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Application of factorial design in optimization of preconcentration procedure for copper determination in soft drink by flame atomic absorption spectrometry

Martha T.P.O. Castro[a,*], Nivaldo Baccan[b]

[a] *Instituto de Química, Universidade Federal da Bahia, Campus de Ondina, CEP 40.170-290, Brazil*
[b] *Instituto de Química, Universidade Estadual de Campinas, Brazil*

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Abstract

In the present paper, a procedure for preconcentration and determination of copper in soft drink using flame atomic absorption spectrometry (FAAS) is proposed, which is based on solid-phase extraction of copper(II) ions as its ion pair of 1,10-phenanthroline complexes with the anionic surfactant sodium dodecil sulphate (SDS), by Amberlite XAD-2 resin. The optimization process was carried out using 2^{4-1} factorial and 2^2 factorial with a center point designs. Four variables (XAD-2 mass, copper mass, sample flow rate and elution flow rate) were regarded as factors in the optimization. Student's *t*-test on the results of the 2^{4-1} factorial design with eight runs for copper extraction, demonstrated that the factors XAD-2 mass and sample flow rate in the levels studied are statistically significant. The 2^2 factorial with a center point design was applied in order to determine the optimum conditions for extraction. The procedure proposed allowed the determination of copper with detection limits ($3\alpha/S$) of 3.9 $\mu g\,l^{-1}$. The precision, calculated as relative standard deviation (R.S.D.) was 1.8% for 20.0 $\mu g\,l^{-1}$ of copper. The preconcentration factor was 100. The robustness of this procedure is demonstrated by the recovery achieved for determination of copper in the presence of several cations. This procedure was applied to the determination of copper in soft drink samples collected in Campinas, SP, Brazil.

Keywords: Copper; Factorial design; Flame atomic absorption spectrometry (FAAS); Soft drink

1. Introduction

Procedures for optimization of factors by multivariate techniques [1–5] have been encouraged, as they are faster, more economical and effective, and allow more than one variable to be optimized simultaneously. This optimization can be accomplished using experimental designs appropriate for determining first and second order models. The experimental designs not only determine the influence of the variables to be optimized for the response, but also enable the response function to be obtained and optimized.

In chemistry, the factorial design [6–15] has been widely used in several situations, such as: optimization of experimental variables in cyclic voltammetry of methylene blue [6]; optimization process for organic synthesis [7]; development of an chemiluminescent flow system for bromate determination [8]; methodology for reverse phase HPLC [9]; investigation of vibrational frequencies of methyl fluoride [10]; improving the Ti/TiO_2 electrodes performance [11]; optimization of an on-line preconcentration system for platinum determination [12]; determination of cadmium in urine specimens by graphite furnace atomic absorption spectrometry [13]; determination of phosphate in natural water employing a monosegmented flow system [14]; automatic on line preconcentration and determination of lead in water by ICP OES [15].

* Corresponding author. Tel.: +55 71 3497 0529; fax: +55 71 235 5166.
E-mail address: pantoja@ufba.br (M.T.P.O. Castro).

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Copper is an essential trace element for humans, stimulating the fundamental metabolic protein synthesis. Copper deficiency causes anemia, loss of weight and bone and cartilage with irregular physiological development. Abnormal ingestion causes neurological anomalies, hepatic and renal disturbances [16,17]. This metal is frequently determined in foods. However, their determination by FAAS is difficult because of its relatively low sensitivity and the high organic concentration [18]. According to the Brazilian legislation, copper concentration in water distributed for public provisioning is established in 20 $\mu g\,l^{-1}$ [19].

The reagent 1,10-phenanthroline (phen) forms complexes with several metal ions, including copper(II). 1,10-Phenanthroline have been used for different analytical determinations, such as: solid-phase extraction using silica gel [20,21] or tetraphenylborate-microcrystalline naphthalene adsorbent [22] and liquid–liquid extraction using several solvents [23,24];

In this work, a procedure for the preconcentration and determination of copper in soft drink using FAAS is proposed. Factorial designs were used for optimization of the experimental variables. It is based on the solid-phase extraction of copper ions as its ion pairs of 1,10-phenanthroline complexes with the anionic surfactant sodium dodecyl sulphate on Amberlite XAD-2 resin (polystyrene–divinylbenzene polymer).

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 5100PC flame atomic absorption spectrophotometer was used for copper determination. The absorption measurements were made under conditions described in Table 1. The calibration curves (0–4.0 $\mu g\,ml^{-1}$) for copper were established with solutions prepared from a 1000 $\mu g\,ml^{-1}$ stock solution. A Procyon pH meter (PHD-10 model) was used to pH values measurements.

2.2. Reagents

All the reagents were of analytical reagent grade. Deionized-distilled water (DDW) was used throughout the experimental work. Laboratory glassware was kept overnight in 10% (v/v) nitric acid solution, and washed with deionized water before use.

Table 1
Operating parameters for flame atomic absorption spectrophotometer

Wavelength (mm)	324.8
Lamp current (mA)	15
Slit width (nm)	0.7
Acetylene flow rate ($l\,min^{-1}$)	2.0
Air flow rate ($l\,min^{-1}$)	10.0
Sample flow rate ($ml\,min^{-1}$)	10.0

The copper stock solution (1000 $\mu g\,ml^{-1}$) was prepared by dissolving the metal (Baker 99.96%) in 5 ml of concentrated nitric acid and diluting with DDW to 1000 ml.

Phen solution ($1.7 \times 10^{-2}\,mol\,l^{-1}$) was prepared by dissolving 0.1680 g of 1,10-phenanthroline (Merck) in ethanol (1 ml) and diluting with DDW to 50 ml.

SDS solution ($1.7 \times 10^{-2}\,mol\,l^{-1}$) was prepared by dissolving 0.4900 g of sodium dodecylsulphate (Merck) in 100 ml of DDW.

Acetate buffer solution (pH 5.0) was prepared by mixing 52.5 g of anhydrous sodium acetate and 21.2 ml of concentrated acetic acid and diluted to 1 l of DDW.

Amberlite XAD-2 (Aldrich) was treated with hydrochloric acid 2.8 $mol\,l^{-1}$ for 60 min. Afterwards the resin was washed with deionized water until neutral pH, and then was washed with methanol, DDW and ethanol. Finally, it was dried in an oven at 85 °C for 35 min. The packing of the column was done using a conditioning solution prepared with 2 ml of the buffer solution in 50 ml of DDW.

2.3. Samples

Reference material supplied by Instituto de Pesquisas Tecnológicas do Estado de São Paulo, Brazil (steel IPT-97) was analysed. Composition: C = 0.165%; Si = 0.231%; Mn = 1.11%; P = 0.015%; S = 0.026%; Cu = 0.129%; Ni = 0.227%; Cr = 1.22%; Mo = 0.064%; Al = 0.028%; Co = 0.012%; V = 0.024%; Nb = 0.023%; N = 0.0119%; Ti = 0.002%; B = 0.0022%. The procedure for chemical decomposition is described as follows: 0.1071 g of the sample was treated in a 50 ml beaker with 20 ml of 37% hydrochloric acid/65% nitric acid [3:1, v/v]. After heating to dryness the residue was then treated with 25 ml of 7 $mol\,l^{-1}$ hydrochloric acid. The obtained solution was extract with 25 ml methyl–isobutyl ketone for iron separation [25,26]. The aqueous phase was heated once again, until dry. The residue was taken with 1 ml of concentrated HNO_3 and the volume was completed to 1 l. This solution was used in the preconcentration step, in order to simulate a synthetic water sample with common metals found in soft drinks at $\mu g\,l^{-1}$ levels, since reference materials for soft drinks are not commercially available.

Soft drink samples were collected in Campinas, SP, Brazil and were mechanically stirred for 6 h to degas. The samples were analyzed directly and after addition of copper to perform a recovery test.

2.4. General procedure

It was transferred 1 ml of sample solution contained copper ions (10 $\mu g\,ml^{-1}$) into a 150 ml becker and 2 ml of buffer solution pH 5.0 was added, followed by 1 ml of 1,10-phenanthroline solution ($1.7 \times 10^{-2}\,mol\,l^{-1}$), 1 ml of SDS solution ($1.7 \times 10^{-2}\,mol\,l^{-1}$). Final concentration of copper in solution is of 1 $\mu g\,ml^{-1}$. This solution was passed through