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Generalized evaluation of environmental radioactivity measurements with UncertRadio Part II: Methods with linear unfolding

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HIGHLIGHTS

- Weighted least squares based on Neyman- or Pearson-type Chi-square criterion.
- Weighted total least squares included for significant input quantities covariances.
- Requires a 6-step procedure for constructing a matrix-based uncertainty function.
- ISO 11929 characteristic values are derived from the uncertainty function.

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ABSTRACT

For the software UncertRadio (UR), designed for a generalized evaluation of environmental radioactivity measurements, the evaluation procedure is given if least squares-fitting is involved. UR is then applied to the simultaneous detection of Strontium-89 and Strontium-90. This method is easily extendable over recent approaches based on the evaluation of two measurements, i.e. on two unknowns with two equations. The evaluation within UR includes ISO 11929 decision thresholds and detection limits. The propagation of distributions with MC simulation is described.

1. Introduction

Evaluations of analyses and measurements in the field of environmental radioactivity may become tedious with respect to calculating values of the decision threshold and the detection limit according to the recent international standard ISO 11929 (International Organisation for Standardisation, 2010). Part I of this work (Kanisch, 2016) presented a proposal of how a set of text form equations describing the value of the output quantity of a measurement procedure may be evaluated by software without a need to let them become part of a program's source code; they only need to have a certain simple structure.

This part of the work gives the details for applying such a software (UncertRadio) to measurement methods in which linear least squares methods, called "linear unfolding" in the ISO standard, for analyzing a decay curve of net counting rates are applied. The combined ^{89}Sr and ^{90}Sr analyses which became more attractive during recent years (AKU, 2008; Günther et al., 2009; Kim et al., 2009; Herranz et al., 2011; EPA, 2011; IAEA, 2013) are well suited for discussing the evaluation details for using linear unfolding.

When simultaneously determining activity concentrations of the two beta-ray emitting radionuclides ^{90}Sr and ^{89}Sr by a so-called "rapid" radiochemical method a liquid scintillation counter is often used. It allows using a few separate energy windows (counting channels) yielding several gross counting rates from a small series of beta counting measurements which form time-dependent decay curves for each window. Different radionuclides appear to have different counting efficiencies in the counting channels as well as different half-lives. A known amount of an ^{85}Sr activity may be added to the sample when starting with the radiochemical analysis. It allows determining the chemical Sr yield by measuring its activity at the end of the analysis, either by a separate gamma-ray spectrometric measurement or by including

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Nomenclature

$\mathbf{A}$	design matrix of the LS problem
A_r	activity of radionuclide r
A_r^0	activity of radionuclide r at the Sr/Y separation time
$A_{r,cal}$	value of the activity used for efficiency calibration of radionuclide r
$A_{Tr,G}$	activity of the (gamma-ray emitting) ^{85}Sr tracer
$\mathbf{B}$	diagonal matrix containing factors for conversion $\mathbf{y}_1 \rightarrow \mathbf{y}_2$
f_d	counting time averaged decay factor; Eq. (5)
F_C, F_L	coefficients of a linear relation between output quantity and net count rate
$k_{1-\alpha}$, $k_{1-\beta}$	standard-normal quantiles associated with (1-α) and (1-β)
K, N,M	counting channel identifiers
$\boldsymbol{p}$, $\mathbf{U_p}$	vector of parameters contained in $\mathbf{A}$ and associated covariance matrix
$\boldsymbol{q}$, $\mathbf{U_q}$	vector of parameters contained in the factors converting $\boldsymbol{y_1}$ to $\boldsymbol{y_2}$, and associated covariance matrix
$\mathbf{C_p}$	matrix of partial derivatives of $\boldsymbol{y_1}$ with respect to $\boldsymbol{p}$
$\mathbf{C_q}$	matrix of partial derivatives of $\boldsymbol{y_2}$ with respect to $\boldsymbol{q}$
$\mathbf{C_{y1}}$	matrix of partial derivatives of $\boldsymbol{y_2}$ with respect to $\boldsymbol{y_1}$
$\mathbf{C_\psi}$	matrix of partial derivatives of $\boldsymbol{y}_1$ with respect to elements of $\mathbf{A}$ (ψ terms)
$\mathbf{D_p}$	matrix of partial derivatives of $\boldsymbol{\psi}$ with respect to $\boldsymbol{p}$
$\mathbf{U_\psi}$	covariance matrix of the elements of $\mathbf{A}$ (ψ terms)
r	radionuclide identifier
$R_K(t_i)$	net counting rate of counting channel K at time t_i
$R_{Tr,K}(t_i)$	net counting rate of a ^{85}Sr tracer in channel K, at time t_i
$R_{g,K}$	gross counting rate measured in channel K
R_{Bl}	integrated (total) background count rate
$R_{0,K}$	background counting rate of channel K
R_n	net counting rate
$\mathbf{R}$	matrix obtained by a Cholesky factorization of the matrix $\mathbf{Up}$
t_m	gross counting duration
t_{As}	time elapsed between Sr/Y separation and start of counting
t_i	time difference between the starts of the first and the i-th measurement
$\boldsymbol{x}$, $\mathbf{U_x}$	vector of net counting rates and associated covariance matrix
y	generally: estimate of an output quantity
$\tilde{y}$	a given or assumed value of an output quantity
$\tilde{u}(\tilde{y})$	uncertainty associated with $\tilde{y}$, estimated by the uncertainty function
$\boldsymbol{y_1}$, $\mathbf{U_{y1}}$	vector of activities and associated covariance matrix; treating the LS problem as a sub-model
$\boldsymbol{y_2}$, $\mathbf{U_{y2}}$	vector of decay corrected activity concentrations and associated covariance matrix (depend on $\boldsymbol{y_1}$, $\mathbf{U_{y1}}$)
$\boldsymbol{z}$	vector of random standard-normal deviates
α, β	error probabilities of first and second kind
1-γ	probability associated with coverage interval
$\varepsilon_{r,K}$	detection efficiency of radionuclide r and counting channel K
η_{Sr}	chemical Sr yield
λ_r	decay constant of radionuclide r
$\psi_{r,K}(t_i)$	decay function value, including detection efficiency, of radionuclide r and counting channel K, at time t_i

the ^{85}Sr in the least squares evaluation of the decay curves of the beta counting rates. If the Sr yield is obtained from a separate gamma measurement, the ^{85}Sr tracer contribution to the beta counting rates produces an additional artificial beta background component.

If the measurement conditions are restricted to using one counting channel (one detector) and only two measurements without applying a ^{85}Sr tracer, two counting rate equations are obtained. This represents a system of two linear equations with two unknowns (activities), which can be solved analytically by using determinants of the equation system. More recently, this “two-point” method has been studied with respect to parameters by analytical solutions (Herranz et al., 2011; EPA (2011) developed a similar solution for determining radiostrontium in water samples after some accidental event with Strontium would have occurred. A similar approach of the system of two equations was also applied to determining the Sr isotopes in milk by a combination of Cerenkov and scintillation counting (IAEA, 2013).

It is recommended to use least squares (LS) methods for evaluating such methods. This easily allows including also a third measurement by simply adding the data as a third line to the decay curve table. However, for the above mentioned case with only two equations, the latter would mean to extend at first the algebraic expressions representing a significant step. This work presents a proposal of how to apply or even to extend the standard ISO 11929 from 2010, the appendix C.5 of which is rather short. This standard is an extension of ISO GUM (JCGM 104:2009 (2009)) in that it does not only treat the primary evaluation of the measurement but also two additional full evaluations for the cases of estimating a decision threshold and a detection limit; both cases refer to “modified values” of the activity concentrations. Furthermore, the results obtained analytically according to ISO 11929 shall be compared with MC simulations. It seems that ISO GUM Suppl. 2 (JCGM 102:2011 (2011)) does not really cover least squares analyses.

Two LS methods will be included in tests, that of (a) classical weighted LS (WLS; e.g. ISO 11929) but extended by including by uncertainty propagation a parameter covariance matrix (EWLS) and that of (b) weighted total LS (WTLS). The WTLS method (see e.g. Malengo and Pennecchi, 2013; Markovsky and Van Huffel (2007); for a straight line fit: see Cantrell, 2008) is the better approach when input data are strongly correlated; within EWLS the fitted parameter values are not changed by including covariances, while WTLS may lead also to slightly modified fitting parameter values. Unfortunately, it requires more computational effort.

The calculations described in the following are performed within the author's Fortran90 based Windows program UncertRadio (UR) designed as a tool for generalized evaluation of measurements in the field of environmental radioactivity in accordance with ISO 11929. For including also WTLS, the package of the subroutine LSQGEN from a textbook (Brandt, 1999) is used in UR, which directly takes into account this covariance matrix. The method behind LSQGEN does not seem to be widely known; it has, however, been used in some Physics applications (Zhao et al. 2009; Dydak and Nefedov, 2004).

2. Primary evaluation

2.1. Modeling counting rates

Net counting rates R_K measured at times t_i in three counting channels K (K=A, B, C) may be represented by sums of