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Optimisation of sensitivity in the multi-elemental determination of 83 isotopes by ICP-MS as a function of 21 instrumental operative conditions by modified simplex, principal component analysis and partial least squares

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ABSTRACT

The optimisation of the sensitivity in the ICP-MS determination of 83 isotopes, as a function of 21 operative parameters was performed by generating an initial experimental design that was used to define, by principal component analysis, the multi-criteria target function. The first PC, which contained an overall evaluation of the signal intensity of all isotopes, was used to rank the experiments. The modified simplex optimisation technique was then applied on the ranked experiments. The increase in signal intensity was, on the average, 3.9 times for the isotopes considered for the simplex procedure. When finally convergence was achieved, a PLS regression model calculated on the available experiments allowed to investigate the effect played by each factor on the experimental response. Simplex and PCA proved to be extremely effective to obtain the optimisation and to generate the multi-criteria target function: they can be suggested as an automatic method to perform the optimisation of the instrumental operative conditions.

1. Introduction

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is becoming one of the most widely used techniques for the determination of elements at trace and ultra-trace level (ppb, ppt). The ICP-MS instruments are characterised by a large set of operative parameters which can exhibit various effects on the analytical results by influencing the interference pattern, the sensitivity of the determination, the time of analysis, etc. These parameters setting must be optimised as a function of the specific analysis. As a rule of thumb, all instruments do present an auto-tuning procedure, usually based on the One-Variable-At-a-Time (OVAT) approach, to search for the optimal setting of the operative parameters. The OVAT approach consists in the optimisation of each instrumental parameter independently, to obtain the maximum signal of a selected isotope: this approach therefore does not take into consideration the interactions that often exist between the operative parameters.

Several papers appeared in the nineties about the optimisation of ICP-MS instrumental conditions. Among them, the paper from Ford et al. [1] reports the multi-elemental optimisation of plasma parameters and ion optics in ICP-MS. The simplex procedure was applied to the optimization of plasma and ion optics parameters. Optimisation was successfully performed on the S/N ratios of 10 elements.

Another paper from van Veen et al. [2] reports the optimisation of ICP-MS conditions with respect to short- and long-term precision. The authors derived an expression of the precision as a function of the mass intensity in terms of the source flicker and shot noise contributions.

More recently, some more dedicated papers have appeared dealing with the optimisation of the instrumental parameters in ICP-MS by experimental design techniques [1–11]. Brennetot et al. [3] applied experimental designs to the optimisation of 10 operating conditions of a Multiple-collector inductively coupled plasma mass spectrometry (MC–ICP-MS) for the isotopic analysis of gadolinium. Ingle et al. [4] applied a multivariate approach to characterise and optimise the dominant H-2-based chemistries in a hexapole collision cell used in ICP-MS: in this case the target function for the optimisation was the S/N ratio. Recently, Gomez-Ariza et al. [5] optimised a two-dimensional on-line coupling for the determination of anisoles in wine using an electron capture detector (ECD) and ICP-MS after solid phase micro-extraction – gas-chromatographic (SPME-GC) separation, by a chemometric approach: different ICP-MS conditions (forward power, carrier gas flow and the addition of small percentages of alternate gases) have been optimised. Other

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applications of experimental designs to the optimisation of ICP-MS analysis are by Gomez-Ariza et al. [5], Darrouzes et al. [6] and Martos et al. [7]. In the paper from Darrouzes the optimisation of ICP-MS equipped with collision/reaction cell (C/RC) technology for the determination of selenium at ultra-trace level. Several parameters were optimised: gas flow rates for helium and hydrogen and the voltage of the different ionic lenses disposed around the C/RC (quadrupole bias, octopole bias, cell entrance, cell exit, plate bias). The paper from Martos et al. is focused instead on the pre-concentration and determination of Pt; various parameters and chemical variables affecting the preconcentration and determination of this metal by ICP-AES were evaluated. Five variables (sample flow rate, eluent flow rate, nebulizer flow rate, buffer concentration and mixing coil length) were considered as factors in the optimisation process. Interactions between analytical factors, and their optimal levels were investigated using two level factorial and central composite designs. The optimum conditions established were applied to the determination of platinum by flow injection inductively coupled plasma atomic emission spectrometry (FI-ICP-AES).

Optimisation procedures are usually applied to ICP-MS analysis focusing on a restricted number of instrumental parameters or of elements, according to the scientists' particular interests; it is important to point out however that one of the potentials of ICP-MS analysis is the possibility of determining a great number of elements contemporarily: this is particularly interesting for routine analyses. From this starting consideration, we focused our attention on the contemporary determination of 83 isotopes, in order to obtain experimental conditions representing the best compromise for the identification of all these isotopes in routine analyses. Due to the large number of isotopes to be determined, an exhaustive study of all the instrumental parameters involved is necessary, in order to achieve the best experimental settings. 21 parameters, described in detail in the experimental section, were thus involved in the study. The modified simplex procedure [12–15] was selected to perform the optimisation of the 21 parameters. Simplex represents in this case the best choice in order to limit the number of experiments needed to accomplish optimisation: due to the large number of factors studied, full factorial designs cannot be applied, while fractional factorial designs generate complex confounding structures and, furthermore, complex variables effects and interactions are possibly expected. The simplex iterative procedure represents thus a good alternative.

The large number of experimental signals to be maximised (the 83 isotopes), requires the definition of an effective and suitable multi-criteria target function. Usually the target function adopted is the sum of all the signals. In this case, the multi-criteria target function, representing the signal of almost all the isotopes simultaneously, was generated by Principal Component Analysis (PCA) [16,17]. The initial simplex (22 starting experiments) was used to generate the multi-criteria target function: PCA was carried out on the signals recorded for the 83 isotopes for the initial pool of 22 experiments. This procedure represents a valid alternative due to the robustness of PCA: considering only the first relevant principal components (PCs), random variations due to experimental noise can be eliminated. Once defined the multi-criteria function, the iterative modified simplex method was applied. At each iteration each new experiment is projected on the space given by the relevant PCs previously calculated in order to evaluate the final multivariate experimental response. The iterative simplex allows to obtain new best settings with respect to the OVAT approach. The results obtained by the Simplex procedure were compared to those obtained from the OVAT approach, representing the default settings.

Simplex optimisation, however, provides no model relating the instrumental parameters and the target function. Therefore, a Partial Least Squares (PLS) [16,17] regression model was built based on the overall set of experiments performed, to shed light on the effect of each experimental factor on the final response. This model can be used to identify which experimental factors are more important and the relationships existing among them.

From an operative point of view, the contemporary optimisation of all the instrumental parameters to obtain the best conditions for the determination of all the detectable elements represents an important application in routine analyses and could represent a valid alternative for default instrumental settings optimisation. Here, the attention is focussed on the proposal of a multivariate procedure for the automatic optimisation of the instrumental settings in ICP-MS.

The present approach represents a valid procedure due to the coupling of simplex optimisation to the establishment of a target function based on principal component analysis: this allows to take into consideration the relationships and the interactions among the variables that cannot be taken into account in standard OVAT procedures where each variable is optimised independently from the others. Moreover, even if the Simplex procedure is stopped before achieving convergence, it can provide experimental settings that are better with respect to the initial ones, due to the iterative method applied. This is important when optimisation has to be undertaken with constraints on the maximum time available to perform the optimisation itself.

2. Theory

2.1. The proposed procedure

The optimisation of the signals of 83 isotopes as function of 21 operative parameters in ICP-MS is carried out here by the application of a procedure consisting in four main steps:

- *Identification of the initial simplex*. The initial set of experiments to be performed was determined by the simplex procedure [12–15]. In the present case 21 operative parameters were studied, thus providing an initial set of 22 experiments ($p+1$ initial experiments, where p is the number of factors to be investigated), called *simplex*. The default settings provided by the proprietary software present on the instrument, were selected as starting conditions for the initial simplex. The initial Simplex establishes a starting pool of experiments where the parameters are varied one-at-a-time.
- *Identification of a multivariate target function by Principal Component Analysis*. For each experiment of the initial simplex the signal of the 83 isotopes was recorded. A multivariate target function was then identified by applying Principal Component Analysis (PCA) [16,17] on the data recorded from the initial simplex. As commonly acknowledged, PCA is a pattern recognition method representing objects in a new reference system characterised by variables called Principal Components (PCs). PCs are orthogonal to each other and are computed hierarchically (the information accounted for by successive PCs is decreasing): in this way they account for independent sources of information and experimental noise and random variations are contained in the last PCs (they contain the least possible information). The optimisation of the instrumental parameters with respect to the simultaneous maximisation of the signal of all the isotopes (expressed as number of counts for each isotope) requires the use of a multi-criteria ranking method: PCA can then be effectively used to this purpose. PCA is then performed on the dataset consisting in the experimental responses of the initial pool of experiments and the final target function can be selected by the identification of the PC mostly related to the overall signal increase. This represents a valid alter-