

Evaluation of Inductively Coupled Plasma—Atomic Emission Spectroscopy Multicomponent Trace Analysis Data by Partial Least-Squares Calibration

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In ICP—AES determination of rare earth elements (REE), interferences can occur even if prominent lines are mainly employed. To overcome this drawback, partial least-squares (PLS) calibration procedure has been applied in this work. Using PLS calibration, a model based on calibration set measurement is developed and, afterwards, used to predict the test set (samples). The only assumption is that these two sets are similar in concentration, acidity, viscosity, *etc.* like in any other analytical method. In the presence of interfering elements in both sets, it is possible to determine REE in their mixtures without the necessity to estimate concentrations of interferents and, even, by using some interfered lines. Existence and origin of interferences need not to be studied.

Advantage of multivariate data evaluation with PLS calibration approach has been demonstrated on analysis of various REE mixtures. The results have been discussed and compared with those obtained by the linear least-squares calibration method.

Inductively coupled plasma—atomic emission spectroscopy (ICP—AES) has virtually no chemical interferences and minimal ionization problems, however, there is a potential for spectral interferences as *e.g.* stray light, direct or wing spectral overlap, overlap of broad lines of high intensity, and continuous emission. Interferences are discussed and basic information on the methods used to overcome this problem is given in monographs [1, 2] and review on emission spectrometry [3].

There are several powerful chemometrics techniques, *e.g.* multiple regression, principal component regression, and partial least-squares (PLS) method, which can be used with advantage in multicomponent analysis. A comparison of multivariate calibration methods for quantitative spectral analysis has been made [4] with conclusion in favour of PLS. The basic design of PLS method was developed by *Wold* [5], history, nature, and applications are reviewed elsewhere [6]. The method has found wide use in analytical chemistry because no physical model has to be assumed. This model is developed from standards of known composition and, subsequently, used to predict

composition of samples or a test set.

The aim of the present work is to show the principal possibility of PLS application in ICP—AES in the same manner as it is used already for a long time in spectrophotometry and to demonstrate advantages of PLS over rather complicated procedures that are being used for correction of interferences. This has been demonstrated on the analysis of samples containing a mixture of rare earth elements (REE) with or without an interfering element.

EXPERIMENTAL

Stock solutions of 2.5 mmol dm⁻³ REE in 0.1 mol dm⁻³ nitric acid were prepared by dissolving their nitrates or oxides and standardized chelatometrically as described elsewhere [7]. Mixtures of REE for ICP—AES measurement were prepared in 0.1 mol dm⁻³ nitric acid. Water was redistilled from a quartz apparatus. All other reagents were of anal. grade purity.

A Model 3410, ICP sequential atomic emission spectrometer with MinitorchTM and ultrasonic nebulizer of the Meinhardt type (Applied Research Labora-

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tories, USA) has been used. Samples were introduced at the flow rate of $1.5 \text{ cm}^3 \text{ min}^{-1}$ by means of a Model M312 four-path peristaltic pump (Gilson, France) equipped with Tygon tubing. Nitric acid ($c = 0.1 \text{ mol dm}^{-3}$) was used as a reference solution (blank).

The PLS calibration sets were prepared by using experimental design. Two-level fractional factorial design, where the number of calibration solutions is equal to 2^{m-1} and m is the number of components, *e.g.* REE, was selected because intensities measured in ICP—AES are linear function of concentration in a wide range, over four to six orders of magnitude. Applying this design, interactions caused by direct or wing overlap can be neglected while in the presence of some other effects, *e.g.* curve shift, dimension number of the model (see below) has to be increased. For ordinary linear least-squares (OLS) calibration, the solution from PLS calibration set containing all REE at the highest concentration and another solution containing these elements at half concentration were used.

The data have been evaluated by means of a PLS program [8] written in Fortran 77 according to literature [5].

Calculation

Intensity of an element emission at a certain line, x , is proportional to its concentration y . In case of peak overlapping, the intensity is a sum of contributions of individual elements in a mixture, *i.e.* in matrix notation

$$\mathbf{X} = \mathbf{K} \cdot \mathbf{Y} \quad (1)$$

where \mathbf{K} are proportionality factors.

We explore here the method of partial least-squares modelling [5] which has been used also in various calibrations [9–15]. In PLS method, solutions of relevant analytes are prepared for calibration set (calibration model). In order to obtain accurate predictions, calibration set must contain all possible interferences that can be expected, however, they need not to be known exactly. If n calibration solutions are prepared and

measurements of intensities are done at p wavelengths, $n \times p$ calibration matrix \mathbf{X} is obtained. Thus, each row of this matrix represents intensities for one solution and each column the intensities measured at given wavelength for different solutions. Corresponding concentrations can be arranged in the same manner in an $n \times q$ matrix \mathbf{Y} .

Usually, a geometrical representation is given [6, 12]. Here, the \mathbf{X} -matrix (\mathbf{Y} -matrix) is presented in a p -dimensional (q -dimensional) coordinate system where each of n samples forms some of the matrix points. Relations between calibration solutions in the two spaces can be described as planes or hyperplanes. The aim of PLS is to model each space as appropriate as possible and to obtain maximum correlation between the blocks. In practice, the model has usually a dimension equal to the number of analytes plus several extradi-dimensions to account for nonlinearities, base line shifts, *etc.*, and/or interactions of other origin.

The first step in evaluation of a calibration model is the scaling of variables by giving each variable a weight according to its importance. If this information is not available, the variables in all data sets are scaled to unit variance. After that, the mean for each column is subtracted. The PLS components which correspond to directions in p - and q -space are subsequently calculated in an iterative procedure where the first component describes the greatest amount of variance, the second the second largest, *etc.* For each PLS component, the scores in the \mathbf{X} and \mathbf{Y} blocks are related to each other by linear regression and this procedure is repeated until no significant information is left. In the prediction phase, the procedure is reversed and unknown concentrations of the test set are calculated.

RESULTS AND DISCUSSION

Case 1. Analysis of Mixtures Containing La, Ce, Pr, and Nd

Review of the lines used for ICP—AES measurement and known interferences [16] are given in Table 1. Four lines per each element, mostly the so-

Table 1. Review of La, Ce, Pr, and Nd Lines Used

REE	λ/nm	I_m/I_b^a	Interferents	REE	λ/nm	I_m/I_b^a	Interferents
La	379.478	30.0	Ca, Fe, V	Pr	414.311	8.0	Ca, Fe, Ti, V, Ce Cr, Fe, V, Th, Pr
	398.852	27.0			422.298	6.3	
	408.672	30.0			417.939	8.1	
	412.323	29.0			390.844	8.1	
Ce	371.637	5.7	Pr Cr, Dy, Fe, Ti, Pr	Nd	406.109	31.0	Eu, Gd, Sm, Ta Fe, Mn, Sm, V Mn, Pr, Tl
	422.26				415.608	28.0	
	418.66				455.157	40.0	
	417.93				430.358	40.0	

a) Value of the intensity ratio of the net analyte to background [16].

All lines of La, Pr, and Nd and the Ce line at 418.66 nm are prominent ones [15]; for all lines the state of ionization is equal to II.

Table 2. Composition of Calibration Solutions Used in PLS Approach ($c/(\mu\text{g cm}^3)$)

Solution	Set No. 1				Set No. 2				Set No. 3				
	La	Ce	Pr	Nd	Ce	Dy	Eu	Gd	Ce	Dy	Eu	Gd	Ca
1	2.50	2.50	2.50	2.50	2.50	1.00	1.00	1.00	2.50	1.00	0.10	1.00	0.10
2	2.50	2.50	15.01	20.00	2.50	1.00	2.50	5.00	6.00	2.50	1.50	2.50	1.00
3	2.50	20.01	2.50	20.00	2.50	5.00	0.10	5.00	15.00	5.00	2.50	5.00	1.00
4	2.50	20.01	15.01	2.50	2.50	5.00	2.50	1.00	2.50	1.00	2.50	5.00	1.00
5	25.00	2.50	2.50	20.00	15.00	1.00	0.10	5.00	2.50	5.00	0.10	5.00	1.00
6	25.00	2.50	15.01	2.50	15.00	1.00	2.50	1.00	2.50	5.00	2.50	1.00	0.10
7	25.00	20.01	2.50	2.50	15.00	5.00	0.10	1.00	15.00	1.00	0.10	5.00	1.00
8	25.00	20.01	15.01	20.00	15.00	5.00	2.50	5.00	15.00	1.00	2.50	1.00	0.10
9	—	—	—	—	6.00	2.50	1.50	2.49	15.00	5.00	0.10	1.00	0.10
10	—	—	—	—	0.00	0.00	1.30	3.70	9.00	2.00	1.30	3.70	0.10
11	—	—	—	—	3.00	1.20	0.80	1.20	3.00	1.20	0.80	1.20	1.00

In solutions 1—8, concentrations of REE in each set were changed according to the two-level fractional factorial design while solutions 9—11 were joined as additional ones. The calcium content in set No. 3 was varied randomly.

Table 3. Average Prediction Errors of the Results of Test Sample Analysis ($c/(\mu\text{g cm}^{-3})$)

Method	La	Ce	Pr	Nd	Dy	Eu	Gd
Case 1							
PLS ^a	0.0135	0.0138	0.0177	0.0085	—	—	—
PLS ^b	0.0139	0.0107	0.0153	0.0122	—	—	—
PLS—A ^a	0.0075	0.0113	0.0149	0.0117	—	—	—
OLS—A	0.1019	0.1987	0.1875	0.1210	—	—	—
PLS—B ^a	0.0138	0.0107	0.0147	c	—	—	—
Case 2^a							
PLS	—	0.2011	—	—	0.0186	0.0083	0.0158
OLS	—	0.2119	—	—	0.0518	0.0164	0.0738
PLS—C	—	—	—	—	0.0081	0.0055	0.0101
PLS—D	—	0.1078	—	—	0.0214	0.0074	0.0380
Case 3^d							
PLS ^e	—	0.0991	—	—	0.0198	0.0623	0.0543
PLS—E	—	0.0417	—	—	0.0499	0.0205	0.0540

a) By the PLS method, values of REE concentrations in individual samples were predicted for four abstract components. b) Predicted for six abstract components. c) Not estimated. d) Predicted for five abstract components. e) Calcium content estimated with average prediction error of $0.017 \mu\text{g cm}^{-3}$. Average prediction error was calculated as $[\sum(y_{\text{given}} - y_{\text{predict}})^2/n]^{1/2}$ for 23 test samples in Case 1, 8 in Case 2, and 14 in Case 3.

called prominent ones, were used. Composition of solutions used in PLS calibration is introduced in Table 2, set No. 1. Test samples containing 0.00 up to $24.80 \mu\text{g cm}^{-3}$ La, 0.00— $19.49 \mu\text{g cm}^{-3}$ Ce, 0.00— $9.99 \mu\text{g cm}^{-3}$ Pr, and 0.00— $19.57 \mu\text{g cm}^{-3}$ Nd at 10 up to 12 different concentration levels were analyzed and evaluated by both, PLS and OLS approaches.

The results are given in Table 3 and a comparison of OLS and PLS prediction errors (residuals) of individual samples can be seen from Fig. 1. With PLS method a very good prediction was obtained even if highly interfered lines were used. Average prediction error was around $\pm 0.014 \mu\text{g cm}^{-3}$. The results of the OLS approach were satisfactory for La, however, high deviations were observed at 379.478 nm. Prominent Ce lines at 371.637 nm and 418.66 nm never gave wrong results, while outliers were observed for 422.26

nm and completely wrong results were obtained at 417.93 nm. Results of Pr analysis were mostly wrong for prominent lines of 422.298 nm and 390.844 nm and those of Nd for the line of 455.157 nm. Thus, as expected, the OLS approach could not yield good results unless the "best lines" with the lowest interferences were chosen for analysis or a high attention would be paid to the use of methods for correction of the interferences [1—3, 16]. The lowest interferences were found at 398.852 nm, 418.66 nm, 414.311 nm, and 415.608 nm for La, Ce, Pr, and Nd, respectively. By using these lines, the results obtained by PLS approach (Table 3, PLS—A) were better as well than those obtained by OLS calibration (OLS—A).

In order to illustrate the ability to compensate the effect of unidentified constituents, PLS calculations were done also for three elements only while the fourth

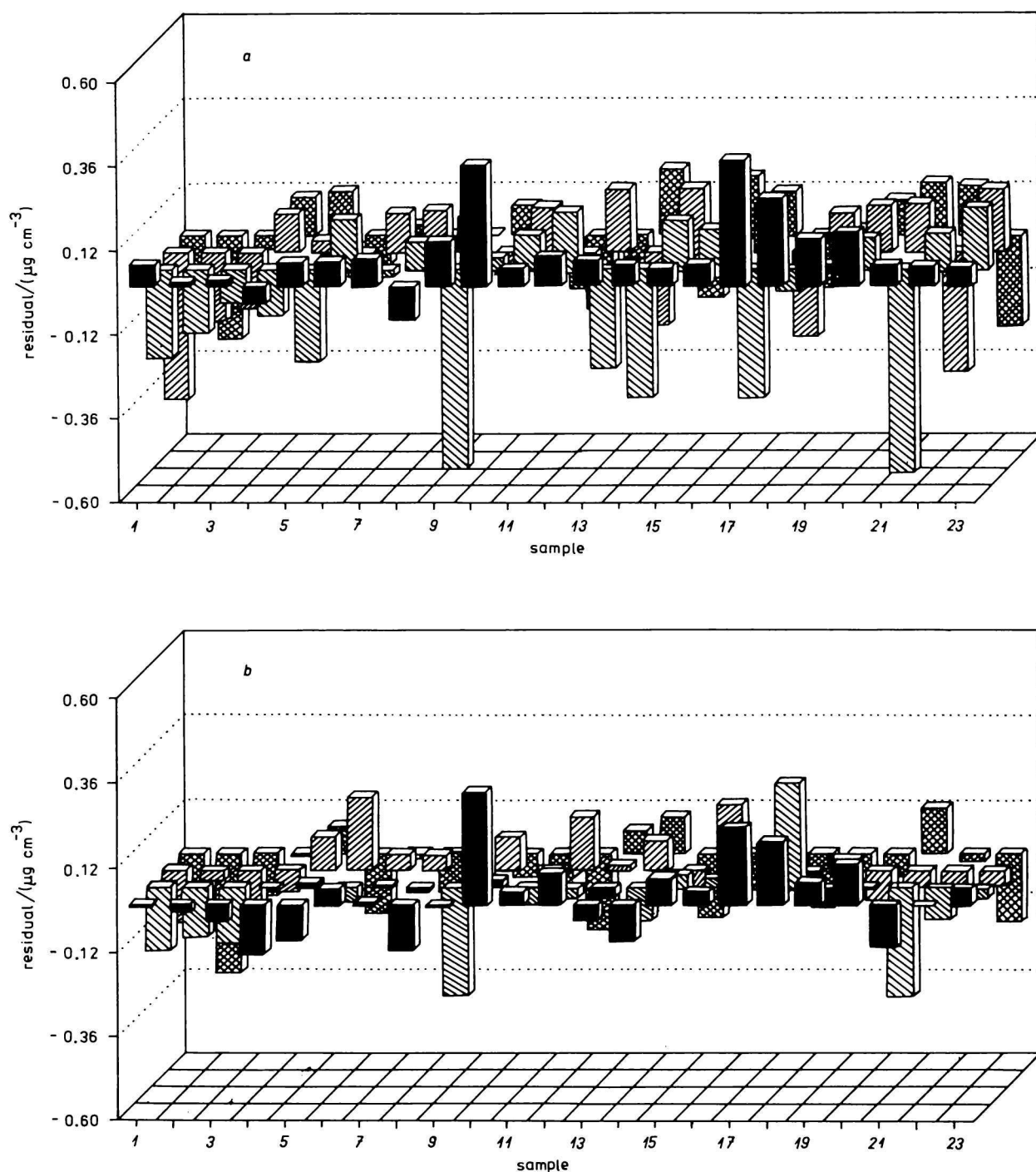


Fig. 1. Residuals obtained by OLS (a) and PLS (b) methods calculated as the difference between predicted and given concentrations of REE. OLS and PLS calibration: ■ La, ▨ Ce, ▩ Pr, ▤ Nd.

one was not taken into account. The results were practically identical with previous ones as demonstrated in Table 3, PLS—B, for the case when the presence of Nd was not taken into account. That is a great advantage of PLS that corrections for unknown constituents if present in both, calibration and test sets, can be easily made.

Case 2. Analysis of Mixtures Containing Ce, Dy, Eu, and Gd

Review of the lines used and interferences referred in the literature [1—3, 16] are given in Table 4 while composition of calibration solutions can be found in Table 2, set No. 2. Concentrations of REE in test sam-

Table 4. Review of Ce, Dy, Eu, and Gd Lines Used

REE	λ/nm	I_m/I_b^a	Interferents	REE	λ/nm	I_m/I_b^a	Interferents
Ce	393.109	5.0	Eu	Eu	381.967	110.0	Cr, Nd, Sm, Ca, Fe, Ti
	413.38	6.0	Gd		393.048	53.0	Ce
	413.765	6.2	Ca, Fe, Ti		412.974	70.0	Cr, Ca, Ti, Gd, Pr
	418.66	5.7	Cr, Dy, Fe, Ti		420.505	70.0	
	401.239	4.0			272.778	37.0	
Dy	364.54	13.0	Sc, Ca, Fe, V	Gd	342.247	21.0	Cr, Fe, Ni, Ti, Ce
	353.17	30.0	Er, Eu, Ho, Tb		376.839	12.0	
	394.468	9.5	Al, Ca		336.223	15.0	
	353.602	10.0	Sc		354.58	9.5	
	396.839	9.5			335.048	14.0	Eu, Ho, Ti, U, Ca

a) Value of the intensity ratio of the net analyte to background [16].

All lines are prominent [15] and with the state of ionization equal to II.

ples were varied at 5 to 7 different levels between 0.00 to 15.00 $\mu\text{g cm}^{-3}$ for Ce, 0.00–4.00 $\mu\text{g cm}^{-3}$ for Dy, 0.80–2.30 $\mu\text{g cm}^{-3}$ for Eu, and 1.20–4.01 $\mu\text{g cm}^{-3}$ for Gd.

As presented in Table 3, prediction errors were relatively low. Highest deviations were observed for Ce where average error was equal to 3.66 %, otherwise for Dy, Eu, and Gd it was 0.54 %, 0.58 %, and 0.68 %, respectively. In order to illustrate the ability to compensate for unidentified constituents, calculations were also done only for Dy, Eu, and Gd while intensities measured at Ce lines were either used (Table 3, PLS—C) or not used (PLS—D) in PLS processing. These results were comparable with those of the previous PLS calculation. A comparison with the OLS approach where the “best lines” of 413.765 nm (Ce), 353.17 nm (Dy), 420.505 nm (Eu), and 376.839 nm (Gd) were employed, was also made. With the OLS method, lower prediction error was obtained only for Ce, otherwise the results of PLS treatment were better for Dy and Gd or, in the case of Eu, without significant difference.

Case 3. Analysis of Mixtures Containing Ce, Dy, Eu, Gd, and Ca

Calcium is interfering the lines of REE and, due to its 10 up to 100 times higher emission intensity than those of majority of REE, the background emission is enhanced significantly under its presence. Determination of REE in samples with calcium content is therefore rather difficult and requires a careful, often tedious and time-consuming correction.

The lines as in Case 2 were used for REE (Table 4), while Ca was monitored only at the single line of 317.933 nm. The composition of the calibration set No. 3 is given in Table 2. Concentrations of REE in test mixtures ranged from 0.00 to 15.00 $\mu\text{g cm}^{-3}$ for Ce, 0.00–5.00 $\mu\text{g cm}^{-3}$ for Dy, 0.00–2.50 $\mu\text{g cm}^{-3}$ for Eu, and 0.00–5.00 $\mu\text{g cm}^{-3}$ for Gd at 6 to 8 different levels and calcium content was varied randomly at 0.10 or 1.00 $\mu\text{g cm}^{-3}$.

The OLS calibration failed completely at the calcium concentrations used. Results of PLS evaluation in Table 3 showed low prediction errors, comparable with those which were found in the absence of calcium. When calcium was not taken into account, *i.e.* being present as an unidentified constituent (Table 3, PLS—E), the results were even better than in the Case 2.

CONCLUSION

PLS calibration method can be successfully applied to evaluation of ICP—AES multicomponent data even if interfered lines are used for the analysis. Also if the lines apparently free of any interferences are employed, better results than those obtained by the OLS method are achieved with the PLS approach. Further, the PLS method can compensate for unidentified components assuming their presence in the calibration set. For a great number of elements to be analyzed simultaneously, the number of calibration solutions could be lowered by using reduced factorial designs or the analysis could be divided into two or more groups with lower number of analytes.

Generally, applying PLS, more precise and reliable results can be obtained and interferences need not be studied or known before. The application of this approach could facilitate the ICP—AES multicomponent analysis.

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