

# Quantification of lanthanides in complex mixtures with X-ray fluorescence: three-point calibration models by correlation constrained MCR-ALS

*B. Debus<sup>1</sup>, D.O. Kirsanov<sup>1,2</sup>, V. V. Panchuk<sup>1,2</sup>, A.A. Goydenko<sup>1</sup>, V.G. Semenov<sup>1</sup>, A. Legin<sup>1,2</sup>*

*<sup>1</sup>Institute of Chemistry, St. Petersburg State University, St. Petersburg, Russia*

*<sup>2</sup>Laboratory of Artificial Sensory Systems, ITMO University, St. Petersburg, Russia*

Total reflection X-ray fluorescence (TXRF) is a technique of choice for various tasks where high sensitivity and selectivity are required. From a single TXRF spectrum both qualitative and quantitative information can be derived based on the position and the intensity of the X-ray fluorescence radiation, respectively. Despite its high sensitivity, the interpretation of TXRF spectra can be challenging in situations where several chemical elements are analyzed simultaneously. Experimentally, the absorption of fluorescence radiation from one element by other chemical elements of the matrix and the overlapping of characteristic lines from neighboring elements may occur. One consequence of such so-called matrix effects is that low detection limit cannot be achieved which hinders the use of TXRF in certain applications.

In an attempt to improve the precision in quantification of individual elements in complex mixtures, first-order calibration methods have been proposed. Recently, partial least-squares (PLS) was proposed for the quantification of a six elements lanthanide mixtures from TXRF spectra [1]. The main advantage of multivariate methods like PLS compared with classical approaches such as ordinary least-squares is that matrix effects can be accommodated by the model yielding adequate calibration with better precision. The only pre-requisite to perform PLS is the number of samples which should be large enough to select a relevant calibration and test sets. This can be a limitation in situation where measurement costs are high or access to the measurement set-up is limited.

To overcome this limitation, we propose to use the correlation constrained MCR-ALS method recently suggested in [2]. This implies the implementation of known concentration values of the target analyte in calibration set during the ALS iteration to reach unique solution. Compared with PLS, correlation constrained MCR-ALS yields similar precision but enables the recovery of pure spectra of individual lanthanides. The most intriguing feature is the possibility to simultaneously predict the concentration of all analytes from a set of three-point calibration models with RMSEP values around  $1.10^5 \text{ mol.L}^{-1}$ . This promising result indicates



that accurate quantification of chemical elements in TXRF spectroscopy can be achieved with a minimal number of calibration samples whereas larger amount of samples is required for PLS.

## **References**

1. D. Kirsanov et al. *SpectrochimicaActa Part B* 113 (2015) 126–131
2. G. Ahmadi et al. *Chemometrics and Intelligent Laboratory Systems* 142142 (2015) 143–150

