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## Use of the Bayesian Concept for the Calculation of Characteristic Limits in Radioanalytical Methods★

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Presented are procedures based on modern Bayesian statistics which are used to calculate characteristic limits, *i.e.* the decision threshold, detection limit and confidence limit in radioanalytical methods. Indicated are also the key elements of this statistics which can be used for measurement of ionizing radiation. The attached example of instrumental neutron activation analysis provides an illustration of the issues discussed.

Przedstawiono procedury postępowania, oparte na nowoczesnej statystyce bayesowskiej, stosowane do obliczania granic charakterystycznych tzn. progu decyzji, granicy detekcji i granic ufności w metodach radioanalitycznych. Podano także podstawowe elementy tej statystyki w aspekcie jej wykorzystania w pomiarach promieniowania jonizującego. Załączony przykład z instrumentalnej neutronowej analizy aktywacyjnej ilustruje omówione zagadnienie.

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

There has been for some decades a controversial debate between supporters of conventional and Bayesian statistics. Those readers who would like to get a closer look at the history and substance of the scientific dispute in this case are referred to a monograph by Jaynes, an outstanding promoter of Bayesian statistics [1].

An important distinction between both types of statistics lies in a quite different approach to the concept of probability. The conventional concept of probability in statistics is associated with the relative frequency of random events. Such a statistics fails in case of systematic effects, non-linear measurement models, values measured close to detection limits, *etc.* [1, 2]. An example of inconsistencies occurring in conventional statistics can also be the Guide which has introduced two different ways for uncertainty evaluation (Type A and Type B) [3].

Probability in Bayesian statistics has a completely different meaning: it reflects the state of our incomplete knowledge of the measured quantity. This state is a result of information obtained from measurements as well as that which was available prior to such measurements (prior information). In other words, this difference can be put as follows: in conventional statistics we ask what our measurements are supposed to bring us, whereas in Bayesian statistics our question is rather about how our measurements will add to our knowledge of the measured value. It should be noted here that information existing prior to a measurement may include the results of any previous measurement, thus creating a chain of consecutive steps toward the expansion of available knowledge.

The term of *characteristic limits* is deemed to refer to the three specific statistics which are vital to ensuring the quality of measurements (determinations): decision threshold, detection limit and confidence limits [4–6]. The theoretical framework and the rules for the calculation of such values for ionizing radiation were developed in the 1960s, in the pioneering works of Altschuler and Pasternack [7], Nicholson [8], and Currie [9]. The author of this article addresses the issue of the decision and detection limits for the measurement of short-lived radioisotopes that are used in neutron activation analysis [10, 11]. These works are based on conventional statistics: they do not comprise the entire analytical procedure as the contemporary Guide does [3], and they relate to the characteristic limits of the signal (counts) from the radiation detector.

In radiological protection, mainly dosimetry [12], as well as in low-activity measurements [13], the idea of Bayesian statistics was already used in the second half of the last century. The Principle of Maximum Entropy (Information), one of the key elements of the modern concept of Bayesian statistics, was not applied in the works of that period.

The Bayesian approach to the calculation of characteristic limits in ionizing radiation metrology was pioneered by Weise and Wöger [14, 15]. Their work helped build a well-documented mathematical base of this concept for the calculation of measurement uncertainties. The Bayesian concept is now becoming increasingly popular in

nuclear engineering, including in radioanalytical and radioecological methods. In its four out of eight parts (parts 5, 6, 7 and 8), the ISO 11929 (2000) standard, which deals with the calculation of characteristic limits in ionizing radiation measurements, is based on the methods of Bayesian statistics [4]. An expression of recognition for the Bayesian concept is also the European Commission's recommendation which advises using this standard (part 7) for radiological monitoring of the surroundings of nuclear facilities [16]. Some reports have recently appeared in the literature of the subject that efforts are underway to replace conventional statistics in parts 1–4 of the ISO 11929 standard with a new solution based on Bayesian statistics [6]. Far-reaching changes are also being made to the Guide's concept [17].

The article is basically meant for practitioners of radioanalytical methods, although it may also be of use to other professionals in ionizing radiation metrology. The theoretical considerations of Bayesian statistics are shown to an extent necessary to understand the concept of characteristic limits. The author hopes that the article will help avoid mistakes and myths that are still relevant when estimating detection limits [18], in particular, make a distinction between the decision threshold and the detection limit and not report negative results (for example,  $0.1 \pm 0.4 \text{ Bq cm}^{-2}$ ).

## MEASUREMENT MODELLING

The modern concept of evaluation of measurement result uncertainty (measurand) is based on the model function, which is also called model equation:

$$Y = f_M(X_1, X_2, \dots, X_N) \quad (1)$$

where  $Y$  stands for the output quantity, that is, the measurand, whereas  $X_i$  for the input quantities. This is a model with one output which is adopted in the current Guide [3]. Knowledge of input quantities, which is incomplete, comes from their probability density function (PDF). While the PDF has good theoretical foundations, the process of measurement modeling does not yet have them. There are no clues about it in the Guide, either. This is, therefore, a task for the researcher/metrologist, and it depends on his experience and knowledge [19].

Input quantities  $X_i$  are assumed to be random variables with values  $x_i$  ( $i = 1, 2, \dots, N$ ) as an estimate. Output quantity  $Y$  is a random variable with measurement result  $y$  as an estimate. Function (1) is required to have only one output value for any set of input values, with various sets of input values being allowed to form a single output value. This rule shows that the dependence is true:

$$y = f_M(x_1, x_2, \dots, x_N) \quad (2)$$

In many analytical methods, especially in radioanalytical methods, the model function is linear or can be considered linear with a good approximation in certain intervals where after expansion into a Taylor series only terms of the first order are used. Then the Guide's rule of uncertainty combination is applied:

$$u^2(y) = \sum_{i=1}^N \left( \frac{\partial f_M}{\partial x_i} \right)^2 u^2(x_i) \quad (3)$$

which is called the law of uncertainty propagation (for non-correlated input values). One should keep in mind, however, that some other procedures should be used to calculate uncertainties  $u(y)$  for non-linear models (1). The issue has been addressed in a new document attached as a supplement to the Guide [20].

Some applications of Bayesian statistics also use an equation that expresses the dependence of the effect (signal) on its cause, which is called measurement equation [19]. The gross signal is typically assigned to input quantity  $X_1$ , and the equation is as follows:

$$x_1 = h(y, x_2, \dots, x_N) \quad (4)$$

Equation (4) can be obtained by transforming equation (2). In more complex cases, such as non-linear dependences, iterative methods should be applied.

## KEY ELEMENTS OF BAYESIAN STATISTICS

Bayesian statistics is based on the theorem of Bayes (1702–1761), which was re-discovered by Jeffreys in 1938 [1]. Bayes' theorem grows from the simple principle that two random variables A and B remain in the following dependence:

$$P(AB) = P(A|B) \cdot P(B) = P(B|A) \cdot P(A) \quad (5)$$

Vertical arrows | indicate conditional distributions. It appears from dependence (5) that:

$$P(A | B) = \frac{P(B | A) \cdot P(A)}{P(B)} \quad (6)$$

In the measurement process, the above probabilities have the following meanings:

- P(A) – pre-measurement probability that value of Y actually falls within interval  $(\eta, \eta + d\eta)$  with prior information I being already known, that is, in a notation using the probability density function for  $\eta$  it will be  $P(A) = g_y(\eta|I)d\eta$ ;
- P(B) – probability that the measurement returns (any) data, that is,  $P(B) = \text{const.}$ ;
- P(B|A) – this factor represents the degree of our belief/hope that the measurement will return new data B if event A occurs; it is called data likelihood and is denominated as  $L(\eta|y, I)$ ;
- P(A|B) – probability that output value of Y actually falls within interval  $(\eta, \eta + d\eta)$  if the measurement return result y.

Following these notes, dependence (6) can be rewritten as follows:

$$g_y(\eta|y, i) = C \cdot L(\eta|y, I) \cdot g_y(\eta|I) \quad (7)$$

Constant C is determined by the normalization of posterior function  $g_y(\eta|y, I)$ . Likelihood function L is not a PDF, and is not subject to normalization. Dependence (7) is often put in a simplified form to leave out I, and then

$$g(\eta|y) = C \cdot L(\eta|y) \cdot g(\eta) \quad (8)$$

Likelihood function L turns into a function of the same name in conventional statistics if this function is symmetrical and  $g(\eta) = \text{const.}$

The goal of further consideration is to use prior and measurement information to determine posterior probability density function  $g(\eta|y)$ , which is also called Bayesian probability density function (BPDF). In modern Bayesian statistics, the Principle of Maximum Entropy (Information) (PME) is used for this purpose. Derived from Shannon's formula, the PME is quite well-known in quantum mechanics and thermodynamics. For continuous variables, the PME is written as follows:

$$S = -\int g(\eta|y) \cdot \ln(g(\eta|y)) d\eta = \max \quad (9)$$

If the measurement returns the amount and variance of measured quantity Y, then equation (9) can be solved by imposing the following constraints:  $E(\eta) = y$  and  $\text{Var}(\eta) = u^2(y)$ . So formulated, it is a problem of the calculus of variations, which is solved by applying the method of Lagrange multipliers [1, 21]. The solution returns a probability density function that makes the best possible use of prior and measurement information about measured value Y:

$$g(\eta|y) = C \cdot g(\eta) \exp(-(\eta-y)^2/2u^2(y)) \quad (10)$$

In radioanalytical methods,  $Y$  usually represents analyte concentration and/or isotope radioactivity. For these figures, actual value  $\eta$  cannot be negative, that is,  $\eta \geq 0$  and prior function  $g(\eta) = \text{const}$  and posterior function  $g(\eta|y)$  have Gaussian forms. It should be noted that in the Gaussian term the random variable is  $\eta$ , and the parameter  $y$ . Constant  $C$  is determined by normalization.

Probability density function  $g(y|\eta)$  for constraint  $\eta$  is needed to calculate the decision threshold. Such a function can be obtained from equations (6) and (10)) by means of conformal transformations:

$$g(y|\eta) = C \cdot \exp(-(y - \eta)^2 / 2\tilde{u}^2(\eta)), \geq 0 \quad (11)$$

An important feature of formula (11) is uncertainty  $\tilde{u}(\eta)$ , which is introduced here as an approximation of uncertainty  $u(y)$ . The determination of  $\tilde{u}^2(\eta)$  requires undertaking certain numerical operations that are necessary for calculation of characteristic limits. A natural approach to the said approximation is to use measurement equation (4). We include signal  $x_1$  in equation (3), replace uncertainties  $u(x_1)$  with function of  $x_1$  (if practicable), and finally use  $\eta$  in place of  $y$  [5, 6]. It is recommended to take the input quantity  $X_1$  as the gross counting rate [6]. The author of this article is of the opinion that in radioanalytical methods due to simple model equations the quantity  $X_1$  can be also taken as the net counting rate  $r_0$ .

In radioanalytical methods the well-known dependence exists:  $u(r_0) = (r_0/t + r_b(1/t + 1/t_b))^{0.5}$ , where  $t$  and  $t_b$  represent the measurement times, respectively, of the sample and the background, and  $r_b$  the background counting rate.

If the procedure described above is impracticable, the approximation specified in the ISO-11929-7 standard could be used [3]. It is assumed that  $\tilde{u}^2(0)$  and  $u^2(y)$  are known and  $\tilde{u}^2(\eta)$  is a slowly increasing linear function of  $\eta$ , hence

$$\tilde{u}^2(\eta) = \tilde{u}^2(0) \cdot (1 - \eta/y) + u^2(y) \eta/y \quad (12)$$

Formula (11) is a PDF that is totally defined as it does not contain any unknown parameters. Therefore, its expected value and standard deviation can be calculated, and not estimated as it is the case in conventional statistics [2].

## CALCULATION OF CHARACTERISTIC LIMITS

As in conventional statistics, the decision threshold and the detection limit are defined here based on zero hypothesis  $H_0(\eta = 0)$  being compared to alternative hypothesis  $H_1(\eta > 0)$ . In the modern approach to this problem, it is measured value  $Y$  which is decisive. Measurement result  $y$ , calculated using model function (2), should be compared to decision threshold  $y^*$ . If  $y \leq y^*$ , the zero hypothesis is assumed to be true. If  $y > y^*$ , it is statistically unreasonable to assume the zero hypothesis, and therefore an assertion is made that measured value  $Y$  occurs in the sample. The probability of this error, called error of the first kind, amounts to:

$$P(y > y^* | \eta = 0) = \alpha \quad (13)$$

To calculate decision threshold  $y^*$ , you must know  $\tilde{u}^2(\eta)$  referred to in the previous paragraph. Placing  $\eta = 0$ , you obtain:

$$y^* = k_{1-\alpha} \tilde{u}(0) \quad (14)$$

Coefficient  $k_{1-\alpha}$  is the quantile of the standard normal distribution for significance level  $\alpha$ . It is usually assumed that  $\alpha = 0.05$  [4–6].

The concept of detection limit relates to actual value  $\eta$ , but not to that of measurement result  $y$  (which is quite often confused). We find such characteristic value  $\eta$ , denominated as  $\eta^*$ , to make the following dependence possible:

$$P(y \leq y^* | \eta = \eta^*) = \beta \quad (15)$$

that is, we define detection limit  $\eta^*$  based on decision threshold  $y^*$  and probability  $\beta$  of taking a wrong decision or accepting a false null hypothesis. This error is called error of the second kind. The detection limit is calculated using the following formula:

$$\eta^* = y^* + k_{1-\beta} \tilde{u}(\eta^*) \quad (16)$$

where coefficient  $k_{1-\beta}$  is also the quantile of the standard normal distribution for significance level  $\beta$ . It is usually assumed that  $\alpha = \beta = 0.05$ .

A general procedure used to determine the value of  $\eta^*$  is the iterative one. if an approximation for  $\tilde{u}(\eta^*)$  can be accepted, which is returned by formula (12), then detection limit  $\eta^*$  is given by formula

$$\eta^* = a + (a^2 + (k_{1-\beta}^2 - k_{1-\alpha}^2) \tilde{u}^2(0))^{1/2} \quad (17)$$

where

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

For  $\alpha = \beta$ ,  $\eta^* = 2a$ .

If approximation  $u^2(y) \cong \tilde{u}^2(0)$  is sufficient, then  $\eta^* = 2y^*$ , that is, the detection limit is twice as high as the decision threshold.

The calculation of confidence limits is applicable when measurement result  $y$  is higher than the decision threshold. In Bayesian statistics, these limits are based on the BPDF. The BPDF has the form of a cut Gaussian distribution.

Given that  $g(\eta) = \text{const}$  and following normalization one obtains the result

$$g(\eta|y) = (1/\sqrt{2\pi}\omega u(y)) \exp(-(\eta - y)^2/2u^2(y)), \text{ for } \eta \geq 0 \quad (18)$$

where  $\omega$  is a value of the standard normal distribution (SND) for quantile  $y/u(y)$ . The calculation of confidence limits is based on the assumption that the actual amount of measured value  $\eta$  lies with Bayesian probability  $(1 - \gamma)$  between the lower ( $\eta_L$ ) and upper ( $\eta_U$ ) limits, and it is a probabilistically symmetric coverage interval, *i.e.*

$$P(\eta < \eta_L) = P(\eta > \eta_U) = \gamma / 2.$$

The limits can be found in the relationships:

$$\int_0^{\eta_L} g(\eta|y) d\eta = \gamma/2 \text{ and } \int_{\eta_U}^{\infty} g(\eta|y) d\eta = \gamma/2 \quad (19)$$

Following integration and some simple transformations using the dependences for the SND distribution function  $F(-t) = 1 - F(t)$ , we arrive at the following equations:

$$F\left(\frac{y - \eta_L}{u(y)}\right) = p = \omega(1 - \gamma/2) \text{ and } F\left(\frac{\eta_U - y}{u(y)}\right) = q = 1 - \omega\gamma/2 \quad (20)$$

The quantiles of function  $F(t)$  which correspond to probability  $p$  and  $q$  should be denominated as  $k_p$  and  $k_q$ , respectively, that is, it appears from (20) that:

$$\eta_L = y - k_p u(y) \text{ and } \eta_U = y + k_q u(y) \quad (21)$$

The Bayesian confidence limits are not symmetric to value  $y$ , but we can assume  $k_p = k_q$  for  $y > \approx 4u(y)$ . In addition, the lower confidence limit is always positive, which results directly from the definition of function  $g(\eta|y)$  in equation (18) and the definition of this limit ( $\eta_l$ ) in equations (19).

In the Bayesian statistics of characteristic limits, the concepts of best estimate value  $z$  and its standard uncertainty  $u(z)$  are also used. The best estimate is expected value  $\eta$ , that is,  $z = E\eta$ , and the standard uncertainty  $u(z) = \sqrt{\text{Var}(\eta)}$ . After performing some calculations using function (18), you arrive at:

$$z = y + \frac{u(y) \cdot \exp\left(-\frac{y^2}{2 \cdot u^2(y)}\right)}{\omega \cdot \sqrt{2\pi}} \quad (22)$$

$$u(z) = \sqrt{u^2(y) - (z - y) \cdot z} \quad (23)$$

As you can see,  $z > y$  and  $u(z) < u(y)$ , but you can already assume  $z = y$  if  $u(z) = u(y)$  for  $y > \approx 4$  as well. If this prerequisite is not fulfilled, values  $z$  and  $u(z)$  should be included in the measurement report.

## SUMMARY

1. The measured value  $y$  and its uncertainty  $u(y)$  are calculated in accordance with the Guide's rules, that is, from model equation (1) and uncertainty combination equation (3). Measurement models with correlated input values are used in radioanalytical and radioecological methods very rarely. The equation for the combination of uncertainties in such cases is omitted in the article, but we can find it elsewhere [3, 5, 6].
2. Subsequently, decision threshold  $y^*$  is calculated from equation (14). For this purpose, an expression for  $u(\eta)$  should be found as indicated in equation (11). Placing  $\eta = 0$  and assuming that  $\alpha$  usually equals to 0.05 and  $k_{1-\alpha}$  to 1.645, we will find  $y^*$ . If  $y \leq y^*$  'not detected' is reported.
3. Detection limit  $\eta^*$  in the methods concerned is usually calculated from equation (17) using approximation (12). The detection limit is compared to the standard amount for the measured value and we evaluate whether or not the method applied is suitable for our task in terms of detectability. The detection limit cannot be used for 'not detected' decisions.
4. Before starting to calculate confidence limits, you must find the  $y/u(y)$  ratio. If this ratio is higher than 4, confidence limits are calculated as in conventional statistics. Otherwise coefficient  $\omega$ , that is a value of standard normal

distribution  $F(t)$  for quantile  $t = y/u(y)$  should be obtained. Having  $\omega$  available and given that the confidence level is  $1 - \gamma$ , values  $p$  and  $q$  are usually calculated for  $\gamma = 0.1$  (or  $0.05$ ) from equations (20). Quantiles  $k_p$  and  $k_q$  can be read for  $p$  and  $q$ , respectively, from the statistical tables for  $F(t)$ . Confidence limits  $\eta_L$  and  $\eta_U$  are finally calculated from equations (21).

5. We should also calculate best estimate value  $z$  and its standard uncertainty  $u(z)$ . These values are calculated from equations (22) and (23) and included in the measurement report.

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### Example:

#### DETERMINATION OF ULTRATRACES OF CESIUM IN TOBACCO LEAVES (CTA–OTL–1) USING INSTRUMENTAL EPITHERMAL NEUTRON ACTIVATION ANALYSIS

The selected example concerns a specific situation in which the determination result is higher than the decision threshold, but lower than the detection limit. In conventional statistics, some difficulties in evaluating the confidence limits for the determination result usually arise in such cases.

The analytical procedure involved gamma-spectrometric measurements of long-lived radioisotopes of 15 elements, including cesium, generated in a stream of neutrons in the sample and the attached sets of relevant standards [22].

The model equation of the method is a NAA-typical linear equation:

$$c = \xi \frac{r}{M} \frac{M}{m} \quad (24)$$

where:  $c$  – cesium concentration in the sample (in  $\text{ng g}^{-1}$ ),  $m$  – sample weight (in grams),  $M$  – standard weight (in ng),  $r$  and  $R$  – net count rates in the 795.8 keV peaks in the gamma spectra of the sample and the standard, respectively,  $\xi$  – correction factor for the microgradient of neutrons.

Count rates  $r$  and  $R$  were calculated by adding up counts  $a_i$  in the channels containing the 795.8 keV peak according to Rogers' formulae often applied in analytical gamma-ray spectrometry [23]. These formulae are defined as

$$A = G - Bg = \sum_{i=2}^{N-1} a_i - \frac{1}{2}(n-2)(\bar{a}_1 + \bar{a}_N) \quad (25)$$

for net area of gamma-ray peak ( $A$ ) and

$$u^2(A) = A + 0.25 \left[ \left( 2 + \frac{N-2}{m} \right) (n-2)(\bar{a}_1 + \bar{a}_N) \right] \quad (26)$$

for uncertainty of  $A$ . The factor  $(N-2)$  is used in Rogers' formula because channels 1 and  $N$  do not contribute counts to the net area. Symbol  $\bar{a}_1$  means average background counts in channel 1 obtained from averaging over channels  $2 - m$  to 1 and symbol  $\bar{a}_N$  means average background counts in channel  $N$  obtained from averaging over channels  $N$  to  $N + m - 1$ . Symbols  $G$  and  $Bg$  means the gross number of counts accumulated in  $N-2$  channels (between  $i = 2$  and  $i = N - 1$ ) and the background number of counts estimated for the 795.8 keV peak with the use of linear approximation, respectively.

We assumed  $N = 11$  channels for determination purposes, with channels 1 and 11 containing average counts  $\bar{a}_1$  and  $\bar{a}_{11}$  from three subsequent channels ( $m = 3$ ). In the so arranged Rogers' rule, standard uncertainty for the net counting rate  $r = A/t$  in the 795.8 keV peak is calculated using the following formula:

$$u^2(r) = r / t + 11.25 (\bar{a}_1 + \bar{a}_{11}) / t^2 \quad (27)$$

where  $t$  – measurement time of the gamma spectrum of samples (in seconds).

The calculation procedure of standard  $u^2(R)$  for measurement time  $T$  is similar.

**Table 1.** Data for the input values in the example

	Quantity	Value	Standard uncertainty	Unit	Type of uncertainty
Sample	$\xi$	1.17	0.03	–	B
	G	9332	96.0	l	A
	Bg	9018	116.3	l	A
	A	314	151.2	l	A
	$\bar{a}_1 + \bar{a}_{11}$	2004	25.8	l	A
	t	14400	–	s	–
	r	0.0218	0.0105	s <sup>-1</sup>	A
	m	1.0	$5 \times 10^{-4}$	g	A
Standard	G	12041	109.7	l	A
	Bg	10094	123.0	l	A
	A	1947	164.8	l	A
	$\bar{a}_1 + \bar{a}_{11}$	2243	27.3	l	A
	T	1800	–	S	–
	R	1.082	0.0916	s <sup>-1</sup>	A
	M	1500	55	ng	A

Calculations are performed using the data in Table 1, in the sequence specified in the Summary.

1. The determined cesium concentration, calculated from formula (24), amounts to 35.3 ng g<sup>-1</sup>.
2. Standard uncertainty  $u(c)$  is calculated in line with the existing principle of uncertainty propagation (3). By applying this principle to function (24) we obtain:

$$\frac{u^2(c)}{c^2} = \frac{u^2(\xi)}{\xi^2} + \frac{u^2(r)}{r^2} + \frac{u^2(R)}{R^2} + \frac{u^2(m)}{m^2} + \frac{u^2(M)}{M^2} \quad (28)$$

and after substitution of the data from Table 1 we obtain  $u(c) = 17.7 \text{ ng g}^{-1}$ .

3. The calculation of decision threshold  $c^*$  requires knowledge of  $\tilde{u}(\eta = 0)$ . For this purpose, in formula (28) expression (27) should be substituted for  $u^2(r)$ , and from the measurement equation, after transformation of model equation (24), we get  $r = c \cdot m \cdot R / \xi \cdot M$ . These substitutions bring an expression for  $u^2(c)$  in the form:

$$u^2(c) = c^2 \left[ \frac{u^2(\xi)}{\xi^2} + \frac{u^2(R)}{R^2} + \frac{u^2(m)}{m^2} + \frac{u^2(M)}{M^2} \right] + \left( \frac{\xi M}{m R t} \right)^2 \left[ c \frac{m R t}{\xi M} + 11.25(\bar{a}_1 + \bar{a}_{11}) \right] \quad (29)$$

Equation (27) is fulfilled for true yet unknown cesium concentration  $\eta$ . By replacing  $c$  with  $\eta$  in (27), and then assuming that  $\eta = 0$ , we arrive at:

$$\tilde{u}^2(0) = 11.25 \left( \frac{\xi M}{m R t} \right)^2 (\bar{a}_1 + \bar{a}_{11}) \quad (30)$$

After substituting the data from Table 1 and assuming probability  $\alpha = 0.05$  we get  $\tilde{u}(0) = 17.0 \text{ ng g}^{-1}$  and decision threshold  $c^* = 1.645 \times 17.0 = 27.9 \text{ ng g}^{-1}$ .

4. Cesium detection limit  $\eta^*$  is calculated using formula (16) by assuming that  $\alpha = \beta = 0.05$ , that is,  $k_\alpha = k_\beta = 1.645$  and the calculated decision threshold  $27.9 \text{ ng g}^{-1}$ . For  $\tilde{u}(\eta)$  both the exact formula (27) and the approximation given by formula (17) were used. Formula (29) allows us to obtain the relationship between  $\tilde{u}^2(\eta)$  and  $\eta$  after inserting the respective data from Table 1 and replacing  $c$  with  $\eta$ :

$$\tilde{u}^2(\eta) = 0.00919 \eta^2 + 0.1126 \eta + 288.7 \quad (31)$$

With the use of the above relationship we get the detection limit  $\eta^* = 57.4 \text{ ng g}^{-1}$ . On the other hand when using the approximation (17) for  $\tilde{u}^2(\eta)$  we obtain the detection limit  $\eta^* = 57.7 \text{ ng g}^{-1}$ . So, in our example is slowly increasing linear function of  $\eta$ .

5. Traces of cesium were detected in tobacco sample ( $c > c^*$ ) and the limits of the confidence interval should be calculated. Since ratio  $c/u(c) = 35.3/17.7 = 4$ , the interval limits are not symmetrical to a cesium determination of  $35.3 \text{ ng g}^{-1}$ . From table of standard normal distribution  $F(t)$  we find for quantile  $t = 1.994$  the value of  $\omega = F(1.994) = 0.9769$ . We assume confidence level  $1 - \gamma = 0.95$ . For these value  $\omega$  and  $\gamma$  substituted in formulas (20) we obtain  $p = 0.9524$  and  $q = 0.9755$ . From table of the above mentioned function  $F(t)$  we find for probabilities  $p$  and  $q$  quantiles  $k_p = 1.6690$  and  $k_q = 1.9683$ . The upper and lower limits of the confidence interval are calculated using formula (21) by placing determined cesium concentration  $35.3 \text{ ng g}^{-1}$ , its

standard uncertainty  $17.7 \text{ ng g}^{-1}$  and relevant values of the quantiles. In our example, the confidence limits amount to  $5.7 \text{ ng g}^{-1}$  and  $70.1 \text{ ng g}^{-1}$ .

From formulae (22) and (23) we obtain for our data  $z = 36.4 \text{ ng g}^{-1}$  and  $u(z) = 16.6 \text{ ng g}^{-1}$ .

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