{-1} and (8.58 ± 0.01) 10^{-4} g (DPKSH) g^{-1} (IRA 402) at pH 12, respectively. The solid lines shown in Figure 3a were calculated by using parameters obtained from experimental values and an excellent fit was observed.

The Freundlich adsorption isotherm[23] gives an empirical expression encompassing an exponential distribution of active sites. The model takes either a monolayer or multilayer adsorption that is indefinitely increased irrespective of the adsorbate concentration. This model also assumes that the adsorbent surface is energetically heterogeneous.
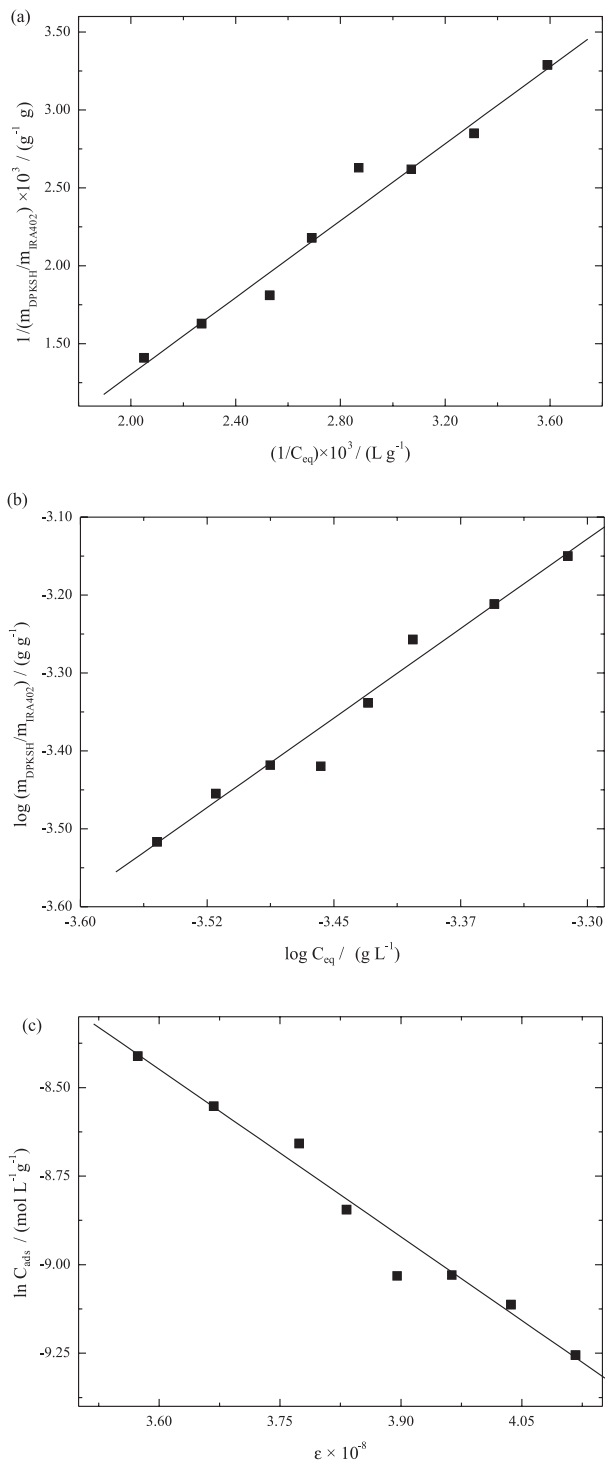
The linearized form of Freundlich isotherm is expressed as follows:

$$\log m_{ads} = \log K_F + \frac{1}{n} \log C_{eq} \tag{8}$$

where m_{ads} and C_{eq} are as indicated in the Langmuir isotherm, K_F is the empirical constant and $1/n$ is related to the energetic heterogeneity of adsorption sites.

The Freundlich constants $1/n$ and K_F were determined from the slope and intercept of plots of $\log m_{ads}$ *vs.* $\log C_{eq}$ at pH 12, which are shown in Figure 3b. Numerical values of the adsorption capacity, K_F and $1/n$, indicate the energy and intensity of adsorption and are (86 ± 9) g g^{-1} and (0.65 ± 0.02), respectively. A value of n between 1 and 10 indicates that adsorption is favored.[19]

To distinguish between physical and chemical adsorption, the experimental data were applied to the

Figure 3. Adsorption isotherms of DPKSH onto IRA 402 at pH 12 (T = 25 ± 1 °C). Solid lines correspond to fitting by the (a) Langmuir (b) Freundlich (c) Dubinin-Radushkevich models.

Dubinin-Radushkevich (D-R) isotherm model.[14,15,19] This model features energy heterogeneity over the entire surface. The linear form of the D-R isotherm is given by:

$$\ln C_{ads} = \log K_{DR} - B\varepsilon^2 \tag{9}$$

where C_{ads} is the amount of DPKSH adsorbed *per* unit mass of IRA 402 (mol $L^{-1}g^{-1}$), K_{DR} is the maximum amount of DPKSH adsorbed, B is a constant with dimensions of energy and ε indicates the Polanyi potential ($\varepsilon = RT \ln [1 + (1/C_{eq})]$), where R is the gas constant in kJ K^{-1} mol^{-1} and T is the temperature in K.

Figure 3c shows the linear regression of the equation $\ln C_{ads}$ *vs.* ε^2. The values of B and K_{DR} were obtained from the slope and intercept yielding $(-1.58 \pm 0.01) \times 10^{-8}$ J^2 mol^{-2} and $(6.29 \pm 0.01) \times 10^{-2}$ mol g^{-1} at pH 12.

According to Antonio *et al.*,[14] Freitas *et al.*[15] and Saeed *et al.*[24] if the surface is considered heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for sites that are energetically equivalent, then the quantity $B^{1/2}$ can be related to the average sorption energy (E) as:

$$E = \frac{1}{\sqrt{-2 B}} \qquad (10)$$

which is the mean free energy of the transfer of 1 mol of solute from infinity to the surface of IRA 402.

The numerical value of E, calculated from equation 10, is 5.62 kJ mol^{-1} at pH 12, indicating physical adsorption. [14, 15]

Flow injection procedure

Originally, some significant parameters in the method development that can also considerably influence sensitivity, such as preconcentration time, sample flow rate, pH, eluent volume, concentration and flow rate, reagent volume and concentration, and reaction coil size were optimized.

The loading time effect (preconcentration time) which influences the sample volume and analyte retention on the solid phase was evaluated ranging from 30 to 90 s (30, 45, 60, 75 and 90 s) with a 63.5 µg L^{-1} Cu(II) solution at pH 4.7 and with a flow rate of 4.0 mL min^{-1}. A linear development in the analytical signal (A) was observed due to the increase in the preconcentration time (t) to 60 s and can be described by the equation A = $(8.7 \pm 0.5) \times 10^{-2} + (3.0 \pm 0.1) \times 10^{-3} t$ (r = 0.996). Thus, under the experimental conditions, the solid phase was not saturated until a 60 s loading time was reached. Therefore, a 60 s loading time was chosen for subsequent experiments.

The analytical signal can also be influenced by the sample flow rate. At a constant loading time, the analytical signal tends to enlarge with an increase in flow rate, which is evidenced by an increase in the amount of analyte that interacts with the adsorbent. However, the kinetics of adsorption needs to be considered and the retention efficiency can diminish with low sample residence time in

the column. Excessively high flow rates can also cause fluid leakage from the connection points due to an increase of backpressure. The flow rate (q) between 1.8 and 10.8 mL min^{-1} was evaluated under experimental conditions similar to those previously described. The analytical signal varied linearly from 1.8 to 6.3 mL min^{-1} according to the equation: A = $(7.6 \pm 0.2) \times 10^{-2} + 0.133 \pm 0.007$ q, r = 0.999. Thus, showing that favorable kinetics is involved in metal retention until a flow rate of 6.3 mL min^{-1} is reached.

The effect of acidity on copper retention was investigated from pH 4.0 to 7.0 using appropriate buffer solutions. An increase in pH led to an increase in the analytical signal, as shown in Figure 4a. The increase in analytical signal was significant until pH 5.5 and was approximately 53% higher than observed at pH 4.0. A pH greater than 7.0 was not evaluated due to the fact that the metal hydrolysis was more favorable. Thus, a buffer solution with a pH of 5.5 was chosen for further experiments.
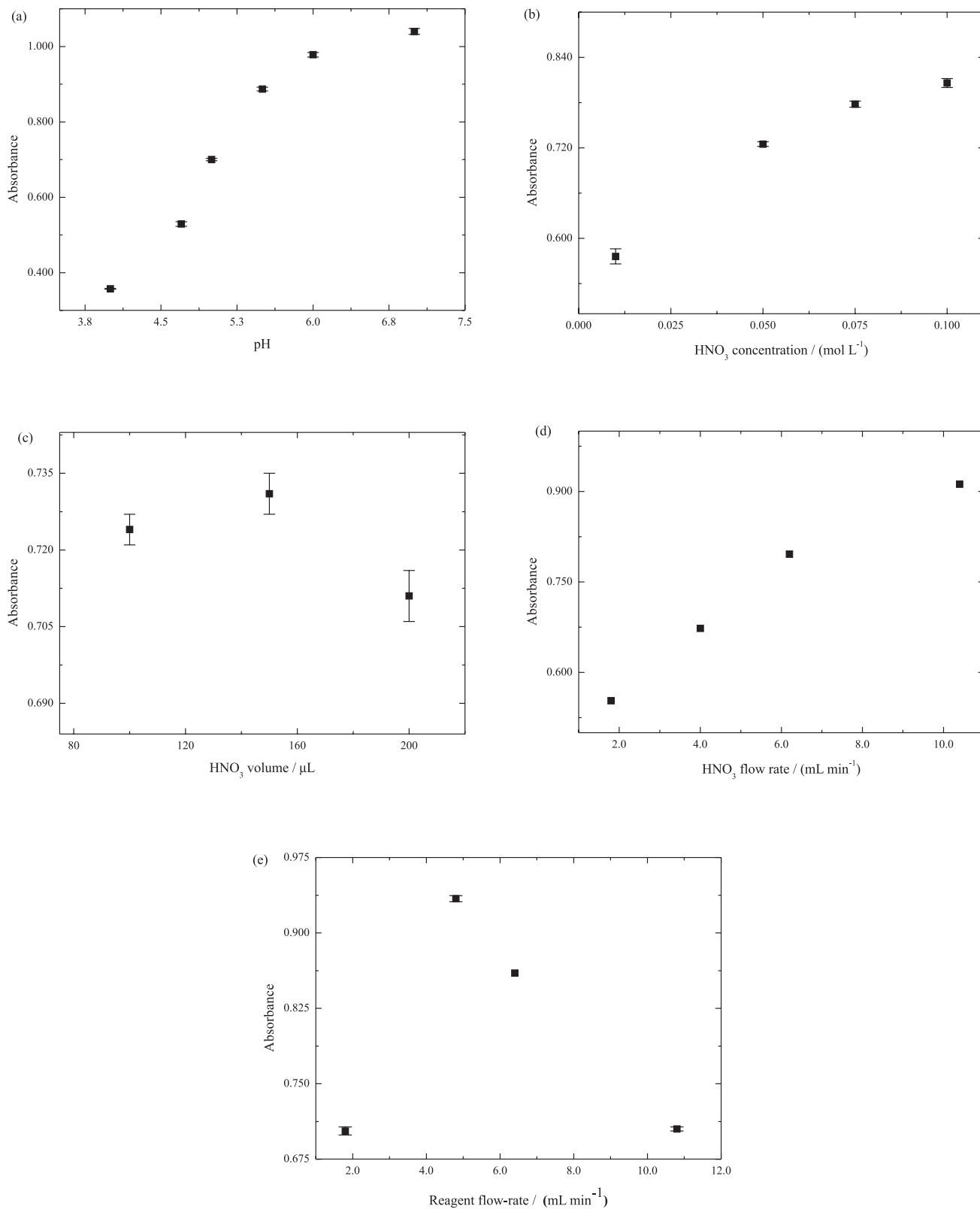
The efficiency of Cu^{2+} elution was evaluated using HNO_3 in varying concentrations, volumes and flow rates. As shown in Figure 4b, HNO_3 concentrations up to 0.10 mol L^{-1} were evaluated and the difference in the resulting analytical signals was not significant. The protonation of DPKSH is favorable in the presence of a high concentration of H^+ and this leads to competition between H^+ and metal ions for binding sites on the modified resin. However, higher eluent concentrations should be avoided to minimize desorption of complexant from the solid phase. Thus, 0.05 mol L^{-1} HNO_3 concentration was maintained in further experiments.

A slightly higher analytical signal was achieved with an increase in eluent volume from 100 to 150 µL. However, a decrease in the analytical signal (-2.8%) was observed with 200 µL of HNO_3 due to greater dilution of the analyte, as shown in Figure 4c. Therefore, an eluent volume of 100 µL was chosen for subsequent experiments.

The eluent flow rate was investigated between 1.8 and 10.4 mL min^{-1}. As shown in Figure 4d, the increase in the analytical signal was proportional to the eluent flow rate to 6.3 mL min^{-1}, demonstrating favorable desorption kinetics. Excessive flow rates may cause fluid leakage, which was observed at the sample flow rate. For further studies, an eluent flow rate of 6.3 mL min^{-1} was used.

The DPKSH concentration was varied at (1.5, 3.0 and 6.0) $\times 10^{-4}$ mol L^{-1} at pH 5.5. The differences between analytical signals were low (*ca.* 1.4%), therefore, a DPKSH concentration of 1.5×10^{-4} mol L^{-1} was selected.

As observed with high eluent volumes, a higher dispersion of the sample zone can cause a decrease in analytical signals. This effect was also observed with an increase in reagent flow rate, shown in Figure 4e. Above

Figure 4. Effect of the (a) pH of the buffer solution, (b, c and d) eluent concentration, volume and flow rate and (e) reagent flow rate on the analytical signal for a 60 s loading time and a sample flow rate of 6.3 mL min^{-1}.

4.8 mL min^{-1}, a significant decrease in analytical signal was observed. Thus, a reagent flow rate of 4.8 mL min^{-1} was chosen for further experiments.

The effect of the reaction coil (RC) length (10, 30 and 50 cm) was evaluated. A decrease in analytical signal was observed with an increase in the length of the reaction coil due to greater dispersion of the sample zone. Therefore, a reaction coil length of 10 cm was chosen.

Analytical features

Using the flow system shown in Figure 1, analytical curves were obtained by pumping aliquots of Cu(II) standard solutions of varying concentrations, with measurements made in triplicate. A linear response was observed from 0.31 to 1.26 µmol L^{-1}. This behavior can be described by the equation A = (2.6 ± 0.4) × 10^{-2} + (2.48 ± 0.04) × 10^5 C$_{Cu(II)}$, r = 0.997, where A is the absorbance measured as peak height and C is the Cu(II) concentration in mol L^{-1}.

The limits of detection and quantification were estimated at 0.5 and 1.8 µg L^{-1} of Cu(II) according to IUPAC recommendations at the 95% confidence level[25] with an enrichment factor of 11. The relative standard deviation was estimated as 2.6% for 20 independent measurements with a 32 µg L^{-1} Cu(II) solution. The sampling throughput for a 60 s loading time was 55 samples *per* hour. The resin modified by the addition of DPKSH was used for at least 288 sampling cycles without significant variation in the analytical response.

Effect of foreign ions

Under optimized conditions, experiments were conducted to evaluate the selectivity of the proposed procedure. The effect of cations and anions often found in different samples was evaluated and the results are presented in Table 1. The tolerance limit (7.8%) was taken as three times the standard deviation (± 0.004) of the average of analytical signal (0.153) for tenfold measurement for solutions with no interfering species.

Some cations and anions (Na$^+$, K$^+$, Co^{2+}, Cl$^-$, NO$_3^-$, F$^-$, CH$_3$COO$^-$ and SO$_4^{2-}$) yield only a slight interference when the concentration of interfering ion was 1000 fold greater than the concentration of Cu(II) (63.5 µg L^{-1}). However, Co^{2+} was an exception and caused a relevant interference at concentrations 1000 times greater than the concentration of Cu(II). HCO$_3^-$ and PO$_4^{3-}$ caused interferences when their concentrations were 100 times greater than Cu(II). Similar effects were observed for Mg^{2+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+} and Cr^{3+} when

Table 1. Tolerance limit of foreign ions on determination of 63.5 µg L^{-1} Cu(II), pH = 5.5, λ = 378 nm, 95 mg modified resin

Foreign ion	Tolerance Limit
Ascorbate	≥ 10.000
Na$^+$, K$^+$, Co^{2+}, Cl$^-$, F$^-$, NO$_3^-$, CH$_3$COO$^-$, SO$_4^{2-}$	≥ 1.000
HCO$_3^-$, PO$_4^{3-}$	≥ 100
Mg^{2+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+}	≥ 10
Al^{3+}	≥ 1

present in concentrations that were 10 times higher than Cu(II). Low Cu(II) retention in the presence of these ions may be attributed to competition for adsorption sites. Only Al^{3+} yields a serious interference when present in concentrations equivalent to Cu(II).

By comparing the absorption maximum wavelength and molar absorptivity of complexes Cu(II)/DPKSH 3.6×10^4 L mol^{-1} cm^{-1} at 378 nm, Ni(II)/DPKSH 4.9×10^4 L mol^{-1} cm^{-1} at 375 nm and Co(II)/DPKSH 4.3×10^4 L mol^{-1} cm^{-1} at 375 nm,[16] the positive interference caused by Ni^{2+} and Co^{2+}, at concentrations 10 times greater than the concentration of Cu^{2+}, may take place as a result of a competition between these ions for modified resin active sites resulting in an increased absorbance value from the elution of Cu(II) and Ni^{2+} or Cu(II) and Co(II). Zn(II)/DPKSH complex also shows a molar absorptivity value 5.3×10^4 L mol^{-1} cm^{-1} [16] greater than Cu(II)/DPKSH, however the absorption maximum wavelength of such complex corresponds to 360 nm.

The interference of metallic ions commonly present in ethanol fuel samples, such as Ni, Zn, Cd and Co,[26, 27] are

Table 2. Recovery of copper spiked and determination of copper in ethanol fuel samples by proposed procedure and F AAS[30]

Samples	Copper amount / (mg L^{-1})		
	Added	Found	Recovery / (%)
A	0.060	0.062 ± 0.002	103 ± 4
	0.080	0.077 ± 0.001	97 ± 1
	Proposed procedure	F AAS	
B	0.021 ± 0.004	0.024 ± 0.007	
C	0.0042 ± 0.0013	< 0.011*	
D	0.017 ± 0.008	0.016 ± 0.008	
E	0.018 ± 0.005	0.021 ± 0.003	
F	0.045 ± 0.003	0.047 ± 0.003	
G	0.037 ± 0.007	0.032 ± 0.005	
H	0.028 ± 0.009	0.028 ± 0.006	

*< limit of detection.

Table 3. Analytical features of some procedures for copper determination

Solid Phase	Sample frequency / (h^{-1})	Limit of detection / ($\mu g\ L^{-1}$)	Coefficient of variation / (%)	Enrichment factor	Sample volume / mL	Reference
Peat Sorb®	12	3.2	3.3	16	13.6	10
XAD-4 functionalized[a]	51	1.1	2.5	29	5	12
XAD-4 loaded[a]	51	1.0	1.9	29	5	12
PUF/Me-BDBD	-	3.4	3.2	7	-	31
XAD-4/PAR	-	2.8	1.1	7.4	2.5	32
IRA 402/DPKSH	55	0.5	2.8	11	6.3	proposed procedure

[a]β-nitroso-α-naphthol; PUF polyurethane foam; Me_BDBD 6-[2´-(6´-methyl-benzothilazolylazo)]-1,2-dihydroxy-3,5-benzenedisulfonic acid; PAR 4-(2-pyridylazo) resorcinol.

not relevant to the proposed procedure, since these species are typically found at levels similar or lower than Cu(II). However, Fe(III) is a concomitant commonly present at levels similar or higher than Cu(II) and must be masked. Based on the values of complexes formation constants Fe(III)/DPKSH (β_1 2.9×10^5)[28] and Fe(III)/F$^-$ (β_6 1.3×10^{16}),[29] Fe(III) ions present in the ethanol fuel samples were masked in these samples by adding F$^-$.

Application to ethanol fuel samples

The recovery of copper spiked into ethanol fuel samples was evaluated to verify the applicability of the proposed procedure (Table 2). Recoveries from 97 to 103% were estimated indicating that the procedure is free from matrix effects.

The results obtained from ethanol fuel samples by the proposed procedure were compared to those attained by F AAS,[30] Table 2, and are in agreement at the 99% confidence level.

Table 3 shows a comparison of analytical features of the proposed method and established methods for the determination of copper after solid-phase extraction.[10,12,31,32] Features such as the limit of detection and enrichment factor are comparable to those obtained by the proposed method. A relevant number of methods have been proposed for the determination of cations from ethanol fuel samples and most of then use atomization techniques - these procedures also need a preconcentration step.[33,34] Advantages of the proposed method include the determination of copper from ethanol fuel samples without the requirement of a pretreatment step, low consumption of sample and reagents and high limit of detection, as well as the UV-Vis spectrophotometric methods are seen as attractive possibilities for determining metallic ions due to their handling easiness and simplicity, low cost and easy access to instrumentation.[35]

Conclusions

IRA 402 resin was modified by the addition of DPKSH, and a kinetic and isotherm adsorption study was performed. The modified resin was used for at least 288 preconcentration/elution cycles to test endurance and reproducibility. The successful application of the proposed method for Cu(II) determination in ethanol fuel samples, without the need for pretreatment such as evaporation, shows the feasibility of IRA 402 resin modified by DPKSH as a solid phase in solid-liquid extraction.

Acknowledgments

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