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Improving precision of X-ray fluorescence analysis of lanthanide mixtures using partial least squares regression

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ABSTRACT

This study addresses the problem of simultaneous quantitative analysis of six lanthanides (Ce, Pr, Nd, Sm, Eu, Gd) in mixed solutions by two different X-ray fluorescence techniques: energy-dispersive (EDX) and total reflection (TXRF). Concentration of each lanthanide was varied in the range 10^{-6}–10^{-3} mol/L, low values being around the detection limit of the method. This resulted in XRF spectra with very poor signal to noise ratio and overlapping bands in case of EDX, while only the latter problem was observed for TXRF. It was shown that ordinary least squares approach in numerical calibration fails to provide for reasonable precision in quantification of individual lanthanides. Partial least squares (PLS) regression was able to circumvent spectral inferiorities and yielded adequate calibration models for both techniques with RMSEP (root mean squared error of prediction) values around 10^{-5} mol/L. It was demonstrated that comparatively simple and inexpensive EDX method is capable of ensuring the similar precision to more sophisticated TXRF, when the spectra are treated by PLS.

1. Introduction

X-ray fluorescence (XRF) is a very convenient tool of express multicomponent analysis and it does not require complex sample pretreatment procedures. Nevertheless there are certain issues hindering wide acceptance of the method in analytical practice. These issues are considerable sample matrix influence and rather high detection limits. During simultaneous analysis of the metals in solutions these matrix effects are mainly twofold: 1) absorption of fluorescence radiation from analyzed element by other chemical elements of the matrix; 2) overlapping of characteristic lines from analyzed elements. While matrix effects can be easily taken into account in aqueous solution by choosing of appropriate standard samples, the sensitivity is still insufficient for certain analytical tasks [1]. A possible way to circumvent these issues can be the application of appropriate multivariate data analysis techniques (chemometrics).

Chemometric tools are not yet applied widely for XRF data analysis, however there is a certain growth in a number of such reports through the last years. The most popular strategy is in application of principal component analysis (PCA) and clustering techniques for classification of samples according to certain features like age, provenance, etc. There are reports on discrimination of ancient pottery [2–4], ceramics [5], on analysis of building materials [6], sediments [7] and atmospheric aerosols [8]. As for quantitative analysis of elements from XRF data the main instrument applied so far was PLS (partial least squares) regression. This method was applied in [9] to eliminate diffraction effects when analyzing sulfur in graphite matrix. The PLS allowed getting mean relative error of 5% in sulfur quantification while ordinary least squares (OLS) failed. The report [10] was addressing the problem of appropriate spectral region selection for PLS regression when dealing with geological sample analysis. It was shown that PLS model precision is superior to OLS and MLR (multilinear regression) for certain metals and comparable for the others, because it allows for taking into account absorption and interference effects in spectral data. In [11] quantitative sulfur determination was hindered by overlapping molybdenum peak and this problem was successfully solved by PCR (principal component regression) and PLS application. Noteworthy, no significant differences in the performance of two methods were observed. Other examples of using PLS technique for quantitative XRF data analysis in soils [12,13], sediments [14], lubricating oils [15], and glasses [16] are reported.

There are certain analytical tasks requiring simultaneous quantification of several lanthanides in complex mixtures, e.g. in spent nuclear fuel reprocessing where lanthanides are fission products that must be removed from the media [17]; during processing of monazite — an important ore for rare earth elements [18] and during technological monitoring of various industrial solutions. This task can be addressed using modern analytical techniques like ICP-MS (inductively couple plasma-mass spectrometry) and AES (atomic emission spectroscopy). These methods, however, are quite expensive and time-consuming and extensive sample pretreatment is often required before the

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analysis. This lead to the search for other appropriate alternatives, e.g. there are some studies reporting application of chemical sensor arrays to resolve the triple mixtures of lanthanides [19], but precision and selectivity attained so far was not very high. Another potential candidate method for lanthanide mixture analysis can be EDX, however, having the above mentioned tasks in mind it appears that concentrations of targeted elements are quite low. Moreover, one can expect strong overlapping of the X-ray lines from neighboring lanthanides.

The purpose of this study is to assess the potential of PLS technique for improving XRF precision in simultaneous analysis of several lanthanides in complex mixtures. For this purpose two XRF methods were tested: EDX (energy-dispersive X-ray fluorescence) and TXRF (total reflection X-ray fluorescence). EDX is a very popular tool due to its simplicity and relatively low costs but it does not allow for high precision comparing to classic wavelength dispersive XRF and TXRF. Among these methods TXRF has demonstrated the lowest detection limits for lanthanides, but it requires much more expensive instruments and more sophisticated sample preparation.

2. Experimental

2.1. Samples

The samples for this study were the mixtures of six lanthanides: Ce, Pr, Nd, Sm, Eu, Gd. These mixtures were prepared from 0.1 M stock aqueous solutions of corresponding lanthanide nitrates in 0.01 M nitric acid that were kindly provided by Khlopin Radium Institute (St. Petersburg, Russia). Lanthanide concentrations in mixtures were varied in a range from 10^{-6} to 10^{-3} mol/L. After dilution the pH of all solutions was adjusted to 2 by nitric acid (pro analysis grade, Vekton, St. Petersburg, Russia). This concentration range was relevant to numerous practical analytical tasks, like quantification of lanthanides in monazite ores, analysis of spent nuclear fuel reprocessing media and other technological solutions. To design the mixtures we employed the approach reported in [20] based on a uniform distribution of samples in a concentration hyperspace. In this case we dealt with a six-dimensional concentration space (as there were six components of interest). The coordinates of each experimental point were given by concentrations of corresponding lanthanides. Algorithm allowed for choosing appropriate coordinates (concentrations) for a given number of experimental points in order to provide for uniform filling of the space. To obtain denser distribution of experimental points in the low concentration range we used logarithmic concentrations in design. The resulted compositions of the mixtures (in mol/L units) are given in the Table 1.

2.2. EDX measurements

EDX spectra of lanthanides' L-series were obtained using energy-dispersive X-ray fluorescence spectrometer Shimadzu EDX-800HS with rhodium anode X-ray tube and Si(Li) nitrogen cooled detector. 5 ml of sample solution was placed in a sample cup (2.5 cm in diameter) and covered by polypropylene film of 20-micrometer thickness. All

Table 1
Composition of the lanthanides' mixtures (mol/L).

#	Ce	Pr	Nd	Sm	Eu	Gd
1	3.5×10^{-5}	5.6×10^{-6}	1.1×10^{-4}	8.3×10^{-4}	1.5×10^{-4}	1.9×10^{-5}
2	1.1×10^{-4}	1.5×10^{-6}	2.4×10^{-6}	1.9×10^{-5}	1.4×10^{-6}	5.1×10^{-5}
3	6.6×10^{-4}	2.6×10^{-4}	3.7×10^{-4}	2.6×10^{-6}	1.3×10^{-5}	3.4×10^{-4}
4	2.5×10^{-6}	2.2×10^{-4}	9.5×10^{-4}	2.6×10^{-4}	2.2×10^{-6}	4.6×10^{-6}
5	1.2×10^{-6}	4.3×10^{-5}	3.5×10^{-6}	3.1×10^{-4}	1.1×10^{-6}	6.3×10^{-5}
6	4.4×10^{-6}	2.6×10^{-4}	2.1×10^{-5}	7.2×10^{-4}	5.2×10^{-4}	5.4×10^{-4}
7	1.1×10^{-6}	5.0×10^{-4}	9.5×10^{-4}	9.8×10^{-4}	3.2×10^{-5}	4.9×10^{-5}
8	1.3×10^{-5}	1.1×10^{-6}	2.5×10^{-6}	2.3×10^{-4}	2.2×10^{-6}	5.8×10^{-6}
9	1.3×10^{-5}	1.1×10^{-6}	1.8×10^{-4}	6.8×10^{-6}	6.5×10^{-5}	1.1×10^{-6}
10	1.7×10^{-4}	3.6×10^{-6}	1.9×10^{-6}	6.3×10^{-4}	1.2×10^{-5}	3.7×10^{-5}
11	6.5×10^{-4}	3.2×10^{-4}	6.2×10^{-4}	3.0×10^{-5}	2.0×10^{-5}	3.5×10^{-6}
12	4.0×10^{-5}	2.5×10^{-4}	5.9×10^{-4}	5.4×10^{-4}	6.9×10^{-5}	3.3×10^{-5}
13	9.5×10^{-4}	1.9×10^{-5}	2.5×10^{-5}	3.7×10^{-6}	3.5×10^{-6}	4.9×10^{-6}
14	6.5×10^{-6}	1.3×10^{-6}	6.5×10^{-6}	1.4×10^{-5}	1.1×10^{-5}	1.0×10^{-6}
15	2.8×10^{-5}	1.9×10^{-5}	7.6×10^{-6}	1.0×10^{-6}	2.0×10^{-6}	3.5×10^{-6}
16	8.3×10^{-5}	1.0×10^{-6}	5.9×10^{-4}	2.1×10^{-6}	5.1×10^{-5}	2.5×10^{-5}
17	2.3×10^{-6}	1.1×10^{-6}	8.3×10^{-4}	1.1×10^{-4}	2.6×10^{-6}	5.8×10^{-5}
18	3.2×10^{-6}	1.6×10^{-6}	1.1×10^{-4}	2.0×10^{-4}	1.7×10^{-4}	1.7×10^{-6}
19	3.7×10^{-4}	4.9×10^{-4}	2.4×10^{-4}	7.4×10^{-4}	5.9×10^{-6}	1.7×10^{-4}
20	4.4×10^{-5}	4.5×10^{-5}	4.3×10^{-6}	3.2×10^{-5}	1.0×10^{-6}	1.1×10^{-6}
21	1.1×10^{-6}	1.0×10^{-6}	1.5×10^{-6}	1.3×10^{-4}	7.4×10^{-4}	5.5×10^{-6}
22	4.4×10^{-6}	1.0×10^{-3}	7.4×10^{-6}	2.8×10^{-6}	5.2×10^{-5}	3.0×10^{-5}
23	8.3×10^{-5}	4.1×10^{-5}	3.0×10^{-5}	8.3×10^{-4}	5.8×10^{-5}	5.9×10^{-4}
24	2.0×10^{-6}	3.7×10^{-5}	5.2×10^{-5}	8.9×10^{-4}	7.9×10^{-6}	3.8×10^{-6}
25	7.9×10^{-5}	3.2×10^{-4}	3.5×10^{-5}	5.0×10^{-6}	1.4×10^{-4}	5.0×10^{-4}
26	2.5×10^{-5}	9.1×10^{-5}	1.1×10^{-6}	2.6×10^{-6}	2.7×10^{-4}	2.9×10^{-5}
27	1.0×10^{-3}	1.0×10^{-6}	2.7×10^{-4}	9.1×10^{-4}	1.7×10^{-4}	1.5×10^{-5}
28	6.2×10^{-5}	1.4×10^{-6}	6.6×10^{-4}	7.8×10^{-6}	1.6×10^{-6}	6.3×10^{-5}
29	1.0×10^{-4}	2.3×10^{-6}	9.3×10^{-5}	1.0×10^{-6}	1.2×10^{-6}	8.1×10^{-4}
30	1.3×10^{-5}	1.0×10^{-3}	9.5×10^{-4}	2.5×10^{-5}	4.3×10^{-5}	1.5×10^{-4}
31	1.4×10^{-6}	9.8×10^{-4}	1.0×10^{-6}	5.6×10^{-5}	2.8×10^{-5}	2.2×10^{-4}
32	1.0×10^{-3}	1.9×10^{-6}	1.2×10^{-4}	1.4×10^{-4}	4.8×10^{-6}	9.5×10^{-4}
33	1.1×10^{-6}	1.0×10^{-6}	6.8×10^{-6}	2.4×10^{-4}	4.3×10^{-4}	6.5×10^{-5}
34	5.4×10^{-6}	1.1×10^{-6}	9.5×10^{-4}	2.2×10^{-4}	5.2×10^{-5}	8.1×10^{-4}
35	4.0×10^{-6}	1.9×10^{-6}	6.8×10^{-5}	8.9×10^{-6}	2.5×10^{-6}	1.9×10^{-6}
36	8.1×10^{-4}	1.0×10^{-6}	2.3×10^{-4}	5.4×10^{-5}	8.5×10^{-4}	3.1×10^{-5}
37	3.6×10^{-6}	4.6×10^{-5}	2.5×10^{-5}	4.9×10^{-6}	1.0×10^{-6}	3.0×10^{-4}
38	4.4×10^{-4}	3.2×10^{-5}	4.9×10^{-4}	1.7×10^{-6}	2.7×10^{-4}	1.0×10^{-6}
39	1.9×10^{-5}	2.8×10^{-5}	5.6×10^{-6}	4.5×10^{-6}	1.5×10^{-4}	1.9×10^{-5}
40	5.5×10^{-4}	2.1×10^{-4}	6.2×10^{-4}	3.2×10^{-5}	4.3×10^{-6}	1.7×10^{-5}