Analytical Atomic Spectroscopy

Multivariate optimization in atomic spectrometry

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Abstract

This work is directed to the dissemination of the multivariate statistical methods applied in the optimization of methods in atomic spectrometry. It was proposed, in particular, work published covering methods of variable selection also called screening methods, response surface design, as well as optimization methods.

Keywords: Multivariate statistical methods, atomic spectrometry.

1. Introduction

The optimization of analytical methods often relies on a trial-and-error approach in which the studies are carried out without a predefined plan of experiments. Using this procedure, conclusions extracted from previous assays may help to propose new experiments to progress in the optimization process. Unsuccessfully, this strategy requires a large number of trials to reach the optimal conditions, and it may be incapable to reveal interactions among the factors. In consequence, the experimental conditions finally chosen might be unacceptable [1].

The design of experiments (DOE) can be used as an alternative to this procedure. Generally, DOE provides a better knowledge of the factors controlling a given process and allows the optimization of the working conditions.

The initial point in the DOE procedure is the establishment an appropriate optimization criterion; it means to define the objective(s). In parallel, a list of potential factors is created to find out the most influential ones. The identification of relevant factors can be carried out using the screening methods such as fractional factorial design or the Plackett-Burman design when the number of factors is higher. After the selection of the factors, the full factorial design can be used to evaluate the factors as well the interactions between the factors. Finally, the surface response methodology can be used to find the optimal conditions through a Doehlert design, a central composite design (CCD), a Box-Behnken design, or a D-optimal design [2-4].

2. Applications using screening methods

The significant factors that influence the cloud point extraction of zinc by flame atomic absorption spectrometry (FAAS), in aqueous extracts of medicinal plants and blood samples, were chosen through the Plackett-Burman design (PBD) because it can be used as the screening method [5].

The optimal conditions for the determination of arsenic in seawater by PVG-ICPMS (Photochemical vapor generation coupled to inductively coupled plasma mass spectrometry) were firstly investigated by the Plackett-Burman as the screening method, and then after the central composite central was used to optimize it [6].

3. Applications using response surface methodology

The determination of copper, iron, nickel, and zinc by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) using an assisted liquid-liquid extraction was optimized through a full factorial design, in two levels, and a Box-Behnken design [7]. The bismuth in urine using hydride generation and atomic fluorescence spectrometry (HG-AFS) was optimized through the same designs, and the proposed method allowed the achievement the high precision even for the low concentration usually found in this sample [8].

The method proposed for the determination of vanadium and copper in seawater by inductively coupled plasma optical emission spectrometry (ICP-OES) was optimized by

way of the full factorial design, in two levels, and Doehlert design. In this work, four factors were investigated (PAN mass, pH, active carbon mass, and shaking time) in the optimization procedure. The limit of detection were 73 and 94 ng L^{-1} for vanadium and copper, respectively [9].

The determination of arsenic in diesel, gasoline, and nafta using graphite furnace atomic absorption spectrometry (GF-AAS) was optimized by the central composite design (CCD). The investigated factors were pyrolysis temperature, atomization temperature, nitric acid concentration in the microemulsion, and sample/propan-1-ol volume ratio in the experimental procedure. The evaluation of the regressors in the multiple linear regression with statistical significance ($p < 0.05$) was carried out by the Pareto chart of standardized effects [10].

The effects of the pyrolysis temperature and atomization temperature in the determination of cadmium and lead in cassava employing slurry sampling and GF-AAS were investigated by the central composite design (CCD). Once more, the Pareto chart of standardized effects was used in the evaluation of the regressors of the regression model [11]. The same design (CCD) was used to investigate and optimize the factors that act on the determination of mercury by cold vapor atomic absorption spectrometry (CV-AAS). The limit of detection was 0.14 µg.kg^{-1} in the original sample [12].

The D-optimal design was used to optimize the flame conditions in the determination of platinum presented from antitumoral drugs in human urine by flame atomic absorption spectrometry (FAAS). The limit of detection was 0.004 mg.L^{-1} of platinum in the original sample [13].

4. Conclusions

This short review shows the importance of multivariate methods in the optimization of spectrometric methods. Nowadays, it is observed that the vast majority of published works use this statistical tool in the optimization stage of the analytical method in detriment to the one-variable-at-a-time (OVAT approach). The use of multivariate optimization reduces the time of the laboratory tests, produces a reduction in costs and improves the quality of the results since it allows to estimate the interactions among the variables.

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