Analytical Note

Application of multivariate curve resolution-alternating least squares for the determination of boron isotope ratios by inductively coupled plasma-optical emission spectrometry

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ABSTRACT

Multivariate curve resolution-alternating least squares (MCR-ALS) was applied to atomic emission data obtained from inductively coupled plasma-optical emission spectrometry analysis of boron for the quantification of $^{10}B/^{11}B$ ratios. The determination of isotopic composition of boron is based on the isotopic shift of ^{10}B and ^{11}B in the emission line of 208.957 nm. After recording of the emission spectra in the range of 208.940–208.970 nm, evaluation of isotopic composition of boron containing samples was performed with MCR-ALS algorithm. MCR-ALS was able to resolve the emission spectra of ^{10}B and ^{11}B mixtures. The performance of the proposed methods was tested by determination of $^{10}B/^{11}B$ ratios in synthetic mixtures and also water samples.

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1. Introduction

Naturally occurring boron consists of two stable isotopes, ^{10}B (19.8%) and ^{11}B (80.2%). ^{10}B isotope has a large thermal neutron capture cross-section and it, therefore, is used widely in nuclear power industry and medical science [1,2]. ^{10}B is used in a primary coolant system in pressurized water reactors in the form of boric acid to control the reactivity in the core [3]. This isotope is also used as a source for the short range α particles in a cancer treatment by a boron neutron capture therapy which is a novel technique for treating cancer by using ^{10}B-labeled compounds and a neutron radiation to kill the cancerous cells [4].

The large difference between atomic mass of boron isotopes leads to significant fractionation in environmental and geological environment [5]. This led to considerable interest in determining the variations in boron isotopic composition. The variation in the ratios of the two B isotopes is represented by $\delta^{11}B$ value expressed in (‰) and calculated as:

$$\delta^{11}B = \left\{ \left(^{11}B/^{10}B \right)_{sample} / \left(^{11}B/^{10}B \right)_{standard} - 1 \right\} \times 1000 \qquad (1)$$

where $(^{11}B/^{10}B)_{sample}$ denotes the ^{11}B-to-^{10}B boron isotopic ratio of the sample and $(^{11}B/^{10}B)_{standard}$ that of a standard. The standard used in most studies is NBS SRM 951 boric acid. In nature, the boron isotopic compositions vary widely from -30 to $+60$‰ [5]. Due mainly to this large variation, boron isotopic composition has been applied to many areas of earth sciences and has provided valuable findings on fundamental processes in natural circumstances [5,6]. The $^{11}B/^{10}B$ ratio in seawater, for example, is much higher than that in typical soils ($\delta^{11}B$ seawater~39.5‰) because of mechanisms such as the preferential adsorption of ^{10}B onto clay minerals and the fractionation that takes place during the precipitation of carbonates [7,8]. Also the isotopic composition of dissolved boron in groundwater can be used to determine the source(s) of boron; this information can be used to infer the source(s) of other co-migrating contaminants [9]. Hence, rapid, precise and low cost methods for the determination of the isotopic composition of boron are of great significance.

Usually, boron isotope ratios have been determined using thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) [10]. TIMS is a magnetic sector mass spectrometry technique that is capable of making very precise measurements of isotope ratios of elements that can be ionized thermally, usually by passing a current through a thin metal ribbon under vacuum. However, time-consuming sample preparation, analyte purification, and sample determination processes may limit the routine application of TIMS for isotope ratio measurements [10,11]. ICP-MS is another method for the determination of boron isotope ratios that uses an Ar inductively coupled plasma (ICP) as an ionization device interfaced to a low-resolution quadrupole mass analyzer [12–15]. Although ICP-MS is attractive for isotope ratio determination due to its rapidity and selectivity, high instrumental and operational costs make it difficult to facilitate this method in routine analysis.

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The isotopic composition of some elements can be determined by spectroscopic techniques, such as atomic emission or atomic absorption [16,17]. These techniques are applicable for the isotopic analysis for those elements, which have a significant isotopic shift in the emission or absorption lines [17]. The isotopic shifts are larger either in very light elements due to the relatively large mass difference of their isotopes or in heavy elements because of the difference in nuclear charge distribution of the isotopes [17]. The determinations of isotope ratios by atomic absorption or atomic emission measurements have been reported for Li [18], Pb [19], U [16,20–23], B [17,24–26] and Hg [27].

Under computer-controlled instrumentation, multivariate chemometric methods play a very important role in the multicomponent analysis of mixtures by spectroscopic techniques [28–30]. The application of quantitative chemometrics to multivariate chemical data is becoming more widespread owing to the availability of digitized spectroscopic data and commercial software for laboratory computers. Multivariate curve resolution is defined as a group of techniques which help resolve mixtures by determining the number of constituents, their response profiles (spectra, pH profiles, time profiles, elution profiles) and their estimated concentrations, when no prior information is available about the nature and composition of these mixtures [31–33].

Multivariate curve resolution-alternating least squares (MCR-ALS) is one of the most recent approaches to elaborate the spectroscopic data [34]. It allows to extract the pure spectra and concentration of the components in a mixture from a set of spectra with different composition. MCR-ALS has been applied to solve the signal overlap problems in UV–vis and fluorescence spectrometry [35,36], voltammetry [37], chromatography [38,39], flow injection analysis [40] and spectroscopic images [41].

In this work, the use of MCR-ALS method is proposed for the quantitative determination of boron isotope ratios by inductively coupled plasma-optical emission spectrometry (ICP-OES). For comparison, partial least squares method was also employed for determination of boron isotope ratios.

2. Theory

2.1. Multivariate curve resolution-alternating least square

The main aim of multivariate curve resolution with alternating least squares is to resolve a data matrix to obtain the concentration and spectra profiles of every important component that provides information to the system. For matrix data, the aim of the analysis can be summarized in mathematical form as:

$$\mathbf{D} = \mathbf{CS^T} + \mathbf{E} \tag{2}$$

where $\mathbf{C}$ is a two dimensional array of the concentration profiles of each component, $\mathbf{S^T}$ is the transpose of a matrix containing the spectra of the pure components, and $\mathbf{D}$ is the original data matrix [34]. The number of component, to be considered in the mathematical decomposition of Eq. (2) can be estimated by singular value decomposition (SVD). To initiate the iterative ALS procedure, an initial estimation is needed for the spectral or concentration profiles for each species. Different methods are used for this purpose like evolving factor analysis or the determination of the purest variables [42,43]. Eq. (2) is solved iteratively using an alternating least square (ALS) procedure based on the following two matrix equations:

$$\mathbf{S^T} = (\mathbf{C})^+ \mathbf{D} \tag{3}$$

$$\mathbf{C} = \mathbf{D}\left(\mathbf{S^T}\right)^+ \tag{4}$$

where $(\mathbf{S^T})^+$ and $(\mathbf{C})^+$ are the pseudoinverse of the $\mathbf{S^T}$ and $\mathbf{C}$ matrices, respectively. The iteration procedure is stopped when convergence is achieved. The resolution can be improve by applying several constraints during optimization. Constraint applied in this work was non-negativity for the concentration ($\mathbf{C}$) and spectra profiles ($\mathbf{S^T}$). When the optimization process ends, the performance of the model can be evaluated from lack of fit (LOF) data as:

$$\text{LOF} = 100 \times \sqrt{\frac{\sum_{i,j} e_{ij}^2}{\sum_{i,j} d_{ij}^2}} \tag{5}$$

where d_{ij} designs an element of the input data matrix $\mathbf{D}$ and e_{ij} is the related residual obtained from the difference between the input element and the MCR-ALS reproduction. Percent of explained variance is calculated according the following expression where d_{ij} and e_{ij} are the same as above:

$$R_{MCR}^2 = \frac{\sum_{i,j} d_{ij}^2 - \sum_{i,j} e_{ij}^2}{\sum_{i,j} d_{ij}^2}. \tag{6}$$

2.2. Partial least squares

Partial least squares regression (PLS) has become the most frequently used method for multivariate calibration because high-performance calibration models are obtained, while the software is not only available but also easily implemented [44,45]. PLS is a linear modeling technique where information in the descriptor matrix $\mathbf{X}$ is projected onto a small number of underlying ("latent") variables called PLS components, referred to as latent variables. The matrix $\mathbf{Y}$ is simultaneously used in estimating the "latent" variables in $\mathbf{X}$ that will be most relevant for predicting the $\mathbf{Y}$ variables. The number of significant factors for the PLS algorithm was determined using the cross-validation method. With cross-validation, one sample was kept out (leave one out) of the calibration and used for prediction. The process was repeated so that each of the samples was kept out once.

2.3. Statistical parameters

For the evaluation of the predictive ability of multivariate calibration models, the root mean square error of prediction (RMSEP) and relative error of prediction (REP) can be used:

$$\text{RMSEP} = \left[\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2\right]^{0.5} \tag{7}$$

$$\text{REP\%} = \frac{100}{\overline{y}}\left[\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2\right]^{0.5} \tag{8}$$

where $\hat{y}_i$ is the estimated value of the ith object, y_i is the corresponding reference value of this object and n is the number of samples in the validation set.

3. Experimental

3.1. Reagents

All reagents used were of analytical grade and were used as supplied. Isotopic standard solutions (1000 µg mL^{-1} as B) of ^{10}B and ^{11}B were prepared by dissolving appropriate amounts of boric-^{10}B acid (99% ^{10}B) and boric-^{11}B acid (99% ^{11}B) (Sigma-Aldrich), in water, respectively. Working solutions were prepared by adequate dilution with ultrapure water.