Journal of Radioanalytical and Nuclear Chemistry, Vol. 245, No. 1 (2000) 137–144

Quality assurance of nuclear analytical techniques based on Bayesian characteristic limits

R. Michel*

Zentrum für Strahlenschutz und Radioökologie, Universität Hannover, Am Kleinen Felde 30, D-30167 Hannover, Germany

(Received November 22, 1999)

Based on Bayesian statistics, characteristic limits such as decision threshold, detection limit and confidence limits can be calculated taking into account all sources of experimental uncertainties. This approach separates the complete evaluation of a measurement according to the ISO Guide to the Expression of Uncertainty in Measurement from the determination of the characteristic limits. Using the principle of maximum entropy the characteristic limits are determined from the complete standard uncertainty of the measurand.

Introduction

Characteristic limits such as decision threshold, detection limit and confidence limits are widely used as part of quality assurance in nuclear and other analytical techniques. Since it is a general problem that a measurand is usually to be determined in the presence of a background or a blank, three questions are essential: (1) Is the analytical method used suited to perform the measurement task? (2) Is there a contribution of the sample analyzed among the signals measured? (3) Which range of true values may be reasonably attributed to the measurand given the measured results?

These three questions are answered by determining the decision threshold, the detection limit, and the confidence limits, respectively. In the past, approaches to determine these characteristic limits[1–3] were based on conventional statistics. A number of national and international standards has been or is being developed for special applications involving nuclear radiation measurements; see Reference 4 for a survey. These standards are, however, handicapped by the fact that they are dedicated to specialized measurement tasks and that they can only account for experimental uncertainties which are due to counting statistics or which can be determined by repeated measurements. Recently, however, a new approach based on Bayesian statistics[5] has been proposed[6] which allows one to take into account all sources of experimental uncertainties. Moreover, it allows one to include all a priori knowledge about the measurement problem and all information obtained from previous experiments. This approach is used in the German standard DIN 25482 part 10[7] and other upcoming German standards[8–10] as well as in the currently prepared standards ISO 11929 parts 5, 7, 8.[11–13] It separates the complete evaluation of a measurement according to the ISO Guide to the Expression of Uncertainty in Measurement[14] from the determination of the characteristic limits. The characteristic limits are then determined from the complete standard uncertainty of the measurand using the principle of maximum information entropy.

Uncertainties in measurements

The starting point of any analysis is the definition of the quantities Y_k ($k = 1,...,n$) to be measured. These measurands* are for instance the concentrations of elements or activities of radionuclides in a sample. The measurands are connected to input quantities X_i ($i = 1,...,m$) which originate from measurement(s) or from other sources of information by a model of evaluation. Examples of input quantities are net peak areas from γ-spectra, efficiency data of a detector, sample masses and chemical yields. The model of evaluation is a set of mathematical relationships:

$$Y_k = G_k(X_1, X_2, \ldots X_m); \text{ in matrix notation } \boldsymbol{Y} = \boldsymbol{G}(\boldsymbol{X}). \quad (1)$$

Note, that the model functions $\boldsymbol{G}$ must not necessarily be explicitly available. The model may also be given in form of a computer code.

Measurement yield estimates x_i of the true values ξ_i of the input quantities X_i. The estimators x_i have the associated uncertainties $u(x_i)$. The evaluation of an analysis yields estimates y_i of the measurands or output quantities using the x_i as estimates of the true values ξ_i in Eq. (1) and one obtains

$$y_k = G_k(x_1, x_2, ..., x_m); \ (k = 1, ..., n). \quad (2)$$

* E-mail: michel@mbox.zsr.uni-hannover.de

* For the proper use of terms of metrology see Ref. 15.

0236–5731/2000/USD 17.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

If the input quantities X_i are not correlated, the combined standard uncertainties $u(y_k)$ associated with y_k are calculated by the law of uncertainty propagation as the positive square root of the combined variance $u^2(y_k)$:

$$u^2(y_k) = \sum_{i=1}^{m} \left(\frac{\partial G_k}{\partial x_i} \right)^2 \cdot u^2(x_i); \quad (k = 1, \ldots n) . \qquad (3)$$

If the input quantities X_i are not independent but correlated the combined standard uncertainty $u(y_k)$ has to be calculated according using covariances (see Reference 14 for details). If the partial derivatives are not explicitly available, they can be numerically sufficiently approximated by using the standard uncertainty $u(x_i)$ as increment of x_i:

$$\frac{\partial G_k}{\partial x_i} \approx \frac{1}{u(x_i)} \cdot (G_k(x_1, \ldots, x_i + u(x_i)/2, \ldots x_m) - G_k(x_1, \ldots, x_i - u(x_i)/2, \ldots x_m)) \qquad (4)$$

The standard uncertainties generally have to be evaluated according to the ISO Guide[14] well in accordance with guidelines of other international bodies.[16,17] In the ISO Guide, uncertainties are evaluated either by "statistical methods" (type A) or by "other means" (type B), i.e., by methods of conventional statistics or Bayesian statistics. Type A uncertainties can be evaluated from repeated or counting measurements, while Type B uncertainties cannot. They are for instance uncertainties given in certificates of standard reference materials or of calibration radiation sources which are used in the evaluation of a measurement. The evident contradiction in using different types of statistics in the definitions of the two types of uncertainties was recently overcome by the establishment of a Bayesian theory of measurement uncertainty[18]. In this theory, uncertainties are consistently determined. They quantitatively express the actual state of incomplete knowledge of the quantities involved.

Bayesian statistics of measurements

The basic difference between conventional and Bayesian statistics lies in the different use of the term probability. Considering measurements, conventional statistics describes the probability $f(\eta|y; w)$, i.e., the conditional probability of the distribution of estimates y given the true value η of the measurand Y under the boundary condition w. Since the true value of a measurand is principally unknown, it is the basic task of an experiment to make statements about the probability distribution of the true value of the measurand. Bayesian statistics allows the calculation of the function $f(\eta|y; w)$, i.e., the probability distribution of the true value η of a measurand Y given the measured estimate y under the boundary condition w.

In Bayesian theory, one uses an Ansatz to establish the probability distribution $f(\eta|y; w)$ which separates the information about the measurand obtained from the actual experiment from all other information available about the measurand by

$$f(\eta|y; w) = f_0(\eta|y; w) \cdot f(\eta). \qquad (5)$$

$f(\eta|y; w)$ is written as a product of two probabilities, the data prior $f_0(\eta|y; w)$ and the model prior $f(\eta)$. The data prior or likelihood $f_0(\eta|y; w)$ is the probability that the measurand has the true value η if only the measured values y are given under the boundary conditions y. It only accounts for the measured values and neglects any other information about the measurand. The model prior $f(\eta)$ represents all information about the measurand existing before the experiment is performed. Therefore, it does not depend y or w. If, for instance, an activity of a radiation source or a concentration of an element is the measurand a meaningful model prior is that the measurand is non-negative ($\eta \geq 0$):

$$f(\eta) = \begin{cases} \text{const} & (\eta \geq 0) \\ 0 & (\eta < 0) \end{cases} \qquad (6)$$

Note, that the actual result of a measurement, for instance a net count rate, can be negative. But the experimentalist knows a priori without performing an experiment that the true value must be non-negative. All non-negative values of the measurand have the same a priori probability since there is no other information about the true value of the measurand before the measurement has been performed.

The data prior $f_0(\eta|y; w)$ represents the information obtained about the true value η of the measurand Y from the actual experiment(s), i.e., from the measured estimates y. Since the data prior exclusively considers the experimental information, $y = \mathrm{E}(\eta)$ and $u^2(y) = \mathrm{Var}(\eta)$ hold for the probability distribution $f_0(\eta|y; w) \cdot \mathrm{E}(\eta)$ and $\mathrm{Var}(\eta)$ are, respectively, the expectation and the variance of η.

According to WEISE and WÖGER[18] the probability distribution $f(\eta|y; w)$ can be determined using the principle of maximum (information) entropy and considering both types (A and B) of uncertainties. The principle of maximum information entropy[19] is given by

$$S = -\int f(\eta|y; w) \cdot \ln(f_0(\eta|y; w)) d\eta = \max . \qquad (7)$$

Equation (7) can be solved by the method of Lagrangian multipliers and one obtains the result

$$f(\eta|y; w) = C \cdot f(\eta) \cdot \exp(-(\eta - y)^2 / 2 \cdot u^2(y)) . \qquad (8)$$

The distribution $f(\eta|y; w)$ is a product of the model prior and a Gaussian $N(y,u(y))$. Note, that the Gaussian in Eq. (8) is not an approximation as in conventional statistics or a distribution of measured values from repeated or counting measurements. It is simply the result of maximizing the information entropy.

If the true value η of a measurand Y is estimated by a mean value $\bar{y}$ of measured values y_i from repeated measurements, one obtains

$$f(\eta|\bar{y};w) = C \cdot f(\eta) \cdot \exp(-(\eta-\bar{y})^2 / 2 \cdot u^2(\bar{y})) . \quad (9)$$

The model prior has to be assumed constant if there is no a priori knowledge about the measurand. In this case, one obtains for a given estimate y with its associated standard uncertainty $u(y)$ a Gaussian, $N(y,u(y))$, as the probability distribution $f(\eta|y; w)$. For a non-negative measurand with a model prior according to equation 6 one obtains for $f(\eta|y; w)$ a truncated Gaussian.

Bayesian theory also allows the calculation of the probability distribution $f(\eta|y; w)$ of the estimate given the true value η of the measurand Y. Using Bayes Theorem one obtains

$$f(y|\eta;w) \cdot f(\eta) = f(\eta|y;w) \cdot f(y;w) . \quad (10)$$

Since $f(y;w)$, i.e., the probability for observing a measurement result y given the boundary condition w, and $f(\eta)$, i.e., the probability for a true value η under boundary condition w, both are constant, one obtains for $f(\eta|y; w)$ from equation 10 by approximating $u(y)$ by a function $\tilde{u}(\eta)$:

$$f(y|\eta;w) = C \cdot \exp(-(y-\eta)^2 / 2 \cdot \tilde{u}^2(\eta)) \; (\eta \geq 0). \quad (11)$$

$\tilde{u}(\eta)$ is the standard uncertainty of the measurand Y as function of its true value η $\tilde{u}^2(\eta)$ can be estimated by $u^2(y)$. The probability distribution $f(\eta|y; w)$ is a Gaussian for a given true value η of the measurand with the standard uncertainty $\tilde{u}(\eta)$. Note, that the true value η of the measurand Y is now a parameter in Eq. 11 and that the variance $u^2(y)$ of the probability distribution $f(\eta|y; w)$ is equal to the variance $\tilde{u}^2(\eta)$ of the probability distribution $f(\eta|y; w)$:

$$u^2(y) = \tilde{u}^2(\eta) \quad (12)$$

Characteristic limits

Without a detailed mathematical foundation of Bayesian characteristic limits, which may be found elsewhere,[6] we can now define the characteristic limits for a non-negative measurand Y which is, for instance, a concentration of an element or an activity of a radionuclide in a sample. The true value η is zero if the element or the radionuclide is not present. Let y be the estimate of the true value η of the measurand Y with the associated standard uncertainty $u(y)$. The decision threshold and the detection limit are defined[6] on the basis of statistical test testing the null hypothesis $H_0: \eta = 0$ against the alternative hypothesis $H_1: \eta > 0$.

A decision quantity Y has to be attributed to the measurand which being a random variable is likewise an estimator of the measurand. It is postulated that the expectation $E(Y)$ of the decision quantity Y is equal to the true value of the measurand. A value y of the estimator Y derived from measurements is an estimate of the measurand. As a result of the measurement, y and its standard uncertainty $u(y)$ are derived according to the ISO Guide[14] as a complete results of the measurement. y and $u(y)$ have to be derived by evaluation of measured quantities and of other information by way of a mathematical model which takes into account all relevant quantities. Generally, it will not be explicitly made use of the fact that the measurand is non-negative. Therefore, y may become negative, in particular, if the true value of the measurand is close to zero.

For the determination of the decision threshold and the detection limit, the standard uncertainty of the decision quantity has to be calculated if possible as a function $\tilde{u}(\eta)$ of the true value η of the measurand. In the case that this is not possible, approximate solutions are described below. η is the value of another, non-negative estimator $\hat{\eta}$ of the measurand. The limits of the confidence interval to be determined refer to this estimator. The expectation $E(\hat{\eta})$ of this estimator is a best estimate z of the measurand and the standard deviation $(Var(\hat{\eta}))^{1/2}$ is the standard uncertainty $u(z)$ of the best estimate z of the measurand.

Then, the decision threshold y^* (Fig. 1a) is a characteristic limit which when exceeded by a result y of a measurement one decides that the element or radionuclide is present in the sample. If $y \leq y^*$ the null hypothesis, $H_0: \eta = 0$, cannot be rejected and one decides that the element or radionuclide is not found in this sample. If this decision rule is observed, a wrong acceptance of the alternative hypothesis, $H_1: \eta > 0$, occurs with the probability α which is the probability of the error of the first kind of the statistical test used. The decision threshold is given by

$$y^* = k_{1-\alpha} \cdot \tilde{u}(0) \quad (13)$$

with $k_{1-\alpha}$ being the $(1-\alpha)$-quantile of the standardized normal distribution. $\tilde{u}(0)$ is the uncertainty associated with the measurand if its true value equals zero. If the approximation $\tilde{u}(\eta = 0) = u(y)$ is sufficient, one gets $y^* = k_{1-\alpha} \cdot u(y)$.

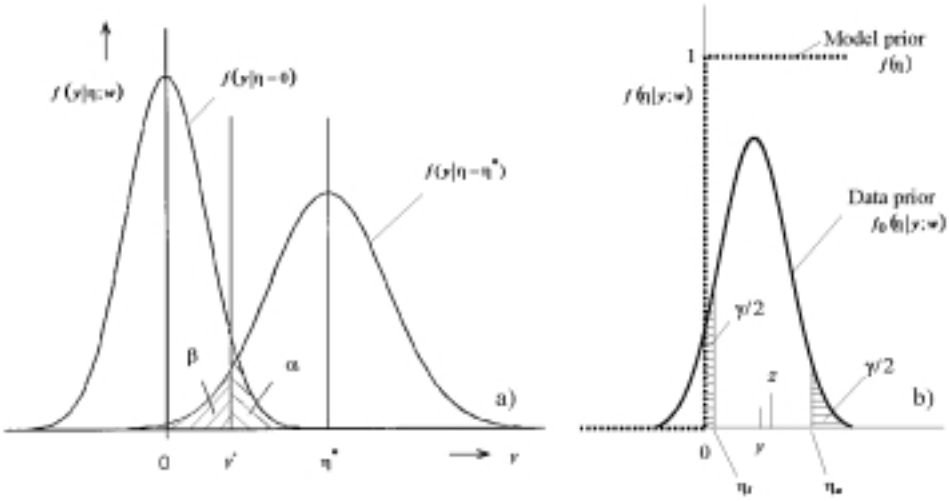

Fig. 1. Illustration of (a) the decision threshold y^* and the detection limit η^* and (b) of the confidence limits η_l and η_u and of the best estimate z of the true value η of a non-negative measurand Y

The detection limit η^* (Fig. 1a) is the smallest true value of the measurand detectable with the measuring method. It is sufficiently larger than the decision threshold that the probability of an error of second kind is equal to β. The detection limit is given by

$$\eta^* = y^* + k_{1-\beta} \cdot \tilde{u}(\eta^*) \qquad (14)$$

with $k_{1-\beta}$ being $(1-\beta)$-quantile of the standardized normal distribution. $\tilde{u}(\eta^*)$ is the uncertainty associated with the measurand if its true value equals the detection limit η^*.

Equation (14) is an implicit one. The detection limit can be calculated from it by iteration using for example the starting approximation $\eta^* = 2 \cdot y^*$.

For the numerical calculation of the decision threshold and the detection limit the function $\tilde{u}(\eta)$ is needed which gives the standard uncertainty of the decision quantity as function of the (true) value η of the measurand. This function generally has to be determined in the course of the evaluation of the measurement according to the ISO Guide.[14] Often this function is only slowly increasing. Therefore it is justified in many cases to use the approximation $\tilde{u}(\eta) = u(y)$. If the approximation $\tilde{u}(\eta) = u(y)$ is sufficient for all true values η, then $\eta^* = (k_{1-\alpha} + k_{1-\beta}) \cdot u(y)$ is valid.

This applies in particular if the primary estimate y of the measurand is not much larger than its standard uncertainty $u(y)$. Frequently, the value of y is calculated as the difference (net effect) of two quantities of approximately equal size with x_1 being the gross effect and x_0 being the background or blank effect, both obtained from independent measurements. In this case of $y = x_1 - x_0$ one gets $\tilde{u}^2(\eta) = u^2(x_1) + u^2(x_0)$ with the standard uncertainties $u(x_1)$ and $u(x_0)$ of x_1 and x_0, respectively. From this, one obtains $\tilde{u}^2(0) = 2 \cdot u^2(x_0)$.

If only $\tilde{u}(0)$ and $u(y)$ are known, the approximation by linear interpolation according to Eq. (15) is often sufficient for $y > 0$:

$$\tilde{u}^2(\eta) = \tilde{u}(0) \cdot (1 - \eta/y) + u^2(y) \cdot \eta / y \qquad (15)$$

In many practical cases $\tilde{u}^2(\eta)$ is a slowly increasing linear function of η. This justifies the approximations above, in particular, the linear interpolation of $\tilde{u}^2(\eta)$ instead of $\tilde{u}(\eta)$, itself.

With the interpolation formula according to Eq. (15) one gets the approximation

$$\eta^* = a + \sqrt{a^2 + (k_{1-\beta}^2 - k_{1-\alpha}^2) \cdot \tilde{u}^2(0)} \qquad (16)$$

with

$$a = k_{1-\alpha} \cdot \tilde{u}(0) + \frac{1}{2}\left(k_{1-\beta}^2 / y\right) \cdot \left(u^2(y) - \tilde{u}^2(0)\right)$$

For $\alpha = \beta$ one receives $\eta^* = 2 \cdot a$.

The confidence interval (Fig. 1b) includes for a result y of a measurement which exceeds the decision threshold y^* the true value of the measurand with a probability $1-\gamma$. It is enclosed by the lower and upper limit of the confidence interval, respectively η_l and η_u, according to

$$\eta_l = y - k_p \cdot u(y) \quad \text{with } p = \omega \cdot (1 - \gamma/2) \qquad (17)$$

$$\eta_u = y - k_q \cdot u(y) \quad \text{with } q = 1 - \omega \cdot \gamma/2 \qquad (18)$$

The parameter ω is given by

$$\omega = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{y/u(y)} \exp(-z^2/2)\,dz = \Phi(y/u(y)) \quad (19)$$

Values of the function $\Phi(t)$, which is the distribution function of the standardized normal distribution, as well as the quantiles k_p of the standardized normal distribution are tabulated.[20]

The confidence limits are not symmetrical around the expectation $E(\hat{\eta})$. The probabilities of $\hat{\eta}<\eta_l$ and $\hat{\eta}>\eta_u$, however, both are equal to γ/2 and the relationship $0<\eta_l<\eta_u$ is valid. If y and $u(y)$ are of similar size this asymmetry of the confidence interval is clearly visible. But, for $y>>u(y)$ the well known formula

$$\eta_{l,u} = y \pm k_{1-\gamma/2} \cdot u(y) \quad (20)$$

is valid as an approximation. Equation (20) is applicable if $y \gtrapprox 2 \cdot k_{1-\gamma/2} \cdot u(y)$.

Assessment of an analytical technique

Thus, having performed a measurement and an evaluation of the measurement according to the ISO Guide,[14] the performance of the analytical technique can be assessed and the three questions asked in the introduction can be answered in the following way:

(1) A measured result has to be compared with the decision threshold calculated by means of equation 20. If a result of the measurement y is larger than the decision threshold y^* one decides that a non-zero effect quantified by the measurand is observed and that the element or activity is present in the sample.

(2) To check whether a measuring method is suitable for the measurement of measurand, the calculated detection limit has to be compared with a specified guideline value, e.g., specified requirements on the sensitivity of the measuring procedure from scientific, legal or other reasons. The detection limit has to be calculated by means of Eq. (14). If the detection limit thus determined is smaller than the guideline value, the measuring procedure is suitable for the measurement, otherwise it is not.

(3) The confidence interval defined by the lower and upper confidence limits according to equations 17 and 18 includes, for a result y of a measurement which exceeds the decision threshold y^*, the true value of the measurand with a probability 1–γ.

If a non-zero effect is observed, i.e., $y>y^*$, a best estimate z of the measurand (Fig. 1b) can be calculated from the expectation of the probability distribution $f(\hat{\eta}|y; w)$ according to Eq. (8). With

$$E(\hat{\eta}) = \frac{\int \hat{\eta} \cdot f(\hat{\eta}|y; w)\,d\hat{\eta}}{\int f(\hat{\eta}|y; w)\,d\hat{\eta}}$$

and using ω from Eq. (19) the best estimate z is calculated by

$$z = E(\hat{\eta}) = y + \frac{u(y) \cdot \exp(-y^2/(2 \cdot u^2(y)))}{\omega \cdot \sqrt{2\pi}} \quad (21)$$

with its standard uncertainty $u(z)$

$$u(z) = \sqrt{\mathrm{Var}(\hat{\eta})} = \sqrt{u^2(y) - (z-y) \cdot z}\,. \quad (22)$$

The following relationships $z \geq y$ and $z \geq 0$ as well as $u(z) \leq u(y)$ are valid. For $y>>u(y)$ the approximations $z = y$ and $u(z) = u(y)$ hold. See Fig. 1b for an illustration of the confidence interval and the best estimate of the measurand.

Numerical example: Analysis of ^{129}I via RNAA

As a numerical example, the determination of the characteristic limits is described for the determination of ^{129}I in an Ukrainian soil sample. For details of the scientific background and the techniques of ^{129}I analyses in environmental samples see Ref.[21,22] In environmental samples the long-lived radionuclide:

$$^{129}\mathrm{I}(T_{1/2} = 15.7\ \mathrm{Ma}) \xrightarrow{\beta^-} {}^{129}\mathrm{Xe}$$

can be analyzed via radiochemical neutron activation analysis (RNAA) or accelerator mass spectrometry (AMS). If RNAA is applied the nuclear reaction

$$^{129}\mathrm{I}(\mathrm{n},\gamma)^{130}\mathrm{I}(T_{1/2} = 12.36\ \mathrm{h}) \xrightarrow{\beta^-} {}^{130}\mathrm{Xe}$$
$$E_\gamma = 536\ \mathrm{keV}$$

is used for the determination of ^{129}I and the measurements are performed by γ-spectrometry. Since there is pre- and post-irradiation chemistry the chemical yield ε is measured via the radioactive tracer ^{125}I (E_γ = 35 keV). ε and its associated standard uncertainty $u(\varepsilon)$ are individually determined for each analysis. In this example ε = 0.72 and $u(\varepsilon)$ = 0.02 were obtained.

As information from previous experiments performed by AMS it is known that in each analysis an ^{129}I activity A_b = 3.5 μBq is brought into the analysis as a blank from chemicals used. It has an associated standard uncertainty $u(A_b)$ = 0.5 μBq.

We use here a somewhat simplified model of the evaluation in order to keep equations short:

$$A_p = \frac{1}{m_p \cdot \varepsilon} \cdot \left(\frac{A_s \cdot NP_p}{NP_s} - A_b \right) \tag{23}$$

with

A_p – ^{129}I activity per unit mass in the sample in Bq/kg,
m_p – sample mass in kg,
ε – chemical yield,
A_s – ^{129}I activity of the standard in Bq,
NP_s – net peak area of the 536 keV γ-line of ^{130}I in the standard,
NP_p – net peak area of the 536 keV γ-line of ^{130}I in the sample,
A_b – ^{129}I activity of the chemistry blank in Bq,
BG_p – background below the 536 keV γ-line of ^{130}I in the sample.

Simplifications made are to assume that the same chemical yields of sample and standard are identical and that the net peak areas of the standard and samples are already decay-corrected to identical counting and decay times.

The combined standard uncertainty $u(Ap)$ associated with Ap is calculated by:

$$u^2(A_p) = \left[\frac{1}{m_p \cdot \varepsilon} \right]^2 \cdot \left\{ \begin{aligned} &\left(\frac{u^2(m_p)}{m_p^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} \right) \cdot \left(\frac{A_s \cdot NP_p}{NP_s} - A_b \right)^2 + u^2(A_s) \cdot \left(\frac{NP_p}{NP_s} \right)^2 \\ &+ \frac{u^2(NP_s)}{NP_s^2} \cdot \left(\frac{A_s \cdot NP_p}{NP_s} \right)^2 + u^2(NP_p) \cdot \left(\frac{A_s}{NP_s} \right)^2 + u^2(A_b) \end{aligned} \right\} \tag{24}$$

For a true value α_p of A_p one expects $NP_p = 0$ and hence $u^2(NP_p = 0) = 2 \cdot BG_p$. Thus, one calculates

$$\begin{aligned} \tilde{u}^2(0) &= \left[\frac{1}{m_p \cdot \varepsilon} \right]^2 \cdot \left\{ \left(\frac{u^2(m_p)}{m_p^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} \right) \cdot A_b^2 + u^2(NP_p = 0) \cdot \left(\frac{A_s}{NP_s} \right)^2 + u^2(A_b) \right\} \\ &= \left[\frac{1}{m_p \cdot \varepsilon} \right]^2 \cdot \left\{ \left(\frac{u^2(m_p)}{m_p^2} + \frac{u^2(\varepsilon)}{\varepsilon^2} \right) \cdot A_b^2 + 2 \cdot BG_p \cdot \left(\frac{A_s}{NP_s} \right)^2 + u^2(A_b) \right\} \end{aligned} \tag{25}$$

Table 1. Data for the example of an analysis of ^{129}I in an Ukrainian soil sample

Quantity	Value	Standard uncertainty	Unit	Type of uncertainty
m_p	0.0400	0.0004	**kg**	**A**
ε	0.72	0.02	–	A
A_b	$3.5 \cdot 10^{-6}$	$0.5 \cdot 10^{-6}$	Bq	B
A_s	0.111	0.003	Bq	A
NP_s	90738	$\sqrt{NP_s + 2 \cdot BG_s} = 334$	–	A
NP_p	254	$\sqrt{NP_p + 2 \cdot BG_p} = 59.9$	–	A
BG_p	3080	55.5	–	A

The probabilities $1-\alpha = 1-\beta = 0.05$ and $\gamma = 0.95$ were chosen. This yields $k_{1-\alpha} = k_{1-\beta} = 1.645$ and $k_{1-\gamma/2} = 1.96$. With the data of Table 1 for the actual analysis one calculates:*

$$\tilde{u}^2(0) = 3.055 \cdot 10^{-6}\ \mathrm{Bq^2/kg^2} \tag{26}$$

and obtains the decision threshold

$$A_p^* = k_{1-\alpha} \cdot \tilde{u}(0) = 1.645.1 \cdot 748\ \mathrm{Bq/kg} = 2.875\ \mathrm{mBq/kg}. \tag{27}$$

The activity per sample mass of the soil sample from Ukraine is calculated to be

$$A_p = \frac{1}{0.04 \cdot 0.72} \cdot \left(\frac{0.111 \cdot 254}{90738} - 0.35 \cdot 10^{-6} \right) \mathrm{Bq/kg} = 10.776\ \mathrm{mBq/kg} \tag{28}$$

with the associated standard uncertainty

$$u(A_p) = 2.581\ \mathrm{mBq/kg}. \tag{29}$$

Since the measured value exceeds the decision threshold a ^{129}I activity of the sample was observed. The complete results of the measurement is: $A_p = 10.8$ mBq/kg, $u(A_p) = 2.6$ mBq/kg.

The interpolation formula of equation 15 yields

$$\tilde{u}^2(\alpha_p) = 3.055 \cdot 10^{-6}\ \mathrm{Bq^2/kg^2} \cdot \left(1 - \frac{\alpha_p}{10.776 \cdot 10^{-3}\ \mathrm{Bq/kg}} \right) + \frac{6.662 \cdot 10^{-6}\ \mathrm{Bq^2/kg^2} \cdot \alpha_p}{10.776 \cdot 10^{-3}\ \mathrm{Bq/kg}} = 3.055 \cdot 10^{-6}\ \mathrm{Bq^2/kg^2} + 3.347 \cdot 10^{-4}\ \mathrm{Bq/kg} \cdot \alpha_p \tag{30}$$

With Eq. (30) one obtains an implicit equation for the detection limit

$$\alpha_p^* = 2.875 \cdot 10^{-3} + k_{1-\beta} \cdot \sqrt{3.055 \cdot 10^{-6} + 3.347 \cdot 10^{-4} \cdot \alpha_p} \tag{31}$$

The equation is solved by iteration with a starting value $\alpha_p^* = 2 \cdot A_p^* = 5.75 \cdot 10^{-3}$ Bq/kg. This yields the result for the detection limit of

$$\alpha_p^* = 6.7\ \mathrm{mBq/kg}. \tag{32}$$

Because of $A_p/u(A_p) = 4.177$ the approximation for $y >> u(y)$ can be applied and one obtains the confidence limits:

$$\alpha_{l,u} = A_p \pm k_{1-\gamma/2} \cdot u(A_p) = (10.776 \pm 1.96 \cdot 2.58)\ \mathrm{mBq/kg} \tag{33}$$

$$\alpha_l = 5.8\ \mathrm{mBq/kg}; \alpha_u = 15.8\ \mathrm{mBq/kg}$$

The calculation of a best estimate z is not needed here because of $A_p/u(A_p) = 4.177$.

Conclusions

Standardized procedures for the calculation of uncertainties and of characteristic limits are an essential part of quality assurance in nuclear and other analytical techniques. Strict adherence to the ISO Guide[14] provides standard uncertainties which take into account all sources of uncertainties in measurements. Based on such standard uncertainties characteristic limits can be consistently calculated using a Bayesian statistical approach. Upcoming parts of DIN 25482[7–10] and of ISO 11929[11–13] will make use of a Bayesian theory of uncertainty for the standardized determination of characteristic limits in nuclear analytical techniques.

*

The author is grateful to K. WEISE for introducing him to a Bayesian view at the evaluation of measurements and for many helpful discussions.

References

1. B. ALTSCHULER, B. PASTERNACK, Health Phys., 9 (1963) 293.
2. W. L. NICHOLSON, Fixed Time Estimation of Counting Rates With Background Corrections, Hanford Laboratories, Richland, 1963.
3. L. A. CURRIE, Anal. Chem., 40 (1968) 586.
4. R. MICHEL, O. MENDE, K. KIRCHHOFF, Kerntechnik, 62 (1997) 104.
5. T. BAYES, Phil.Trans. Roy. Soc., 53 (1763) 370; reprinted and commented by G. A. BARNARD, in Biometrika, 45 (1958) 293.
6. K. WEISE, Kerntechnik, 63 (1998) 21.
7. DIN 25482-10, Detection limit and decision threshold for ionizing radiation measurements – Part 10: General applications, Deutsches Institut für Normung e.V., Berlin, yellow print, 1998.
8. DIN 25482-11, Detection limit and decision threshold for ionizing radiation measurements – Part 11: Measurements with albedo-dosimeters, Deutsches Institut für Normung e.V., Berlin, draft, 1999.
9. DIN 25482-12, Detection limit and decision threshold for ionizing radiation measurements – Part 12: Unfolding of spectrometric measurements, Deutsches Institut für Normung e.V., Berlin, draft, 1999.
10. DIN 25482-13, Detection limit and decision threshold for ionizing radiation measurements – Part 13: Counting measurements at moving objects, Deutsches Institut für Normung e.V., Berlin, draft, 1999.

* In this example we give more digits than significant in order to make it easier recalculate.

11. ISO 11929-7, Determination of detection limit and decision threshold for ionizing radiation measurements – Part 7: Fundamentals and general applications, ISO/DIS, 1999.
12. ISO 11929-5, Determination of detection limit and decision threshold for ionizing radiation measurements – Part 5: Fundamentals and application to a transient measurement mode, ISO/DIS, 1999.
13. ISO 11929-8, Determination of detection limit and decision threshold for ionizing radiation measurements – Part 8: Fundamentals and application to unfolding of spectrometric measurements without the influence of sample treatment, ISO/DIS, 1999.
14. ISO Guide to the Expression of Uncertainty in Measurement. ISO International Organization for Standardization, Geneve 1993, corrected reprint, 1995.
15. ISO International Vocabulary of Basic and General Terms in Metrology. ISO International Organization for Standardization, Geneve, 1993.
16. L. A. CURRIE, Pure Appl. Chem., 67 (1995) 1699.
17. EURACHEM, Quantifying Uncertainty in Analytical Measurement, CITAC, 1995.
18. a. K. WEISE, W. WÖGER, Meas. Sci. Technol. 4 (1993) 1.
18. b. K. WEISE, W. WÖGER, Meßunsicherheit und Meßdatenauswertung, Wiley-VCH, Berlin, 1999.
19. E. T. JAYNES, Papers on Probability, Statistics and Statistical Physics, R. D. ROSENKRANTZ (Ed.), Kluwer Publ., Dordrecht, Boston, New York, 1989.
20. F. KOHLRAUSCH, Praktische Physik, Band 3, 24th ed., Teubner, Stuttgart, 1996, p. 613.
21. A. SCHMIDT, Ch. SCHNABEL, J. HANDL, D. JAKOB, R. MICHEL, H.-A. SYNAL, M. J. M. WAGNER, M. SUTER, Sci. Tot. Environ., 223 (1998) 131.
22. S. SZIDAT, A. SCHMIDT, J. HANDL, D. JAKOB, R. MICHEL, H.-A. SYNAL, M. SUTER, this Proceedings.