Comments on "Quality assurance of nuclear analytical techniques based on Bayesian characteristic limits"

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A paper by R. MICHEL in this journal (J. Radioanal. Nucl. Chem., 245 (2000) 137) describes, among other things, a numerical example: the calculation of characteristic limits in an analysis of ¹²⁹I via radiochemical NAA. A key problem in Bayesian characteristic limits is a proper formulation of the expression for the uncertainty associated with the measurand if its true value is equal to zero, $\tilde{u}(0)$. We show that MICHEL's expression for $\tilde{u}^2(0)$ is not correct and propose a new one. Some numerical errors found in the paper are also indicated.

Introduction

MICHEL presents an example of the calculation of Bayesian characteristic limits (i.e., decision threshold, detection limit and confidence limits) for the determination of 129 I in an Ukrainian soil sample by radiochemical neutron activation analysis (RNAA).¹ The attached model equation in MICHEL's example is attractive for practitioners of nuclear analytical methods since it takes into account also the information about the blank value. In some cases, e.g., in NAA of biological materials the blank values can be of significance, comparable with the element content to be determined.²

In the course of the adoption of MICHEL's example to our analytical work³ with high blank values we have noticed that MICHEL's formula¹ for the uncertainty $\tilde{u}(0)$ is incorrect and some numerical errors exist in the calculations. Hence, the values of characteristic limits in question should be again calculated.

MICHEL's uncertainty $\tilde{u}(0)$

The simplified model equation in MICHEL's paper l is as follows:

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

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

The combined standard uncertainty, $u(A_p)$, is calculated according to the concept of the GUM law of

uncertainty propagation⁴ as the positive square root of the variance $u^2(A_n)$. Thus

$$u^{2}(A_{p}) = \left[\frac{1}{m_{p} \cdot \varepsilon}\right]^{2} \cdot \left[\left(\frac{u^{2}(m_{p})}{m_{p}^{2}} + \frac{u^{2}(\varepsilon)}{\varepsilon^{2}}\right) \cdot \left(\frac{A_{s} \cdot NP_{p}}{NP_{s}} - A_{b}\right)^{2} + \left(\frac{NP_{p}}{NP_{s}}\right)^{2} \cdot u^{2}(A_{s}) + \left(\frac{A_{s} \cdot NP_{p}}{NP_{s}}\right)^{2} \cdot u^{2}(NP_{s}) + u^{2}(A_{b})\right]$$

$$\left[\frac{A_{s}}{NP_{s}}\right]^{2} \cdot u^{2}(NP_{p}) + \left(\frac{A_{s} \cdot NP_{p}}{NP_{s}^{2}}\right)^{2} \cdot u^{2}(NP_{s}) + u^{2}(A_{b})\right]$$

Substituting in Eq. (2) a true activity of ¹³⁰I in the sample $\alpha_p = 0$ and $NP_p = 0$ MICHEL¹ get:

$$\begin{split} \widetilde{u}^{2}(0) &= \left[\frac{1}{m_{p} \cdot \varepsilon}\right]^{2} \cdot \left[\left(\frac{u^{2}(m_{p})}{m_{p}^{2}} + \frac{u^{2}(\varepsilon)}{\varepsilon^{2}}\right) \cdot A_{b}^{2} + \\ &+ 2 \cdot BG_{p} \cdot \left(\frac{A_{s}}{NP_{s}}\right)^{2} + u^{2}(A_{b}) \right] \end{split}$$
(3)

where $u^2(NP_p=0)=2 \cdot BG_0$. However, in Eq. (3) should be $(-A_b)^2$ not A_b^2 . This misunderstanding is the reason why Eq. (3) can not be accepted.

The proposed expression for $\tilde{u}^2(0)$

The above mentioned discrepancy relating Eq. (3) one can explain using the measurement equation.⁵ From Eq. (1) we obtain:

$$NP_{p} = \frac{NP_{s}}{A_{s}} \cdot (m_{p} \cdot \varepsilon \cdot A_{p} + A_{b}) =$$

$$NP_{n}^{(1)} \text{ (sample)} + NP_{n}^{(2)} \text{ (blank)}$$
(4)

thus, the symbol NP_p in Eq. (1) means the net peak area of the 536 keV γ -line of ¹³⁰I in the measured spectrum,

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