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Analytical Methods

Analytical strategies for determination of cadmium in Brazilian vinegar samples using ET AAS

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ABSTRACT

This paper proposes two methods for determination of cadmium in vinegar employing electrothermal atomic absorption spectrometry. The optimization step was performed using two-level full factorial and Box–Behnken designs, being that a new multiple response function was established. Under experimental conditions of pyrolysis temperature of 640 °C and atomization temperature of 2000 °C, the direct method allows the analysis using the external calibration technique, with limit of quantification of 14 ng L^{-1} and characteristic mass of 1.2 pg, having aluminium as chemical modifier. This method was applied in six samples of vinegar acquired from Salvador City, Brazil. The cadmium content varied from 20 to 890 ng L^{-1}. Other method was also proposed by digestion using nitric acid and hydrogen peroxide in reflux system employing cold finger, being cadmium determined by ETAAS. The results obtained with the complete digestion procedure were in agreement with those found by the direct method proposed herein.

1. Introduction

Vinegar is a condiment used in food preparation throughout the world. Generally, vinegar is produced by the fermentation of raw plant materials such as grapes, apples and sugarcane, among others. Vinegar is primarily composed of acetic acid and ethyl alcohol. The mineral content is derived from the plant material used and from contamination during the production process and storage. Given the importance of vinegar in human food, several methods for the determination of the levels of toxic chemical elements in this condiment have been proposed. A paper evaluated different sample preparation procedures for the determination of lead concentrations in vinegar using ICP-MS and GFAAS (Ndung'u, Hibdon, & Flegal, 2004). Another study determined and evaluated possible sources of lead in vinegar (Ndung'u, Hibdon, & Flegal, 2007). A method using stripping chronopotentiometry was proposed for determination of lead, cadmium, copper and zinc in commercial Iranian vinegars (Saei-Dehkordi, Fallah, & Ghafari, 2012). A direct method for the determination of lead in vinegar by ETAAS was established employing bismuth as internal standard, and the chemical modification was performed with ruthenium as the permanent modifier and co-injection of palladium–magnesium (de Oliveira & Gomes Neto, 2007). Another work of the same research group used tungsten as permanent chemical modifier and co-injection of palladium–magnesium also for direct determination of lead in vinegar (Oliveira, Oliveira, & Gomes Neto, 2007). In a method proposed for the determination of cadmium and lead in vinegar leached from pewter cups by ET AAS the chemical modification was performed using palladium–magnesium (Dessuy et al., 2011).

The Box–Behnken design is a chemometric tool often used for the optimization of analytical methods (Garcia-Rodrigues, Cela-Torrijos, Lorenzo-Ferreira, & Carro-Diaz, 2012; Khajeh, 2011; Kishore & Kayastha, 2012; Singh et al., 2014; Zarena, Sachindra, & Udaya Sankar, 2012). This tool enables quadratic models showing the critical condition (maximum, minimum or saddle point) to be obtained (Ferreira et al., 2007). The optimization of analytical methods involving two or more chemometric responses requires use of multiple responses. These multiple responses are established by considering the objective of the analytical system that is being optimized. The most common method employed to obtain multiple responses makes use of a desirability function *D*, where individual response surfaces are determined for each response (Derringer & Suich, 1980). An on-line sequential preconcentration system using chemically modified silica was developed for determination of Cr(III) and Cr(VI) by flame atomic absorption

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spectrometry. The optimization was performed using a multivariate methodology and a desirability function was established (Tarley et al., 2012).

In this study, two methods for determination of cadmium in vinegar using ETAAS were proposed. Also a new strategy was established to qualitatively and quantitatively evaluate the peak profiles obtained during the optimization step.

2. Experimental

2.1. Instrumental parameters of the ET AAS

The experiments were performed using a ZEEnit 600 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with a graphite atomizer with transverse heating and Zeeman effect background correction. A MPE 60 automatic liquid autosampler (Analytik Jena AG, Jena, Germany) was used to introduce the samples. In all analyzes, pyrolytic graphite-coated tubes and a L'vov platform were employed. A cadmium hollow cathode lamp (Varian, Mulgrave, VA, Australia) with wavelength of 228.8 nm and a spectral bandwidth of 0.5 nm was used as the radiation source. Argon (purity, 99.997%) at an internal flow rate of 2.0 L min^{-1} was used as the purge gas during all steps (White Martins, Salvador, Brazil) except atomization, during which the flow was stopped. The protocol proposed in this work is presented in Table 1.

2.2. Reagents and solutions

All solutions and standards used were prepared with high-purity water obtained from a Milli-Q system (Millipore, Bedford, USA) and had a specific resistivity of 18 MΩ-cm. All reagents used were of the highest analytical grade. The standards were prepared by the successive dilution of a 1000 mg L^{-1} stock solution of cadmium (Merck, Darmstadt, Germany) in 0.5% nitric acid. A volume of three microlitres of a 1000 mg L^{-1} ICP-MS aluminium solution (Merck) was used as chemical modifier (da Silva et al., 2011; Ferreira et al., 2011; Lima et al., 2013), being that the samples and standards volumes injected in the graphite furnace for the direct method was 20.0 µL. The accuracy of method was evaluated using a certified reference material of bovine liver furnished by the National Institute of Standard and Technology.

2.3. Sample digestion using digester block and reflux system

Samples were digested using a digester block and a reflux system that included a cold finger (Ferreira et al., 2013). Aliquots (5 mL) of each sample were placed into individual glass tubes. 4 mL of concentrated nitric acid (Merck) and 2.0 mL of 30% (v/v) hydrogen peroxide (Merck) were added to each tube. The samples were then digested for 60 min at 110 °C. Subsequently, the digested samples were transferred to a 25-mL volumetric flask, and ultrapure water was then used to fill the volumetric flask to 25 mL. During the determination of cadmium the sample volume injected in the graphite furnace was also 20.0 µL.

Table 1
Temperature program used for cadmium content determinations; an internal gas flow rate of 2.0 L min^{-1} was used in all stages except during atomization, when the gas flow was turned off.

Step	Temperature (°C)	Ramp (°C/s)	Hold time (s)
Drying	110	15	10
Drying	120	10	15
Pyrolysis	640	100	7
Atomization	2000	FP[a]	4
Cleanout	2550	FP	5

[a] Full power.

2.4. Determination of the qualitative evaluation index (QEI)

Given that the "ideal peak" for ET AAS methods should be large (a greater integrated area ensures greater sensitivity) and narrow (resulting from a process of fast atomization), the qualitative evaluation index was calculated as the ratio of the height of the peak to the width of the peak at half maximum. Fig. 1 shows the expression for calculating the QEI.

$$\mathrm{QEI} = (\boldsymbol{a}/2)/\boldsymbol{l} \qquad (1)$$

where $\boldsymbol{a}$ is the height of the peak and $\boldsymbol{l}$ is the width of the peak at half maximum.

The height and width of each peak were measured using EXCEL to five significant digits.

The multiple response (MR) was calculated by normalising the integrated absorbance and the QEI to the highest values of these parameters found in the experiments.

$$\mathrm{MR} = (\mathrm{abs}/\mathrm{abs}_{\mathrm{maximum}}) + (\mathrm{QEI}/\mathrm{QEI}_{\mathrm{maximum}}) \qquad (2)$$

2.5. Optimization of the experimental conditions

The optimization of the experimental conditions established for the determination of cadmium employing ETAAS were performed using two-level full factorial design for preliminary evaluation of the factors and also Box–Behnken design for determination of the critical conditions of these factors. All experiments were performed in random order. Chemometric data were processed using the statistical program Statistica 6.0.

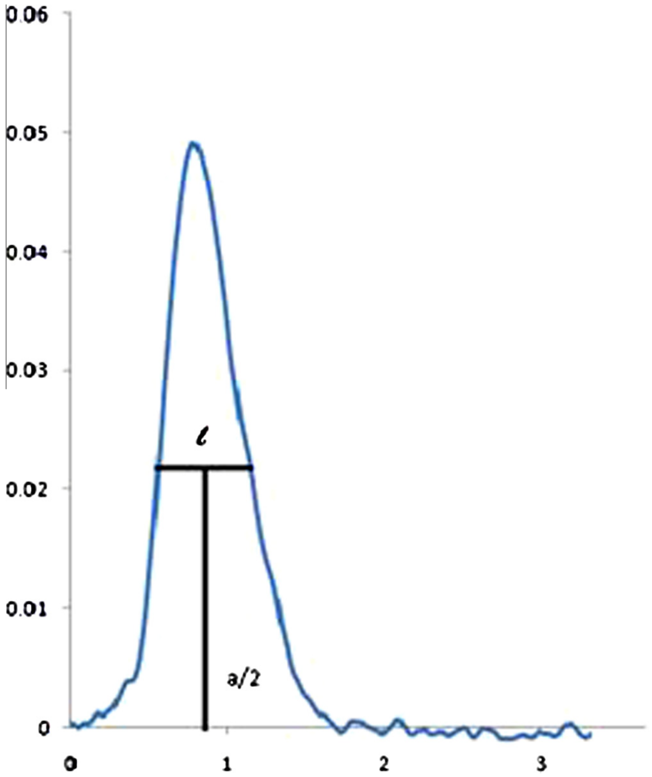

Fig. 1. Determination of QEI in analytical signal obtained for cadmium by ETAAS.