Supplementary Information

Solid Phase Extraction Using $SiO_2/Al_2O_3/TiO_2$ Ternary Oxide for Cu^{2+} Preconcentration

Evelyn F. Pinheiro,[a] José Guilherme A. Rodrigues,[a,b] Gláucio G. Honório,[a] Jéssica N. da Cunha,[a] Carlos Eduardo R. de Paula,[a] Débora F. de Andrade,[a] Emerson S. Ribeiro [iD] *,[a,b] and Eliane D'Elia[a]*

[a]*Instituto de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, 21941-909 Rio de Janeiro-RJ, Brazil*

[b]*Instituto Nacional de Tecnologias Alternativas para Detecção, Avaliação Toxicológica e Remoção de Micropoluentes e Radioativos (INCT-DATREM), Instituto de Química, Universidade Estadual Paulista (Unesp), CP 355, 14800-900 Araraquara-SP, Brazil*
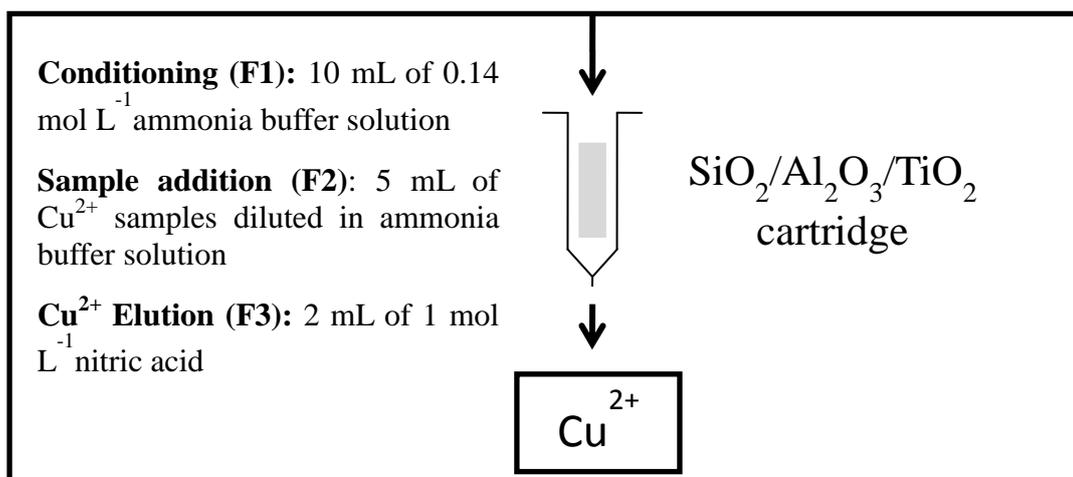
Conditioning (F1): 10 mL of 0.14 mol L^{-1} ammonia buffer solution

Sample addition (F2): 5 mL of Cu^{2+} samples diluted in ammonia buffer solution

Cu^{2+} Elution (F3): 2 mL of 1 mol L^{-1} nitric acid

$SiO_2/Al_2O_3/TiO_2$ cartridge

Cu^{2+}

Figure S1. Schematic representation of the solid phase extraction procedure.

_____

*e-mail: emersonsr@iq.ufrj.br

Table S1. Parameters used for the determination of copper ions by SW-ASV

Parameter	Value used
Support electrolyte	0.1 mol L^{-1} HCl
pH	1
f / Hz	50
Δ_{ep} / mV	5.0
A / mV	50
υ (calculated value) / (mV s^{-1})	250
E_{dep} / V	−0.6
T_{dep} / s	300
T_{eq} / s	10
Potential range / V	−0.25 a + 0.045

f: frequency; Δ_{ep}: potential increment; A: amplitude; υ: sweep rate; E_{dep}: deposition potential; T_{dep}: deposition time; T_{eq}: equilibrium time.

Table S2. Temperature program used for the determination of copper by GFAAS

Stage	Temperature / °C	Ramp / s	Landing / s	Air flow / (mL min^{-1})
Drying	110	1	30	250
	130	15	30	250
Pyrolysis	1200	10	20	250
Atomization	2000	0	5	0
Cleaning	2450	1	3	250

Partial validation of the proposed method

Linearity

The linearity study was performed by triplicate injections of samples with concentrations throughout the analytical curve: 29.7, 39.5, 49.2, 58.8 and 68.4 µg L^{-1}. The coefficient of determination (R^2) of the straight line was employed to verify the linearity of the method; values above 0.99 were generally acceptable.[1]

The Cochran test was used to evaluate the homogeneity of variances and thus confirm the linearity of a given group of samples. This test was calculated according to equation 1.

$$C = \frac{s_{max}^2}{\sum_{i=1}^{k} s_i^2} \qquad (1)$$

where s_{max}^2 is the largest variance and $\sum_{i=1}^{k} s_i^2$ is the sum of all sample variances.

Limit of detection and limit of quantification

The limit of detection (LOD) was calculated using the standard deviation and slope of the analytical curve, through equation 2.

$$LD = \frac{3\,s}{b} \tag{2}$$

where: s is standard deviation of the intercept, and b is the slope of the analytical curve. The limit of quantification (LOQ) was determined by multiplying the value of the LOD by 3.3.[2]

Precision (repeatability and intermediate precision)

Precision was evaluated in terms of repeatability and intermediate precision. Repeatability, which expresses the precision over the same operating conditions, i.e., the same equipment, day, operator and method, can be evaluated by estimating the relative standard deviation (RSD), also referred to as the coefficient of variation (CV), represented by equation 3.[3]

$$RSD\% = \frac{\sigma}{\overline{C}} \times 100 \tag{3}$$

where σ is the standard deviation and $\overline{C}$ is the average concentration.

To evaluate intermediate precision, a comparative study was performed in triplicate between two analytical curves generated by the same operator on different days, with concentrations ranging from 29.7 to 68.4 µg L^{-1}. The comparative study evaluated the variances through the hypothesis test, as well as implications through Student's *t*-test.

References

1. Lopes, P. A.; *Publicação Interna do Curso de Validação de Método*, 1ª ed.; Rede de Tecnologia: Rio de Janeiro, Brasil, 2008.

2. Brett, C. M. A.; Brett, A. M. O.; *Electroanalysis*, 1st ed.; Oxford Chemistry Primers: Oxford, USA, 1998.

3. Ribani, M.; *Quim. Nova* **2004**, *27*, 771.