DECLAB: a software for liquid scintillation spectra deconvolution

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Abstract

The deconvolution of liquid scintillation (LS) spectra is meaningful in several scenarios like supporting incomplete radio-chemical separations, for screening purposes and determining different isotopes of the same element, which is explored in this paper for the case of ^{89}Sr/^{90}Sr. In this paper *DECLAB*, an online application for liquid scintillation spectra analysis is presented. The software considers the classical calibration modes like constant efficiency and quenching curve and further-more, the deconvolution of multicomponent spectra by means of Partial Least Square Regression. *DECLAB* is designed to analyse Perkin Elmer Wallac Quantulus 1220 spectra. However, in further upgrades, the applicability of this tool will be extended to other LS spectrometers.

Keywords Liquid scintillation spectrometry · Deconvolution · Beta emitters · Strontium · Data analysis software ·
DECLAB

Introduction

Liquid scintillation spectrometry (LSS) is a commonly used technique for the determination of alpha and beta emitters, and it has played a leading role in the radiometric charac-terization of several kind of samples, from surveillance of the environment to managing of nuclear waste produced in industrial facilities. Due to its high detection efficiency LSS has become the standard technical solution for the quan-tification of hard to measure radionuclides, which usually are low energy beta emitters. LSS has high efficiency due to its 4π geometry but poor resolution, which hinders the identification of specific radionuclides in mixtures because of the spectra overlapping. In the case of beta emitters, this overlapping is unavoidable due to its continuous spectra. For this reason, the sample dissolution is usually preceded by a chemical isolation of the target radionuclides before LSS measurement. Therefore, the common procedure for hard to measure radionuclides determination is, in a first step, the dissolution of the sample, after that, the isolation of the target radionuclides by means of physical or, more often, a chemical separation and finally its measurement by LSS. However, is not always possible to obtain pure LS spectra. The main reason is that, in some cases, the sam-ple could contain different radionuclides from the same element, which cannot be separated chemically. Another non-minor issue is the difficulty in removing all the radio-chemical interferents in samples with a huge amount and relative high activity of them. In those cases, either for an ineffective radiochemical procedure or due to the complexity of the sample (kind of matrix or number and activity of the interferers), the complete isolation of the target radionuclide cannot be achieved. Furthermore, in these cases the incom-pleteness of the chemical separation can just be noticed after LSS measurement. In those instances, deconvolution of the obtained spectrum could be an interesting strategy to iden-tify the interferers, to improve the radiochemical separation, and even subtract their contribution in the determination of the target radionuclides. Furthermore, the analysis of the spectra obtained from different screening parameters like gross alpha and gross beta, which have taken an increasing importance as a result of the drinking water European direc-tive [1], can provide additional information from the sample without further measurements.

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For this reason, several authors put their effort to achieve the quantification of several radionuclides from the same LS spectrum using different approaches. Among these approaches stand out, for binary mixtures, the definition of counting windows with contribution of one or both radionuclides [2, 3] and the use of the mass centre of the spectrum [4].

The advances in computation also permitted the development of new deconvolution techniques as the fitting of the sample spectrum to a combination of single emitter standard spectra [5], to a linear combination of tailed Gaussian functions [6, 7] or to a Fourier series [8, 9].

Other approaches for the unfolding of multicomponent spectra are based on the use of multivariant calibrations like Partial Least Squares regression (PLS) [10, 11] which in turn may be improved using artificial neural networks (ANN) to select the channels used for the PLS model construction [12]. ANN may be also used directly to accomplish the aim of separating the contribution of different beta emitters at the same LS spectra [13].

The approach followed by our research group is the construction of PLS models using spectra obtained from standard solutions in a calibration step. In a subsequent step of sample analysis, the quantification of the radionuclides included in the calibration is performed. PLS is a statistical method that reduces the predictors (in the studied case, the counts in each channel of LS spectrum) to a smaller set of uncorrelated principal components and performs least-squares regression on these components, instead of on the original data.

LS spectra deconvolution using PLS has several advantages in front of other approaches. Since the spectrum of the sample is not compared to theoretical shapes but to measured standard spectra, it can be used for the determination of several emitters (α, β^+, β^- and EC). It also allows the construction of libraries considering a range of quenching levels for each radionuclide in order to determine the activity of mixtures at different quench levels. This calculation method has been proved useful for the determination of up to 6 radionuclides from the same spectrum obtaining promising results [14]. However, in PLS quantification the calibration set must be representative of the sample, so in order to ensure a fit result, it is necessary to use a calibration set which contain all radionuclides included in the test sample, and with the same quench level of the sample.

In previous works, our research group proved the feasibility of multivariate calibration by PLS for LS spectra deconvolution with a method developed using the software *Matlab*™, a licensed software of *MathWorks*®, to support non-complete chemical separations and for screening purposes. For non-complete chemical separations, we achieve the simultaneous determination of ^{226}Ra, ^{228}Ra and ^{210}Pb in water samples using Radium RAD disks with biases lower than 10% for ^{226}Ra and ^{228}Ra, and below 15% for ^{210}Pb [15]. In that case, PLS deconvolution enhances the separation between ^{228}Ra and ^{210}Pb, which is not complete with RAD disk separation. Regarding screening parameters like gross alpha and beta, we demonstrate that it is possible to quantify specific radionuclides by PLS regression obtaining biases lower than 15% for all the studied radionuclides [16]. It should be noted that the more information of the sample is known the fitter the model constructed can be, and hence, better results are obtained as it is demonstrated in a previous work [17].

Finally, the separation of isotopes of the same element by PLS-LSS using *Matlab* has been explored in this paper for the ^{89}Sr/^{90}Sr case.

Nevertheless, the calculations involved in PLS deconvolution are not easy to perform in routine laboratories since the use of a specialized software is required. For these reasons, in order to provide Spanish laboratories involved in radiological environmental surveillance with a tool for LS spectra deconvolution, we developed *DECLAB*, an online *Python* application based on PLS model construction.

PLS method

Even though PLS in not a common technique for LS spectra analysis, it is a widely used method for infra-red (IR) and near infra-red (NIR) [18–20] spectra analysis. This method relates X (the spectra) and Y (the concentration of some analytes) via a multivariate linear model which can process data in the presence of multicollinearity, and in cases in which the number of calibration spectra is less than the number of predictor variables (channels of the spectrum). The PLS regression model can be expressed by the following Eqs. 1 and 2 [21]:

$$X = \mathrm{TP}' + E \tag{1}$$

$$Y = \mathrm{TC} + F \tag{2}$$

where *X* is a matrix that contains the standard spectra, *T* is the X-score matrix of latent variables (LV), *P* is the matrix of X-loadings, Y is a matrix of analyte concentration, C are the PLS regression coefficients, and where *E* and *F* are the random errors of X and Y, respectively.

The aim of PLS is to maximize the covariance between *T* and *Y*. Previously to the model construction it is necessary to perform a mean-centring [22] of both *X* and *Y*, which is performed by subtracting the mean of each column from each of the observations within that column; or standardize to unit variance, wherein the mean of each column is subtracted from each of the observations within that column, and then divided by the corresponding column standard deviation.

Radionuclide	Half-life (T$_{1/2}$)	Daughter products and their T$_{1/2}$	Maximum energy
^{89}Sr	50.57 d	^{89}Y (stable)	1495.1 keV
^{90}Sr	28.8 y	^{90}Y (2.67 d)	545.9 keV
^{90}Y	2.67 d	^{90}Zr (stable)	2278.7 keV

To define the number of LV needed for the construction of the model and to evaluate the fitness of the calculated PLS model, a cross validation step is usually performed, which involves the construction of the model using a subset of the standard spectra, and its evaluation using all other standard spectra.

In PLS regression, the emphasis is on developing predictive models (the calibrations step) that can subsequently be used to predict the analyte concentration from the sample spectrum (in the analysis step).

LSS-PLS deconvolution for determining isotopes of the same element

^{89}Sr and ^{90}Sr are strontium isotopes present in different nuclear fields such as medicine or nuclear reactors. As it is shown in Table 1, both radionuclides are beta emitters, and chemical separation is not possible because of their equal chemical properties. An added issue for their quantification is the presence of ^{90}Y as a daughter radioisotope of ^{90}Sr and consequently, an extra peak on the ^{90}Sr pure fraction will be observed. ^{90}Y is a high energy beta emitter and the relation between this isotope and its mother is the secular equilibrium achieved 21 days after separation. The measuring date plays a crucial role on the quantification step due to the grow of ^{90}Y and the increase of the spectral interference. Since all the radionuclides (^{89}Sr, ^{90}Sr and ^{90}Y) are beta emitters, a separation step is needed to remove all the beta interferences on the fraction.

Taking all these aspects into account, we propose deconvolution as a promising alternative for the simultaneous quantification of ^{89}Sr and ^{90}Sr. In a first step, a solid phase extraction (SPE) using a specific resin (Sr-resin) is performed in order to remove other beta radionuclides from the pure fraction (containing all strontium radioisotopes). The measurements have been performed in a Perkin Elmer Wallac Quantulus 1220. Quantulus 1220 is an ultra-low level liquid scintillation counter able to separate alpha and beta radiation by means of a pulse shape analyser. The quenching control of the samples is performed by means of the Spectral Quench Parameter of the External Standard (SQP[E]) with a source of ^{152}Eu. The reduction of the background caused by gamma and cosmic radiation is performed by the combination of a passive shield, based on an asymmetric block of 630 kg of old lead, and an active shield, which consists of an asymmetric liquid scintillation guard formed by a cylinder that contains a mineral-oil scintillator. Two photomultipliers are used to detect scintillation produced in the guard by gamma rays and cosmic radiation. When a signal is detected in coincidence in both guard photomultipliers and sample photomultipliers, the count is registered in another MCA and rejected from the sample counting. For the simultaneous quantification of both target radionuclides, a PLS model is constructed using LS spectra of standards for both ^{89}Sr and ^{90}Sr, with different activity concentrations which are measured at different times after separation, to consider variable contributions of ^{90}Y.

Once all the parameters (e.g., ratio LS cocktail: sample, background signal, SQP[E]) are fixed, the spectra of the pure fractions (^{89}Sr and ^{90}Sr) are measured to define windows where overlapping occurs due to ^{90}Y interference (Fig. 1.)

Several *Matlab* scripts are used to convert the output data obtained from the detector in continuous spectra. Once all the spectra are converted, a data matrix is created by adding all the vector spectra in the same order as the one used for *Y* block, which contains the activity of the standards at measuring time, calculated considering the known activities of the standards, the elution fraction preconcentrated, the amount of sample added in the vial and the chemical recovery. Once the activity in Bq/vial is calculated, the time correction to the reference date is performed for each sample. The activity of ^{90}Y is also calculated considering the initial activity of ^{90}Sr and the delay between the separation and the measurement.

For the calibration model construction *Matlab Statistical Toolbox* is used for the spectra treatment. The treatment for all the whole set of spectra is performed in the same way and considering the type of model created. A blank spectrum is subtracted from each spectrum coming from spiked samples. The spectra treatment also includes the data mean centering
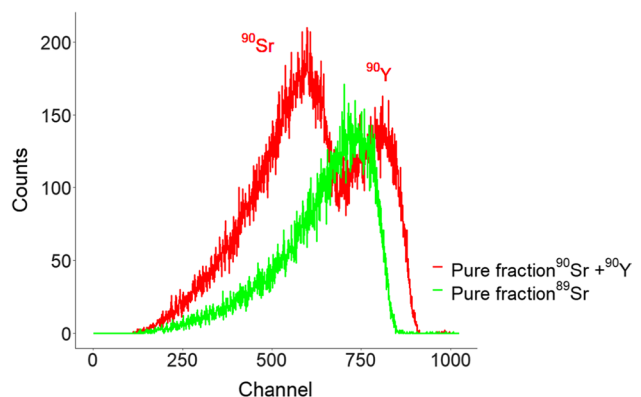

Fig. 1 Spectral overlapping between ^{90}Y and ^{89}Sr on the high energy channels

and its smoothing using Savitsky-Golay filter with a linear polynomial and window length of 31 which have been optimized in previous work. For the Y-block, data mean centring is used.

The PLS model is constructed using the X-block, a matrix that contains all the treated standard spectra and the Y-block which contains the activity of all the radionuclides for each standard spectrum considering the decay corrections. First, the number of latent variable (LV) is chosen as the one with the lowest squared error of the cross validation (RMSECV): 2 LV for a model with ^{90}Sr and its daughter ^{90}Y and 3 LV for ^{89}Sr, ^{90}Sr and ^{90}Y.

The method validation is carried out in two ways: preparing different type of mixtures with different ratios of the activity level of ^{90}Sr and ^{89}Sr and different times (between the separation and the measurement), and simulating spectra by adding pure spectra of ^{90}Sr and ^{89}Sr at different times following the activity ratios tested in mixtures and checking the final results. The simulated spectra (adding pure spectra of ^{90}Sr and ^{89}Sr) and the mixtures tested gave an idea of the methods quantification. The biases, with respect to the theoretical activity, obtained following these procedures are in the range of 1% to 20% for ^{90}Sr and between 10 and 30% for ^{89}Sr.

This example of spectra deconvolution is intended to be used in case of emergency scenarios (nuclear accidents), where a fast method is needed. The results obtained gave a good approach of the application of the method in case of emergency (where the concentration of ^{90}Sr would be higher) and the expected activities would be significatively higher than the detection limit, which allows a better identification and quantification.

Even the results obtained are satisfactory, all the steps of the deconvolution process (reading the output data of the spectrometer, data treatment (mean centring, and smoothing), model construction, cross validation, and application of the model to obtain the activity concentration of the samples) were carried out using *Matlab* scripts and its statistical Toolbox. This makes the deconvolution a work-demanding and time-consuming process. To make deconvolution available for routine analysis of LS spectra we developed *DECLAB*.

Software description

DECLAB is an on-line tool developed by the Laboratory of Environmental Radioactivity of the University of Barcelona in collaboration with Aktios, with the aim of LS spectra analysis. It considers three different analysis modes: the classical like constant efficiency and quenching curve and furthermore, the deconvolution of multicomponent spectra by means of PLS which have been described in Fons-Castells et al. [16] with some additional features such as an automated choice of the number of latent variables or reference date decay correction. For all three modes, *DECLAB* works in two steps. In the first one (the calibration) spectra of standards are uploaded to the application to calculate the efficiency, either as a value, for constant efficiency mode; as a second-degree polynomial for quenching curve mode; or as a PLS model for deconvolution mode. In the second step, spectra of the samples are uploaded to *DECLAB*, and the previously calculated efficiency is used to determine their activity for one or more radionuclides.

The main window of *DECLAB* contains a list of all the calibrations carried out which can be filtered by name, mode, or date. It is possible to switch between the list of calibration and the list of all the analyses performed.

Calibration step

The input data for calibration are loaded in "New calibration" window (Fig. 2). The main inputs in calibration step are spectra of the standards and blanks, selection of α and/or β mode, windows definition, and activity of all the standards. For deconvolution mode, there is also a selector to
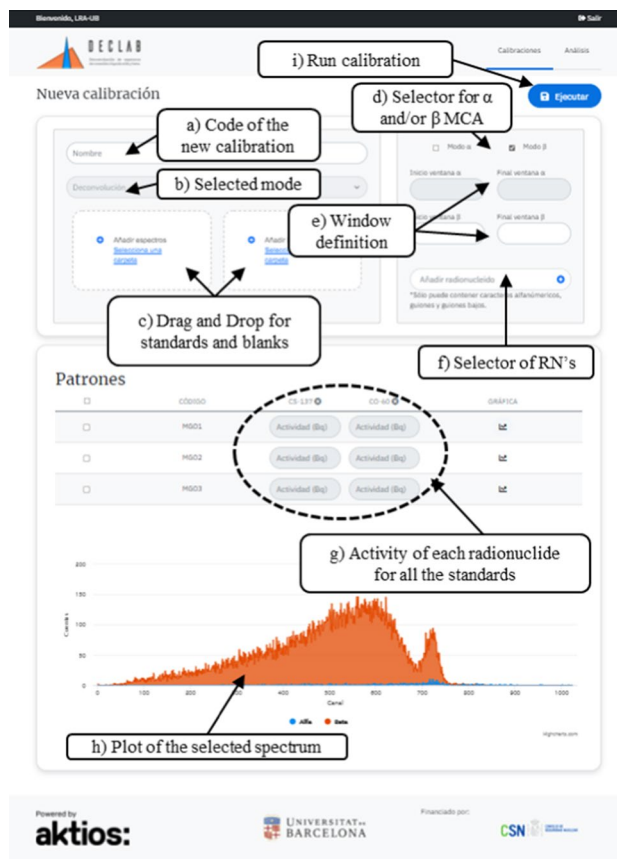

Fig. 2 DECLAB new calibration display

include all the radionuclides that will be considered in the calibration.

The output data for constant efficiency mode is the efficiency of detection, which is calculated following Eq. 3.

$$Eff = \sum_{0}^{s} \frac{\left(\frac{\left(\frac{\sum_{cmin}^{cmax} cpm(stds)}{t(stds)} \right) - \sum_{0}^{b} \frac{\left(\frac{\sum_{cmin}^{cmax} cpm(blb)}{t(blb)} \right)}{b}}{Act(stds)} \right)}{s} \tag{3}$$

where Eff is the detection efficiency; s and b are the number of standards and blanks, respectively; c_{min} and c_{max} are the minimum and maximum channels of the counting window; $cpm\ (std\ s)$ are the counts per minute of the standard s; $cpm\ (bl\ b)$ are the counts per minute of the blank b; t is the counting time in minutes; and $Act\ (std\ s)$ is the activity of the standard s.

In quenching mode, the output of the calibration is a quadratic polynomial which relates the quenching parameter (SQP[E]) with the efficiency, calculated following Eq. 3.

In the deconvolution mode, the output of the calibrations are the matrixes of scores, loadings, and regression coefficients shown in Eqs. 1 and 2, which allow the quantification of the calibrated radionuclides in the analysis step.

Furthermore, in quenching and deconvolution modes, RMSE (Root Mean Square Error) of the calibration is also calculated following Eq. 4:

$$RMSE_{RN} = \sqrt{\frac{\sum_{1}^{n} (A_n^o - A_n^i)^2}{n}} \tag{4}$$

where $RMSE_{RN}$ is the Root Mean Square Error for a specific radionuclide RN; n is the number of input spectra in the calibration set; A_n^o is the output activity for the radionuclide RN for each spectrum; and A_n^i is the input activity for the radionuclide RN for each spectrum.

RMSE can be considered as the standard deviation of the unexplained variance of the model. It has the useful property of being in the same units as the response variable, in the studies case $Bq \cdot L^{-1}$. This variance is considered the uncertainty of the model and it is used in the analysis step for sample uncertainty calculation.

Analysis step

The main inputs in the analysis step are the spectra of samples and blanks. Additionally, DECLAB also allows input data from the sample treatment and preparation (as initial and final amount of sample, chemical recovery, time elapsed between measurement and reference date) which will be considered in activity calculation. Furthermore, the outputs of the selected calibration can be also considered inputs for the analysis.

The output data for the analysis are the activity, its uncertainty, and the detection limit for each sample (and each radionuclide for deconvolution mode). For constant efficiency and quenching curve mode, activity uncertainty and minimum detectable activity is calculated following Eqs. 5, 6 and 7 respectively.

$$Act_{sp} = \frac{\frac{\sum_{cmin}^{cmax} cpm(samp_{sp})}{t(samp_{sp})} - \sum_{0}^{b} \frac{\left(\frac{\sum_{cmin}^{cmax} cpm(blb)}{t(blb)} \right)}{b}}{Eff} \times e^{-\lambda \Delta t} \times \frac{Mf}{R \times Mi \times Mv} \tag{5}$$

$$u(Act_{sp}) = \frac{Act_{sp}}{\frac{cpm(samp_{sp})}{t(samp_{sp})} - \frac{cpm(blb)}{t(blb)}} * \sqrt{\frac{cpm(samp_{sp})}{(t(samp_{sp}))^2} + \frac{cpm(blb)}{(t(blb))^2} + (RMSE \times \sqrt{N})^2} \tag{6}$$

$$MDA(Act_{sp}) = \frac{\left(3.29 \times \sqrt{\frac{cpm(samp_{sp})}{(t(samp_{sp}))^2} + \frac{cpm(blb)}{(t(blb))^2}} + 2.71 \times \left(\frac{1}{t(samp_{sp})} + \frac{1}{t(blb)} \right) \right) \times e^{-\lambda \Delta t} \times Mf}{Eff \times R \times Mi \times Mv} \tag{7}$$

where Act_{sp} is the activity of the sample, in Bq·L^{-1} or Bq·kg^{-1}; *cpm (samp sp)* are the counts per minute of the sample *sp*; M_i is the amount of sample at the beginning of the treatment, in L or kg; M_f is the amount of sample at the end of the treatment, in L or kg; M_v is the amount of treated sample added to the counting vial, in L or kg; *R* is the chemical recovery of the treatment; λ is the decay constant of the radionuclide of interest, in s^{-1}; Δt is the delay between measurement and reference date, in seconds and it is internally calculated by DECLAB using measurement and reference date; *RMSE,* is the Root Mean Square Error (just in quenching and deconvolution modes); and *N* is the number of standard spectra of the calibration (just in quenching and deconvolution modes).

For deconvolution mode, the activity is calculated from the PLS model following Eqs. 1 and 2. The uncertainty is calculated following Eq. 6 and considering RMSE of the PLS model. Finally, the MDA for each radionuclide is established as the arithmetical mean plus two times the standard deviation of the determined activity for the radionuclide considered in in the model in these spectra which was not actually present.

A more detailed description of all the features of DECLAB as well as guide of use is included as Supplementary Material.

DECLAB development

From the development point of view, *DECLAB* consists of two clearly distinguished layers. A server layer, where the application performs the calculations and manage them, and a visual layer, through which the user can create, edit, and delete calibrations and analysis.

The main task of the tool is to allow to create calibrations and analysis using three different methods: constant efficiency, quenching curve, and deconvolution. For the moment, these calibrations are carried out from output files of Wallac Quantulus 1220, but further upgrades to include more LS spectrometers are scheduled. As it is previously mentioned, PLS calibration requires several standard spectra to consider all the radionuclides and quenching range expected in the sample, therefore it is critical to make it possible the reuse of the treated data in different calibrations as well as the created calibrations in different analyses. For this reason, a structure to store the pre-processed data has been created in the Data Base.

To generate a calibration, the user must introduce the identifying parameters and upload the files of the standard spectra. These files are processed in the server layer, and it returns to the visual layer so that the user can select the standards with which they want to perform the calibration.

At the end of this process, the system stores all the spectra, whether selected or not, so it is possible to reuse that pre-processing standard files in a new calibration created from it. Once the calibration has been generated, the user can select which calibration mode to use in the analysis. The results of the calibrations and the analysis can be consulted, displayed graphically, and exported to Excel format at any time.

Python, the most used language nowadays for data analysis and scientific applications, has been used for the development of the logical layer of the application (or server layer). *Python* is an easy-to-use programming language that offers great adaptability, and which could be integrated with application programmed in other languages. It also offers a command line that could be considered as an extension of those used in scientific programs as well as a wide variety of modules for data analysis [23].

To make it easy the calculation of the most complex operations, a series of specific libraries has been used:

- *Scikit-learn*, an open-source machine learning library that provides a variety of methods and algorithms for data analysis [24], which have been used for the operations required for the deconvolution method: partial least squares regression, mean square error, and cross validation.
- *Pandas*, a library that facilitates the handling and manipulation of data structures in tabular format [25]
- *Sigfig*, a module that offers several methods for rounding numbers [26]
- *Statistics*, a native Python module that provides simple functions to calculate mathematical statistics from numerical data [27]

To build the visual layer of the application, the *Django* framework has been used, which is a versatile, flexible, and complete framework that allows agile development, since it includes many modules that makes it easy the development, especially regarding application security and data handling and administration. *Highcharts* library, written in JavaScript, has been incorporated to display the data. This library allows the graphical representation in a rapid and dynamic way, allowing the user to modify the visualization and export it.

Software validation

To ensure the fitness of results reported by *DECLAB*, the same spectra analysed using *Matlab* scripts in previous publications [14, 15, 23], as well as the ones obtained for ^{89}Sr/^{90}Sr and shown in the previous section "*LSS-PLS deconvolution for determining isotopes of the same element*", have been analysed with *DECLAB*, obtaining in all the cases a complete agreement.

It should be pointed out that in the previous investigations, no significant differences on quenching parameters were observed between standards used for model creation and samples. This was because both, standards and samples, where analysed after a radiochemical separation, which entails a constant media, or in the case of gross alpha and gross beta, there were performed in drinking water samples. However, it is well known the effect of quenching on efficiency and specially in spectrum shape, could entail a complexity for LS spectra deconvolution and even make it not possible.

Quenching mis-match effect in identification and quantification of mixtures of radionuclides, as well as the way to correct it is not already implemented in the current version of *DECLAB* but will be studied in further investigations.

Nevertheless, to prevent the user of *DECLAB* from improperly using the tool, the match between quench of standards and samples is checked during the analysis calculations. When the quench parameter of a sample is not in the quench range of the calibration standards DECLAB warns the user.

Conclusions

PLS based deconvolution has been successfully applied for the determination of isotopes of the same element in the case of ^{89}Sr and ^{90}Sr. The biases between the actual activity and the determined by PLS deconvolution were satisfactory. This scenario (determination of isotopes of the same element), together with the previous studied scenarios like non-complete separation and screening methods, presented PLS based deconvolution as a promising alternative for the analysis of radionuclides mixtures, reducing the number of radiochemical separations. Even though PLS requires a calibration set with a significatively high number of spectra, it allows the determination of several radionuclides in a rapid way.

To facilitate the deconvolution by PLS, *DECLAB*, an on-line LS spectra analysis software has been developed. This application also allows the quantification by means of constant efficiency and quenching curve methods, for the time being, for spectra obtained with Wallac Quantulus 1220 LS spectrometer. Regarding the issues of PLS deconvolution, *DECLAB* allows the model construction, spectra treatment and cross validation of the model in a simple way, for users without mathematical model background. The agreement between the results obtained using DECLAB and those obtained with *Matlab* scripts allowed to validate the software. However, further investigation is needed to supply an appropriate evaluation of the crosstalk between radionuclides and uncertainty estimation when quenching of the sample is out of the range of quenching of the standards.

Further upgrades are scheduled to make *DECLAB* compatible with the output files of other LS spectrometers and to translate it into English.

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