SIMULTANEOUS DETERMINATION OF IRON AND COPPER BY THIRD-DERIVATIVE SOLID-PHASE SPECTROPHOTOMETRY

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ABSTRACT

A simultaneous microdetermination of iron and copper at sub-µg/L level by solid phase derivative spectrophotometry has been developed. The compounds TPTZ (2,4,6-tripyridyl-1,3,5-triazine) and Neocuproine (2,9-dimethyl-1,10-phenan-throline hydrochloride), were used as chromogenic reagents to form a blue iron complex and an orange copper complex, respectively (pH = 5.0), which are fixed and concentrated on a cation-exchange resin sephadex sp C-25. The influence of experimental variables on the retention of the complexes on the resin are discussed. The signals in derivative units were measured directly on the solid, packed in a 1 mm spectro-photometric cell. The characteristic amplitude of the signals at 622.0 and 477.0 nm in third-derivative spectra are useful

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for quantitative determination of iron (0.195–$120\,\mathrm{ng\,mL^{-1}}$; RSD $= 1.8\%$) and copper (0.451–$300\,\mathrm{ng\,mL^{-1}}$; RSD 1.3%). The method was applied to the iron and copper determination in different types of water, respectively.

INTRODUCTION

The use of a preconcentration previous to the instrumental measurement is an excellent alternative for the analyte determination at ultratrace levels without the required sophisticated instrumentation. This preconcentration step is mandatory in the treatment of the sample before the instrumental measurement, when the analytes to be determined are present in the sample at levels below to the determination limits of various methods such as in spectrophotometry (1,2), spectrofluorimetry (3,4), electroanalysis (5) and flow injection analysis (6).

The increasing importance of the determination of iron and copper in different fields, particularly in environmental samples, has made it necessary to develop simple, inexpensive and sensitive methods for the determination of traces of these analytes in different samples.

Traditionally, a number of spectrophotometric methods have been proposed for the single determination of copper or iron (7–9). When the sample contains two or more analytes, which are required to be determined simultaneously, the selected method must be more elaborate and sophisticated techniques are required (10–13).

In this work, a method for the simultaneous determination of iron and copper by third derivative spectrophotometry is proposed. In order to obtain a more selective method, a mixture of ligands Neo. (2,9-dimethyl-1,10-phenantroline) and TPTZ (2,4,6-tripyridyl-s-triazine) were used. On the other hand, the analytes were preconcentrated as binary complexes on a cationic resin sephadex sp C-25 increasing considerably the sensitivity. The signals were measured directly on the solid phase in a cell of $1\,\mathrm{mm}$ by derivative spectrophotometry. The digital spectrophotometry technique was selected in order to remove the noise improving considerably the information obtained. In this work the optimization of chemical, spectral and preconcentration variables are included. The method was validated with certified reference material, obtaining a good performance. It was also applied successfully in the determination of the analytes in drinking and river waters.

EXPERIMENTAL

Apparatus

A Shimadzu UV-PC 1603 spectrophotometer with 1 mm cells was used for measurements of the absorbance and derivative absorption spectra. An Orion Research Digital Ion-Analyzer 701 with glass and saturated calomel electrodes was used for pH determinations. A magnetic stirrer HI 190 M, Hanna instruments for the preconcentration step was used.

Reagents

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

Standard Iron (II) solution (titrisol Merck, $1000 \mu g \, mL^{-1}$).

Standard copper (II) solution (titrisol Merck, $1000 \mu g \, mL^{-1}$).

Standards of the cationic and anionic solutions for interferent evaluation (titrisol Merck, $1000 \mu g \, mL^{-1}$).

Solutions of $10 \mu g \, mL^{-1}$ of the analytes were prepared by diluting the standard solutions. Other ranges of concentration were prepared by appropriate dilution. All these solutions were stored in polyethylene containers.

2,4,6-tripyridyl-1,3,5-triazine, (TPTZ). An approximately 5.0×10^{-3} M solution was prepared by dissolving 0.15615 g of TPTZ (Aldrich Chemical Co.) in a few drops of concentrated hydrochloric acid and diluting to 500 mL with water.

2,9-dimethyl-1,10-phenanthroline hydrochloride, (Neo.). A 0.15 M solution was prepared by dissolving 18.3525 g of Neo. (Aldrich) in 500 mL of water.

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) solution. This solution was prepared by dissolving 10.0 g of the salt in 100 mL of water.

Sodium acetate–acetic acid buffer (pH = 5.0). This solution was prepared by dissolving 20.5 g of sodium acetate (Merck) in 100 mL of water and then 8.05 mL of concentrated acetic acid (Merck) was added and diluted to 1000 mL.

Resins, sephadex sp C-25 (sulfopropyl sephadex) cation exchanger, sigma, sephadex sp C-50 (sulfopropyl sephadex) cation exchanger, Sigma, Dowex 50WX2–100 (strongly acidic) cation exchanger. Sigma, chelating (iminodiacetic acid), mesh 50–100. Sigma, ionenaustauscher I, mesh 30–70, Sigma, ionenaustauscher V, mesh 30–70, Sigma, permutit QHPF, mesh 30–70. Sigma, permutit H-70, mesh 16–50. Sigma, permutit

zeo-dur, mesh 16–50, Sigma, permutit decalso, mesh 10–40, Sigma were used.

In the validation of the method a river sediment certified, high-purity standards were used. This sample had the following content in $\mu g \, mL^{-1} \pm$ 0.5% in HNO_3 5%: Fe, 1200.0; Al, 250.0; K, 150.0; Cu, 10.0; Ni, 0.50; V, 0.25; Ca, 300.0; Na, 50.0; Co, 0.10; Tl, 0.01; As, 0.60; Se, 0.50; Cr, 300.0; Pb, 7.0; Th, 0.02; Sr, 0.02; Ba, 0.50; Mg, 70.0; Cd, 0.10; Mn, 80.0; U, 0.01; Zn, 15.0.

Procedure

Place in a 600 mL beaker an aliquot of sample solution containing less than 2 µg of iron and 4 µg of copper, add 10 mL of acetic-acetate buffer (pH = 5.0), 2 mL of 10% $NH_2OH \cdot HCl$ solution, 5 mL of 5.0×10^{-3} M TPTZ solution, 5 mL of 0.15 M Neo. solution, and adjust the total volume to 200 mL. Stir the mixture for 2 min. Add 60.0 mg of sephadex sp C-25. Stir 12 min. Discard the solution and add de-ionized water to wash the resin. Discard the washed water and repeat twice again. Then pack the resin into a cell of 1 mm. Record the zero-order spectra over the range from 400 to 800 nm against a resin reagent blank prepared under the same experimental conditions. Record also the third derivative spectra over the same wavelength range and use a smoothing factor of 40 and a scaling factor of 10^5.

RESULTS AND DISCUSSION

TPTZ reacts with iron in presence of hydroxylamine hydrochloride solution (pH = 5.0) to give a blue cationic chelate. Similarly, copper under the same conditions reacts with Neo. to give an orange cationic complex. It is important to indicate that the $Fe(TPTZ)_2^{++}$ and $Cu(Neo.)_2^+$ are more stable than Fe(II)-Neo. and Cu(I)-TPTZ (Figure 1).

Considering that both complexes have a positive charge, these can be retained on a cation-exchange resin. It was observed that the retention is practically irreversible. Thus, the aromatic structure must be important for the retention of the complexes by interaction with the organic structure of the polymer. In order to obtain the best solid phase for the analytes, we studied the retention of Fe(II)-TPTZ and Cu(I)-Neo., at pH = 5.0 on each of the following solid supports: chelating; dowex 50WX2; sephadex sp C-25; sephadex sp C-50; permutit decalso; permutit QHPF; permutit ZEO-DUR and permutit H-70. Considering the sensitivity of the signal the cation-exchange sephadex sp C-25 was found to be the best for the retention of both the complexes.
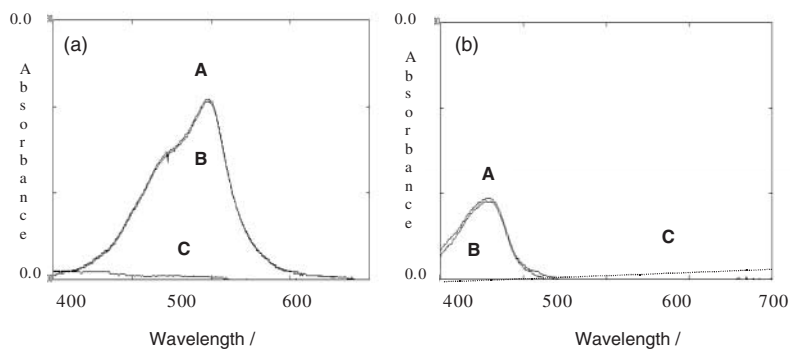
Figure 1. Absorption spectra in solution of Fe(II)-TPTZ and Cu(I)-Neo. complexes, in presence and absence of Neo. and TPTZ ligants, respectively, measured against reagents blank. (a) (A) Fe(II)-TPTZ; (B) Fe(II)-TPTZ en presence of Neo. (C) Fe(II)-Neo. Fe, $50\,\mathrm{ng\,mL}^{-1}$. (b) (A) Cu(I)-Neo. (B) Cu(I)-Neo. in presence of TPTZ and (C) Cu(I)-TPTZ; Cu, $100\,\mathrm{ng\,mL}^{-1}$.
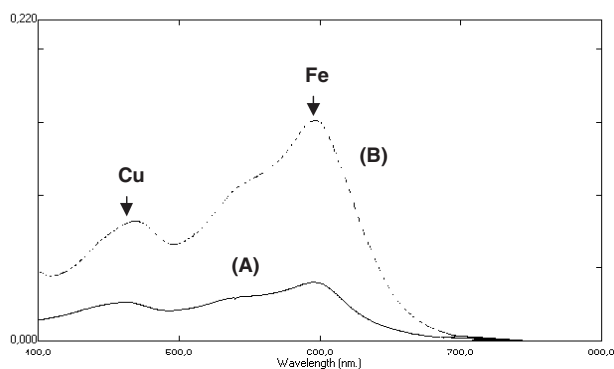

Figure 2. Absorption spectra of mixtures of Fe(II)-TPTZ and Cu(I)-TPTZ complexes in aqueous solution and on solid phase (sephadex sp C-25) measured against the corresponding reagent blank. (A) Complexes in aqueous solution (cell, 10 mm); Fe, $50\,\mathrm{ng\,mL}^{-1}$ and Cu, $100\,\mathrm{ng\,mL}^{-1}$. (B) Complexes retained on resin (cell, 1mm); Fe,$10\,\mathrm{ng\,mL}^{-1}$ and Cu, $20\,\mathrm{ng\,mL}^{-1}$.

The Fe(II)-TPTZ and Cu(I) Neo. complexes fixed on a sephadex sp C-25 cationic-exchange resin, showed an absorption maximum at 600 nm and at 457 nm, respectively. The spectra of the complexes in solution and on the solid phase are shown in Figure 2.

As can be seen, in both cases a strong increase in sensitivity in the solid phase compared with of the solution were found.

Taking into account that the spectral bands are overlapped and that the purpose of this work is to develop a simple, precise and accurate method for simultaneous determination of both analytes the derivative spectrophotometry technique was adopted, because permits, resolution and determination of binary mixture of constituents (14,15).

On the other hand, the spectral signals were evaluated directly in the solid phase, where the dispersion phenomena of the radiant energy become more evident, which can be minimized by the use of a small path of light. In this same context, the digital derivative spectrophotometry was also used in order to control the influence of the dispersion phenomena which increases the noise of the baseline. The digital derivative spectrophotometry used, was proposed by the Savitzky-Galay (16), which uses the least squares procedure for to smooth and to differentiate the spectra numerical data. Under this condition the higher signal/noise ratio were found.

Selection of Spectral Variables

Derivative Order

Derivative spectra of different orders were obtained from stored zero-order spectra using digital differentiation with the program, of the software Shimadzu kit version 3.7 (P/N 206-60570-04), as can be seen in Figure 3.

As can be seen in Figure 3a–d, the second, third and fourth derivatives are more resolved, but these also showed more noise than the first derivative. By using the first derivative, the copper determination is not feasible because the iron spectrum does not present a zero crossing point to carry out this determination. When the second derivative is used, it is possible by simultaneous determination, but taking account the shape of these spectra, it is possible to wait better analytical results when the third derivative is used, because the copper and iron spectra present much better defined zones for determination of each analyte. A wavelength of 622.0 and 477.0 nm for iron and copper determination was used, respectively.

Selection of the Smoothing Factor

Using the third derivative, the smoothing factor was varied and the following values were used: 5, 10, 20 and 40. These values are defined by
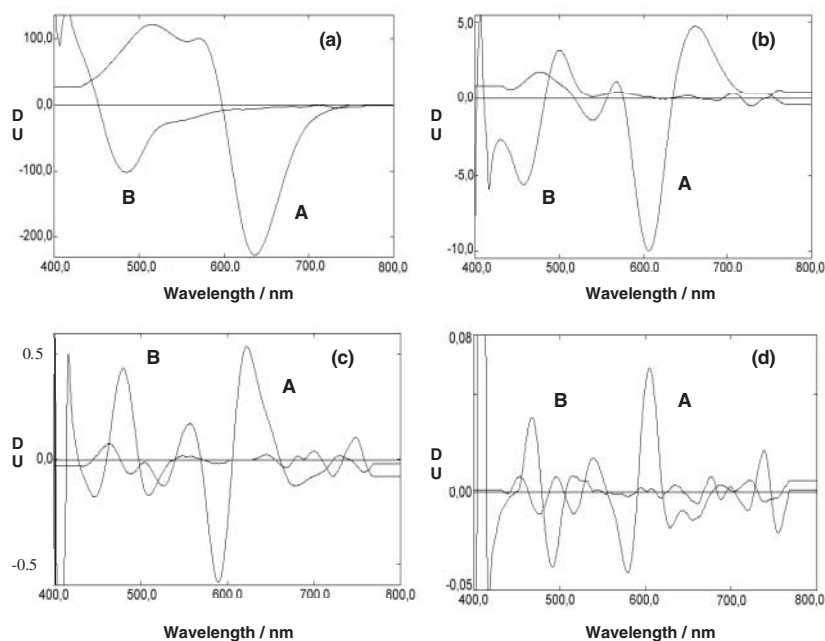
Figure 3. Derivative spectra of Fe(II)-TPTZ and Cu(I)-Neo. complexes retained on sephadex sp C-25 measured against resin of reagent blank. (A) Fe(II)-TPTZ, (B) Cu(I)-Neo.; (a) First derivative spectra; (b) Second derivative spectra (c) Third derivative spectra and (d) Fourth derivative spectra. DU: Derivative unit. Fe, $10 \, ng \, mL^{-1}$ and Cu, $20 \, ng \, mL^{-1}$.

default, which are in relation with the range of wavelength in which the spectra were scanned.

The $\Delta\lambda$ value of differentiation is constant and correspond to 400 nm, when the smoothing factor is increased the heights of the derivative signal decrease but the noise decrease faster, increasing in this way the signal/noise ratio. A value of 40, was selected.

Selection of the Scale Factor

This factor must be studied in order to observe if the system present a distortion effect. Further, the selection of this parameter permits to improve the reading of the analytical signal. Considering this fact, a factor scale of 10^5 was selected.

Optimization of Preconcentration Variables

Variables were optimized by the univariate method, for each analyte separately. This study was carried out at room temperature, because this process was independent of temperature in the range of 15–40°C.

The effect of the mass of the resin on the analytical signal was optimised, in which the general procedure was followed, but the mass of the resin was varied (Figure 4).

As can be seen in the Figure 4, the signal decrease exponentially with the increment of the mass of the resin. For the selection of this variable was also considered mandatory to have enough mass of resin to pack a cell of 1 mm. In this context, a mass of 60 ± 0.01 mg of sephadex sp C-25 was selected. This variable must be strongly controlled because the signal is very dependent of the resin mass.

The effect of the stirring time on the retention for both complexes was also studied in the range from 1 to 20 min. When a final sample volume between 100 and 400 mL was used, the stirring time for maximum retention for the copper and iron complexes were 8 and 10 min, respectively (Figure 5).

On the other hand, the effect of the total volume of sample on the retention for both complexes was also studied, keeping the amount of analyte constant, in the range from 100 to 2000 mL. When a final volume
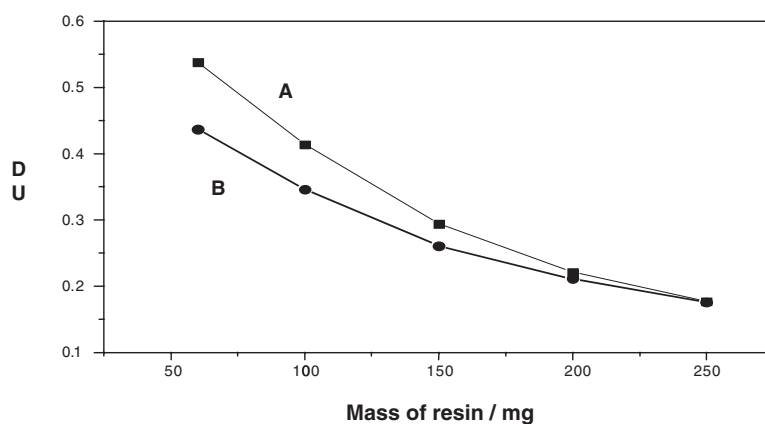

Figure 4. Effect of the mass of resin on derivative units (DU) evaluated by third derivative for Fe(II)-TPTZ and Cu(I)-Neo. complexes retained on resin measured against resin of reagent blank. (A) Fe(II)-TPTZ (B) Cu(I)-Neo.; Fe, $10 \, \text{ng} \, \text{mL}^{-1}$ and Cu, $20 \, \text{ng} \, \text{mL}$.
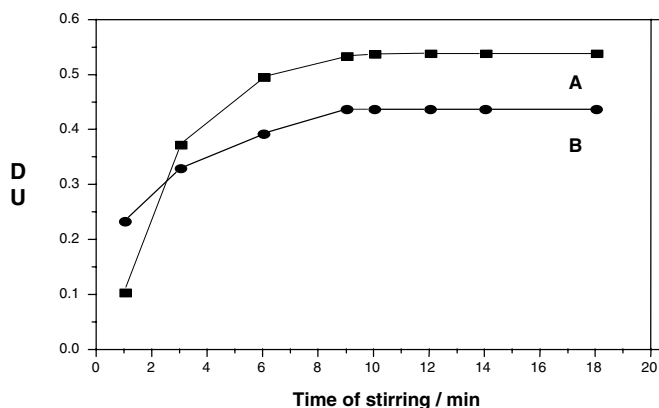
Figure 5. Effect of the stirring time on derivative units (DU) evaluated by third derivative for Fe(II)-TPTZ and Cu(I)-Neo. complexes retained on sephadex sp C-25 measured against resin of reagent blank. (A) Fe(II)-TPTZ (B) Cu(I)-Neo.; Fe, $10\,ng\,mL^{-1}$ and Cu, $20\,ng\,mL^{-1}$.

between 100 and 400 mL was used for the quantitative retention of both complexes, a stirring time of 12 min was found optimum. In the range from 500 to 2000 mL, it was necessary to use a stirring time of 24 min for to obtain a quantitative retention.

Optimization of Chemical Variables

The effect of pH was studied in a range between 1.0 to 12.0. In this study a buffer HAc/NaAc was used, but sodium hydroxide and hydrochloric acid was added for adjustment. The result are shown in Figure 6.

For iron complex at pH values below 3.0 or above 7.0, the derivative units decreases significantly, and for the copper complex the maximum derivative unit was found between 4.0 and 7.0 and the signal also decreases in higher and lower pH values. In this context a pH value of 5.0 was selected.

A study of TPTZ and Neocuproine concentration shows that the analytical signal and the baseline increase when the TPTZ and Neocuproine concentration are increased. Using 200 mL as total sample volume, the signals were maximal and constant from 5 mL of 1.0×10^{-3} M TPTZ and from 5 mL of 0.10 M Neo., for iron and copper, respectively. In order to have an excess of reagent, 5 mL of 5.0×10^{-3} M TPTZ and 5 mL of 0.15 M Neocuproine were used.
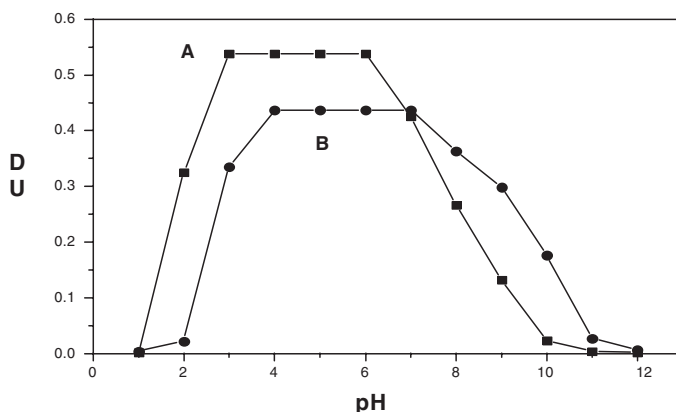
Figure 6. Effect of the pH on derivative units (DU) evaluated by third derivative for the Fe(II)-TPTZ and Cu(I)-Neo. complexes retain on sephadex sp C-25 measured against resin of reagent blank. (A) Fe(II)-TPTZ (B) Cu(I)-Neo.; Fe, $10\,\mathrm{ng\,mL^{-1}}$ and Cu, $20\,\mathrm{ng\,mL^{-1}}$.

As the buffer contains sodium ion, an excess of this cation could change the spectral signals. For this reason a study of the buffer concentration ($10\,\mathrm{mL}$) on the analytical signal was carried out. The analytical signals for both analytes were constant between 0.1 and $0.4\,\mathrm{M}$, from this value the analytical signals decrease when the buffer concentration is increased. A $0.25\,\mathrm{M}$ of buffer was selected.

Analytical Features

The determination of the analytical features, for the simultaneous determination of iron and copper by third order derivative spectrophotometry at 622.0 and $477.0\,\mathrm{nm}$, respectively, was carried out using a smoothing factor of 40 an amplification factor of 10^5 and a total sample volume of $200\,\mathrm{mL}$. The equations for the simultaneous determination of copper and iron obtained by the method of the least squares are the following:

$$H_1 = 0.0222 \cdot C \ (\mathrm{ng\,mL^{-1}}) - 0.0958 \quad r = 0.999, \ \lambda = 477.0\,\mathrm{nm} \ (\text{copper})$$

$$H_2 = 0.0514 \cdot C \ (\mathrm{ng\,mL^{-1}}) - 0.0434 \quad r = 0.999, \ \lambda = 622.0\,\mathrm{nm} \ (\text{iron})$$

$H = $ Arbitrary derivatives units, given by the software and C corresponding to concentration expressed as $\mathrm{ng\,mL^{-1}}$.

For a total volume of 200 mL the ranges in which this simultaneous determination could be made were found to be 0.195–120 ng mL^{-1} for iron and 0.451–300 ng mL^{-1} for copper.

The detection limits (calculated by using the 3σ criterion) were found to be 0.044 ng mL^{-1} for iron and 0.140 ng mL^{-1} for copper. The repeatability of the method expressed as relative standard deviations for ten standard samples containing 74 ng mL^{-1} of copper and 24 ng mL^{-1} were 1.3 and 1.8%, respectively. The detection and quantification limits can be improved if the total volume of the sample is increased, this fact is the main advantage of the solid-phase spectrophotometry.

Interference Studies

A systematic study of the effect of common foreign ions on the simultaneous determination of 10 ng mL^{-1} iron and 20 ng mL^{-1} copper was studied to define the tolerance limit (amount of species that produced an error not exceeding ± 5% in the determination of these analytes). The tolerance values obtained are shown in Table 1. The interference of alkaline and earth alkaline cations can be explained because these species also interact with the active charged sites of the resin. But, it is very important to indicate that the spectral bands of the complexes are not altered. In this context, when the matrix has a high saline content, the standard addition method is mandatory.

Application of the Method

The validation of this method was carried out by using a sample of certified river sediment. To 1 mL of the certified sample, 1.8 mL of copper of 1000 mg L^{-1} was added in order to enrich the copper content and then this solution was diluted to 100 mL. An aliquot of 0.4 mL of this solution was diluted with de-ionized water to 200 mL (iron concentration = 24 ng mL^{-1}, copper = 72 ng mL^{-1}).

In this case the standard addition method was used in order to avoid matrix effects. The recovery percentages for iron and copper were of 98.67 and 101.79%, respectively. In all cases the relative standard deviation was <3.0%.

The method was applied in natural water and drinking water and in all instances the standard addition method was used in order to avoid matrix effects. In drinking water, obtained from our laboratory in April, 2000, a concentration of 17.5 ng mL^{-1} of iron and 7.8 ng mL^{-1} of copper were

Table 1. Effect of Interferents. Tolerance Limit for Cations and Anions

Cations	Iron ($ng\,mL^{-1}$)	Copper ($ng\,mL^{-1}$)
K(I)	11 000	11 000
Na(I)	11 000	11 000
Mg(II)	7000	6000
Ca(II)	11 000	9000
Ni(II)	3000	4000
Al(III)	4000	3000
Cr(III)	7000	6000
Cd(II)	3000	4000
Mn(II)	4000	3000
Sr(II)	8000	5000
Anions	Iron ($ng\,mL^{-1}$)	Copper ($ng\,mL^{-1}$)
Cl^-	*	*
F^-	*	*
SO_4^{-2}	*	*
NO_2^-	*	*
PO_4^{-3}	*	*
Oxalate	8000	7000
Citrate	6000	6000

*No interference.
**Maximum tested $10\,000\,ng\,mL^{-1}$.

obtained. The results for river water collected in San Fernando, VI Región Chile were; $60\,ng\,mL^{-1}$ of iron and $37.8\,ng\,mL^{-1}$ of copper.

CONCLUSIONS

A new application of solid-phase extraction as a system to collect colored complexes from a solution and the direct measure in the solid phase by third derivative spectrophotometry was developed. In this method the use of two specific reagents were considered in order to increase the selectivity. The proposed method shows the possibility of the simultaneous determination of ultratrace levels without the use of sophisticated instrumentation. In the proposed method the preconcentration on the solid phase increases the sensitivity by the formation and preconcentration of complexes on solid phase previous to the instrumental measurement. In this context, the proposed method is more sensitive than others where the

simultaneous determination of both analytes is carried out directly in aqueous solution or by liquid–liquid extraction. The method is fast and simple because the equilibrium involves the formation and retention of the complexes are rapid and kinetic phenomena are not present. The proposed method was successfully applied in different types of water and it is possible to apply the method to other matrices.

ACKNOWLEDGEMENTS

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