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Talanta

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# A combination of dynamic measurement protocol and advanced data treatment to resolve the mixtures of chemically similar analytes with potentiometric multisensor system

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## ARTICLE INFO

### Article history:

Received 14 July 2013

Received in revised form

30 October 2013

Accepted 3 November 2013

Available online 13 November 2013

### Keywords:

Multisensor systems

Lanthanides

Mixture analysis

Chemometrics

## ABSTRACT

Data processing techniques and measuring protocol are very important parts of the multisensor systems methodology. Complex analytical tasks like resolving the mixtures of two components with very similar chemical properties require special attention. We report on the application of non-linear (artificial neural networks, ANNs) and linear (projections on latent structures, PLS) regression techniques to the data obtained from the flow cell with potentiometric multisensor detection of neighbouring lanthanides in the Periodic System of the elements (samarium, europium and gadolinium). Quantification of individual components in mixtures is possible with reasonable precision if dynamic components of the response are incorporated thanks to the use of an automated sequential injection analysis system. The average absolute error in prediction of lanthanides with PLS was around  $1 \times 10^{-4}$  mol/L, while the use of ANNs allows the lowering of prediction errors down to  $2 \times 10^{-5}$  mol/L in certain cases. The suggested protocol seems to be useful for other analytical applications where simultaneous determination of chemically similar analytes in mixtures is required.

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## 1. Introduction

There are a number of analytical applications that require quantitative analysis of mixtures, where the constituents have a very similar chemical nature. As an example, one can consider lanthanides determination in various technological solutions or in PUREX (Plutonium–Uranium Extraction) process raffinate of spent nuclear fuel reprocessing. Being close neighbors in the Periodic System of the elements, lanthanides have closely similar chemical properties and the task of their simultaneous determination can be effectively handled with “heavy” instrumental methods, such as e.g. ICP-MS (inductively coupled plasma mass spectrometry). However, these ICP-based methods are usually hard to implement in on-line mode and they require significant amount of consumables, skilled personnel and long sample preparation. There is a need for simple and inexpensive methods that could allow simultaneous quantification of several chemical

substances of very analogous properties. One of the reasonable alternatives for existing “heavy” methods could be electrochemical sensors. There are a lot of reports in literature on the development of potentiometric sensors for selective determination of lanthanides, such as cerium [1,2], samarium [3,4], europium [5,6], etc., but the pH working range reported in these papers is usually around 4–8 pH units. It is not quite clear which ions promote sensor response at these pH level, since  $\text{Me}^{3+}$  is only present in strongly acidic media. Besides that the reported selectivity values of such sensors are usually rather high ( $\log K_{M,RE} < -2$ ) even in the presence of neighboring lanthanides, and this is quite surprising taking into account very similar ionic radii and chemical properties of lanthanides. The authors of these papers usually do not discuss the nature of such outstanding performance. In most of the cases the measurements are performed in individual solutions of the lanthanides. There are reasonable doubts if the reported data can be extrapolated to the real performance of the sensors in complex mixtures. One of the possible ways for development of fast and inexpensive methods for lanthanides detection is the employment of a multisensor system approach [7]. The main idea of this approach (also called as an electronic tongue) is to measure the samples with an array of chemical sensors with high cross-sensitivity

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towards variety of analytes and to process the resulted unresolved analytical signal from this array by means of multivariate statistics techniques [8]. As an output from this system one can have both qualitative and quantitative chemical information depending on the scope of study and on the methods employed. This type of systems was recently successfully applied for simultaneous determination of rare earth metals (REs) concentrations in complex mixtures simulating spent nuclear fuel reprocessing media [9]. As a further extension of this approach it seems reasonable to try an application of such a system in flow cell conditions. Besides the obvious advantage of simple automation this type of measurement implementation has another important issue – a possibility of dynamic potentiometric measurements, i.e. one can track the evolution of the sensor response in time, and this kinetic information can be used in data processing. The shape of the sensor response curve in a time domain can contain valuable chemical information about the sample and this information is lost when only stationary signal of sensor is employed for processing. It was shown that this approach is quite viable in other applications [10–12]. However, dynamic potentiometric data are more complex in nature compared to the ordinary potentiometric signals and pose a certain challenge from the data processing point of view. One of the possible divisions of chemometric techniques (however quite artificial) is to distinguish linear (e.g. principal component analysis (PCA) and projections on latent structures (PLSs)) and non-linear (e.g. artificial neural networks (ANNs) and support vector machines (SVMs)) methods. Both of these data processing groups are in use in the multisensor systems field. Furthermore, in [13] a wide literature survey was performed which revealed that most of the papers devoted to electronic tongues are mainly dealing with only three data processing techniques: PCA, PLS and ANN. This confirms that these methods are powerful and reliable for extracting valuable chemical information from multisensor system's experimental data. When quantitative chemical analysis is in sight both linear and non-linear regression methods can be employed.

This paper is devoted to the comparison study of the linear and non-linear regression techniques applied to the dynamic potentiometric data from double mixtures of chemically similar lanthanide ions. As linear methods three different PLS modes were implemented: ordinary PLS with stationary potentiometric signals as input variables, PLS with the whole response curves unfolded over time axis and multi-way PLS (nPLS) with time axis as a third dimension in data (samples  $\times$  sensors  $\times$  time). As non-linear methods, different approaches based on artificial neural networks (ANNs) were evaluated including the use of steady state signal and the compression of the dynamic profile employing the *windowed slicing integral* (Int) method [14].

## 2. Experimental

### 2.1. Sensor preparation

The sensor array employed in this study consisted of eight polymeric PVC-plasticized sensors described previously [9]. Active compounds for sensor membranes were various neutral ligands adopted from liquid extraction systems plus chlorinated cobalt dicarbollide (CCD) as a cation-exchanger. All sensor membranes contained 50 mmol/kg of a neutral ligand and 10 mmol/kg of CCD (0.53 wt%). The details on active substances are given in Table 1. Also each sensor membrane contained 33 wt% of poly(vinylchloride) (PVC), and the rest was of *o*-nitrophenyloctyl ether (NPOE) as a solvent-plasticizer (both PVC and NPOE were Selectophore grade from Fluka).

Sensor membranes were prepared according to the standard procedure: weighted amounts of membrane components were dissolved in freshly distilled tetrahydrofuran (THF) and poured

**Table 1**  
Sensor membrane compositions.

Sensor	Active substance	Concentration (wt%)
s1	Tetraphenylmethylenediphosphine dioxide	2.08
s2	Phenylloctyl- <i>N,N</i> -di- <i>i</i> -butylcarbamoylmethylen phosphine oxide	2.03
s3	1,9-Bis-(diphenylphosphynyl)-2,5,8-trioxanonane	2.67
s4	1,6-Bis-(benzylphenylcarbamoyl)-3-benzo-2,5-oxahexane	2.78
s5	1,9-Bis-(diphenylcarbamoyl)-2,5,8-trioxanonane	2.62
s6	<i>N,N,N',N'</i> -tetraoctyldiamide of diglycolic acid	2.90
s7	<i>N,N'</i> -diethyl- <i>N,N'</i> -di- <i>p</i> -tolylidamide of dipicolinic acid	1.53
s8	5,11,17,23-Tetra (diethylcarbamoylethoxymethylcarboxamido)-25,26,27,28-tetrapropoxycalix[4]arene	6.67

into a flat-bottomed Teflon beaker and left overnight for solvent evaporation. Disks 4 mm in diameter and 0.5 mm thick were cut from the parent membranes and covered on one side with a suspension of fine graphite powder in a PVC–cyclohexanone mixture. After drying for 24 h the membranes covered with solid electric contact composition were mounted in the flow cell and fixed in the channel with clamping plastic bodies. On the top of each body there was a gold spot to provide electric contact. Thus the sensor design employed in this study was similar to the coated wire type. The resulting sensors were encoded as s1, s2, ..., s8 in the order of appearance above. The whole construction made of the sensors mounted in the flow cell is shown in Fig. 1.

The flow cell was developed in the framework of FP6 WARMER project and was produced by MedbrytSp. z o.o (Warsaw). This flow cell consists of poly(methylmethacrylate) segments (PMMA) that can be hermetically attached to each other to produce the flow cell with necessary number of sensors. For this study we used nine segments, eight for polymeric sensors and one for Ag/AgCl reference electrode (MedbrytSp. z o.o). Reference electrode was mounted in the middle of the flow path to minimize electric resistance of the system. The inner diameter of the flow path was 1 mm.

### 2.2. Potentiometric measurements

Potentiometric measurements were performed in a sequential injection system (SIA) which provides the automated operation and generation of RE metal mixtures, plus the measuring and data acquisition stages. The SIA system was formed by two differentiated parts: the fluidic system and the measurement system [15,16].

The first part was the fluid system which consisted of an automatic microburette (Crison 2030 microburette, Crison, Spain) equipped with a 5 mL syringe (Hamilton, Switzerland), a holding coil (5 m  $\times$  1 mm i.d. PTFE tubing, Bioblock, France), a 8-way Hamilton MVP valve (Hamilton, Switzerland) and a 7 mL Perspex mixing cell (home built) with a magnetic stirrer. The multiport valve is connected to the burette with the holding coil placed in between. The burette is fed through a carrier solution reservoir. By commanded sequence, the common port of the valve may access any of the other ports which leads to the sample, standard stock solutions, mixing chamber or sensor array by electrical rotation. All the elements were connected together using low pressure liquid chromatography connectors.

The second part was the measurement system that comprised the sensor array, a reference electrode (miniaturized silver/silver chloride electrode with a double junction) and an 8-channel signal conditioning circuit connected to the data acquisition

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