APPLICATION OF MULTI-WAY PARTIAL LEAST SQUARES CALIBRATION FOR SIMULTANEOUS DETERMINATION OF RADIOISOTOPES BY LIQUID SCINTILLATION TECHNIQUE

by

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Three-way partial last squares (3-PLS2), as a multi-way calibration method was applied for determining the $^{235}U/^{238}U$ isotope ratio to overcome problems with spectral interferences in liquid scintillation spectra of these radioisotopes. The alpha energy spectra of samples in different energy channels and different cocktail to sample ratios were used as input data for 3-PLS2. The model was applied to a prediction set and satisfactory results were obtained. The 3-way PLS2 prediction results were compared with 2-way PLS2 and it was shown that 3-way PLS2 results are more accurate than the results of PLS2. Thermal ionization-mass spectrometry was used as a reference method for calculating the accuracy of our method.

Key words: multiway calibration, 3-PLS2, liquid scintillation, uranium isotopes

INTRODUCTION

Uranium isotopes are important radioactive species in natural samples. Determination of the isotopic composition and concentration of uranium is an important concern in the nuclear industry and environmental studies [1-3]. Various techniques such as thermal ionization mass spectrometry (TI-MS) and inductively coupled plasma mass spectrometry (ICP-MS) can be employed for the isotopic analysis of uranium [4, 5]. In the absence of mass spectrometric techniques, other techniques such as alpha and gamma spectrometry [6, 7] and liquid scintillation counting (LSC) can also be used for this purpose. Inductively coupled plasma atomic emission spectrometry can also be used for uranium isotope ratio measurements [8]. LSC is one of the important techniques for analysis of low level radionuclides in environmental samples [9-13]. Due to severe spectral interferences between energy spectra of some radionuclides, their simultaneous determination by LSC has a serious problem [14]. Several efforts have been made to overcome this problem. Forte *et al*. [3] determined uranium isotopes in food and environmental samples by LSC, using Canberra Genie 2000 Interactive Peak Fit Software (v. 1.0) designed for gamma and alpha spectrometry. They successfully determined ^{238}U and ^{234}U but could not determine ^{235}U. Recently, Bianchi *et al*. proposed a procedure for determination of the uranium isotope ratio in liquid samples using LSC. They proposed a method for measurement of isotopic content of ^{234}U with respect to ^{238}U, which is an indirect measure of ^{235}U enrichment. Another approach for determination of $^{235}U/^{238}U$ in enriched uranium fuel samples using LSC has been proposed by Alumela [1]. In this method, a linear correlation between $^{235}U/^{238}U$ and the ratio of total count rate to the Cerenkov count rate (due to ^{234m}Pa) has been obtained.

Multivariate calibration techniques have been increasingly used for overcoming spectral interference problems [14-18]. As the dimension of the output data is increased, the multi-way approach has become an attractive subject in chemometrics for modeling and interpretation of multi-way data [19-29]. These techniques can decompose the data array and process the data. Lohmoller *et al*. [30] showed that a 3-way array can be decomposed as a Kronecker product of a vector and matrix. Wold *et al*. [31] used the optimality proof by Lohmoller *et al*. [30] to develop the NIPALS algorithm for decomposing a multi order array. This method is known as unfold-PLS because it is the result of unfolding or metricizing the predictor array and

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then modeling the matrix using ordinary PLS [32]. Stahle [33] also tried to construct a trilinear PLS algorithm. These algorithms lack the maximum covariance between scores and the dependent variables in a trilinear sense. Bro [34] proposed a generalization of PLS to multi-way situations, called multi-linear PLS. This method is a combination of a trilinear model (PARAFAC) and PLS and was commented on by Smilde [7, 35] and de Jong [7]. An improved model of a multi-way array was later introduced which, however, maintains the same predictions as the original model [36]. Multi-linear PLS algorithm is fast and easy to interpret and can be used for solving spectral overlap problems.

In this paper, a new procedure for determination of ^{235}U/^{238}U has been proposed. In this method 3-PLS2, as a multi-way technique, was applied for determination of the ^{235}U/^{238}U ratio. The prediction results were compared with 2-PLS2. Thermal ionization mass spectrometry has been used as the reference method.

MATERIAL AND METHODS

Reagents

High capacity cocktail Optiphase Hisafe 3 (Wallac Oy, Turku, Finland) and ultrapure water were used throughout the work. Depleted uranyl nitrate (Merck, Darmstadt, Germany) and natural U_3O_8 were used for preparation of standard solutions. All other reagents were of analytical grade and were purchased from Merck (Darmstadt, Germany) or Sigma-Aldrich (Saint Louis, USA).

Apparatus

An ultra-low level liquid scintillation spectrometer Quantulus 1220 (Wallac Oy, Turku, Finland) was used for measuring counting rates. A shaker Heidolph Vibramax 100 (Heidolph Co., Schwabach, Germany) was utilized for mixing the cocktail and sample. The samples and cocktail were mixed in 20-ml polyethylene vials, Polyvial (Zinsser Analytical Co., Frankfurt, Germany).

Software and data processing

Wallac spectrum analysis (v.2.15) allows data collection from the Quantulus instrument and analysis of emission spectra. This program was run on a computer (Pentium II 300 MHz) with the MS-DOS operating system. The output files were ASCII; thus, a laboratory-written program in Turbo Pascal v.7.0 (Borland International, Inc.) was used for data extraction from output files. N-way Toolbox for MATLAB (by Rasmus Bro and Claus A. Anderson, University of Copenhagen) was used for 3-PLS2 modeling. These programs were run in MATLAB (R 2010 a, Version 7.10) on a PC (Pentium IV 2.5 GHz) with the Microsoft windows 7 operating system.

Procedure

Stock solutions of depleted and natural uranium samples were prepared from depleted uranyl nitrate and natural uranium oxide. Nitric acid 1% volume to volume ratio was added to stock solutions for avoiding the aging effect. Known volumes of stock solutions, cocktail and ultrapure water with final volume of 20 ml were mixed in polyethylene vials. Eighty mixtures in 8 different total uranium concentrations (60, 70, 80, 90, 100, 110, and 120 μg/ml) from natural and depleted solutions in 5 different cocktail to sample ratios (2.33, 3, 4, 5.67, and 9) were prepared. The sample vials were placed in a shaker for 5 minutes and the outer surfaces were cleaned with acetone. The vials were stored in a cool, dark shield in a refrigerator (7 °C for 2 hours) for eliminating cocktail fluorescence. All of them were analyzed by LSC for about 70 minutes and the resulting counting rate for alpha particles in different channels (1024 channels) was used for the next step. In the final step the data were preprocessed and subjected to 3-PLS2 modeling. The model was applied for prediction of ^{235}U and ^{238}U in new synthetic samples.

Thermal ionization mass spectrometry was used as a reference method. The analysis of samples was performed using a thermal ionization mass spectrometer (MAT-260, Finnigan) during three steps and with a one week interval. The rhenium filaments (9.5 mm 0.6 mm 0.04 mm dimension and under 10^{-6} mbar vacuum) were cleaned by 4 A current for 25 minutes. Two microliters of samples were deposited on the filaments by micropipette. The filaments were dried by a preparation heating unit with a 2 A current for 5 minutes and a homogenous layer was formed on the filaments. The ion source and analyzer were under 10^{-7} and 10^{-8} mbar respectively. For a stable ionic current the ionization and vaporization filaments were heated by 5.5 A and 2.6 A. The magnetic field for the mass range was changed with 10 kV accelerating voltage.

RESULTS AND DISCUSSION

In the present work, the activity of synthetic mixtures (counts per minute, cpm) was recorded in 1024-channels. The difference between the alpha energy peak of ^{235}U and ^{238}U is lower than the resolution of the instrument (according to the manual, the resolution of the Quantulus 1220 is 300 keV for alpha energy peaks [37])

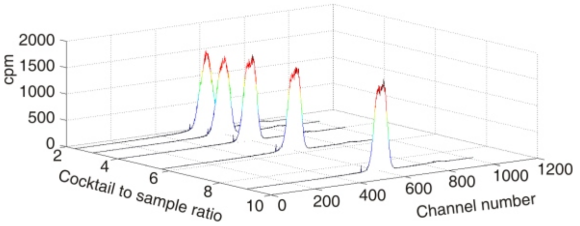

Figure 1. Waterfall of natural uranium samples (60 g/ml) in different cocktail to sample ratios

and severe spectral interference prevents a baseline separation for these radioisotopes. A three dimensional figure of natural uranium samples (60 μg/ml) in different cocktail to sample ratios is shown in fig. 1. As shown in fig. 1, despite the fact that the cocktail to sample ratio can affect the spectra of natural uranium samples, the severe spectral interference is present in all of the samples.

Two types of variables were used: energy channels of alpha emissions and sample to cocktail ratios. The cocktail to sample ratio variable was used as a second type variable. The counting rates of alpha particles at 1024 channels were used as a first type variable. Due to the large number of variables in the data set that results in complexity and due to zero count rates in some channels, the channels that have zero count rates for about 90% of the samples were removed from the data set. After this, the numbers of first type variables were reduced from 1024 to 806. The second type variable has an important limitation so the cocktail to sample ratio must be in the range that the sample dissolves in the cocktail and produces a homogeneous mixture.

Data preprocessing

Extension of mean centering and scaling from two-way data to three-way data were discussed by Bro *et al*. [38]. In this study, centering across the first mode [39] and scaling within the second mode were performed. The results showed that preprocessing on this data set results in lower errors and produce a better model. The results before and after preprocessing are shown in tab. 1.

Selection of the optimal number of factors

In N-PLS regression, such as in other latent variable based methods, the optimal number of components must be determined for obtaining the most reliable predictions. Determining the number of components in three-way regression models is usually performed in a similar manner as is done in two-way analysis. One approach that can be used for this purpose is cross validation [36]. The minimum point in the plot of the sum of square of differences between the predicted and the actual values versus the number of latent variables in the model can be used as the optimum number of factors. In our cross validation procedure, the number of optimal components was selected according to the minimum of the root mean square error of prediction (RMSEP) versus the number of latent variables , *i. e.* five factors with respect to fig. 2.

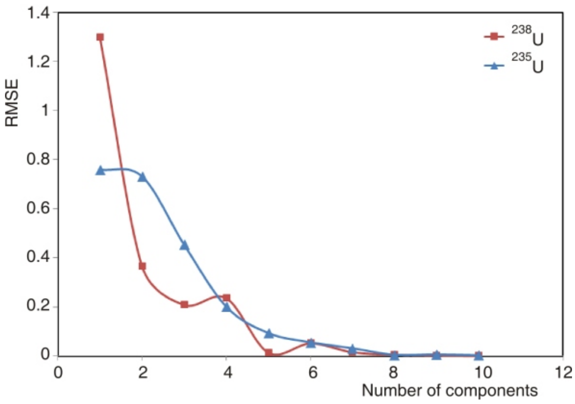

Figure 2. RMSE *vs.* the number of components for prediction by 3-PLS2

Modeling and prediction by 3-PLS2

The data set containing the 16 677 5 array of energy spectrum of samples in different energy channels and different cocktail to sample ratios were fed into the training (13 677 5) and prediction set (3 677 5). The training set was modeled by the

Table 1. Prediction results and relative error of prediction (RE) for ^{238}U and ^{235}U concentrations by 3-PLS2 with and without preprocessing

Sample	^{238}U					^{235}U				
	Actual [ppm]	Prediction^a	RE	Prediction^b	RE	Actual [ppm]	Prediction^a	RE^c	Prediction^b	RE
1	79.76	82.11	–2.95	83.80	–5.06	0.24	0.24	1.93	0.27	–13.11
2	89.37	96.34	–7.8	86.97	2.68	0.63	0.63	–0.55	0.57	9.77
3	59.7	61.67	–3.30	47.15	21.02	0.30	0.30	–0.25	0.22	27.00

[a] with 5 components for the preprocessed data set
[b] with 5 components for without the preprocessing data set
[c] the prediction results were reported with two significant figures and errors were calculated with all figures

Table 2. Prediction results of ^{238}U and ^{235}U by the 3-PLS2 calibration model

Sample	Type	^{235}U			^{238}U			^{235}U/(^{235}U + ^{238}U) [%][a]	^{235}U/(^{235}U + ^{238}U) [%][b]	TIMS [%][c]
		Actual [ppm]	3-PLS2	2-PLS2	Actual [ppm]	3-PLS2	2-PLS2			
1	Depleted	0.24	0.24	0.24	79.76	82.11	83.82	0.29	0.28	0.3
2	Natural	0.63	0.63	0.663	89.37	96.34	91.27	0.65	0.72	0.7
3	Mixture[d]	0.30	0.30	0.31	59.70	61.67	60.33	0.49	0.51	0.5

[a] the isotope abundance percent for the 3-PLS2 model result
[b] the isotope abundance percent for the 2-PLS2 model result
[c] the isotope abundance percent was obtained from thermal ionization mass spectrometry
[d] A 1:1 mixture of natural and depleted uranium

3-PLS2 method. The constructed model was used for prediction of uranium isotopes concentrations (^{235}U and ^{238}U) in the prediction set for the assessment of the model. Table 2 shows the prediction results by 3-PLS2 on the prediction set.

Comparison with 2-PLS2 and TI-MS

The data set containing the 13 766 matrix of the net count rates of 13 synthetic natural and depleted uranium samples in a selected cocktail to sample ratio (2.33) was used for two-way analysis. The constructed model was applied to the prediction set (3 677). The results of prediction by 3-PLS2 and 2-PLS2 were compared with thermal ionization-mass spectrometry as a reference method (tab. 2). The results show that the proposed method is a rapid and economical technique for determination of ^{235}U and ^{238}U in comparison with TI-MS.

CONCLUSIONS

Combination of multi-way PLS (3-PLS2) with the liquid scintillation counting technique was developed as a quick and simple procedure for determination of the ^{235}U and ^{238}U isotope ratio. This method was applied for simultaneous determination of ^{235}U and ^{238}U in synthetic uranium samples. It was shown that the predicted results are more accurate than the results by two-way PLS2. In this study, the 3-PLS2 model was constructed in the absence of the ^{235}U pure spectrum. This method can be applied for quantitative determination of other radionuclides (alpha and beta emitters).

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ПРИМЕНА КАЛИБРАЦИЈЕ ВИШЕСТРУКОМ МЕТОДОМ ПАРЦИЈАЛНИХ НАЈМАЊИХ КВАДРАТА ЗА СИМУЛТАНО ОДРЕЂИВАЊЕ РАДИОИЗОТОПА ПОСТУПКОМ ТЕЧНЕ СЦИНТИЛАЦИЈЕ

Метода троструких парцијалних најмањих квадрата (3-PLS2) употребљена је као начин вишеструке калибрације за одређивање односа изотопа ^{235}U и ^{238}U, ради превазилажења проблема са спектралном интерференцијом у поступку течне сцинтилације ових радиоизотопа. Спектри енергија алфа честица узорака на различитим енергетским каналима и при различитим односима коктела и узорака, коришћени су као улазни подаци за 3-PLS2. Модел је примењен на изабрани узорак и добијени су задовољавајући резултати. Предикција 3-PLS-а упоређена је са резултатима добијеним уз помоћ 2-PLS2 и показало се да су тачнији резултати добијени методом 3-PLS2. Као референтна метода за одређивање течности коришћена је масена спектрометрија термалном јонизацијом.

Кључне речи: вишеструка калибрација, 3-PLS2, течна сцинтилација, уранијумски изотопи