P39: UNCERTAINTY AT VERY LOW ANALYTICAL LEVELS – THE PROBABILISTIC APPROACH

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Abstract – Chemical metrology is a specific field where the process in order to achieve a traceable and comparable results is difficult to be standardized. Moreover, a more holistic approach is required for the evaluation of their reliability. On the other hand, a continuous increasing number of contaminants are intended to be determined in foods and for a high percentage of them e.g. the more toxic, at very low quantification levels. At these low levels, close to detection, the classical way of GUM using statistical techniques for the determination of uncertainty, as the range of values that could reasonably attributed to the measurand, becomes weak.

Probabilities have been used for the determination of type B uncertainties. The probabilistic approach is regarded appropriate in order to determine the concentration level of the analyte and to estimate its uncertainty at the detection and quantification level of the method. More specifically Monte Carlo Simulation and Bayesians can be considered as useful approaches. Bayesians are very useful in case of detection methods where the measurement is not a deterministic procedure but it is based on the capability of the method to classify or identify the analyte from an indication which could lead to false positive or false negative observation.

In the present work, Bayesians are applied in order to estimate the value of the analyte and its uncertainty in the determination of food contaminants at very low levels as well as in identification techniques.

Keywords: uncertainty, probabilistic, Bayesians, low cncentrations

1. INTRODUCTION

It is undeniable that reliability of measurement results is established by comparability and traceability along with uncertainty estimation. In the field of chemical metrology, including chemical analyses, microbiological examinations and clinical and molecular tests, achievement of traceability and estimation of uncertainty cannot be established by a rational system such as in physical measurements and according to GUM estimation of uncertainty statistical model.

Furthermore, in laboratory medicine, as clinical chemistry, clinical microbiology, e.t.c. the samples' examinations (measurements or observations) originating from humans reflect a dynamic "in vivo" state. Taking into account that many of these observations are qualitative the question on their quantitative character is emerging.

However, even in quantitative testing, specifically in case of toxic contaminants, where the safety limits are very low, the methods of analysis should have the capacity to measure at these low levels and close to detection limit.

At these levels, instead of statistics, probabilities are the appropriate tool to provide the likelihood analytes or observants under examination are present and therefore probabilistic estimation of uncertainty, type B, should be applied [1].

2. EXPERIMENTAL

2.1. The Bayesian approach

In "grey zones" of chemical metrology as at detection limits or qualitative observations and measurement should be handled with a holistic approach which is properly served by Bayesians.

Bayesians operate at a similar way as statistics but there are principal differences. Considering parameter ϑ of a statistical population which should be estimated and probability $f(x|\vartheta)$ which defines the probability of the observation of x, under different values of parameter ϑ. The fundamental difference between the two approaches is found on the fact that ϑ is used as a random quantity [2].

The aim of Bayesian approach in the estimation of uncertainty in chemical metrology is to coding the level of knowledge with regard the quantity of the measurand in the form of a probability density function (PDF).

In fact, Bayesian approach is based on *f(ϑ|x)* instead of *f(x|ϑ)*, that is the probability of distribution of *ϑ* for given *x* (data) instead of *x* given to *ϑ*. In order to achieve that probability prior probability distribution of *ϑ* is required.

The four fundamental points that differentiate Bayesian approach from classical statistics are (a) precious knowledge of the measurement, (β) subjective probability, that is the fact that probabilities are subjective and depend on confidence and knowledge of the observer with regard the observant/measurand which is based on a "a posteriori" distribution, (c) self-consistency, which means that all conclusions come from probabilities and (d) detachment from statistical «recipes» but conformation of independent criteria based on posterior distributions. Bayes' theorem is provided in formula (1)

$$\mathrm{P(B(B/} = \frac{\mathrm{P(A(A/B)P(}}{\mathrm{P(A)}} \quad (1)$$

2.2. Chemical metrology and probabilities

Many attempts have been referred to the application of probabilities and Bayesians in chemical metrology [3,4,5,6].

The aim is to estimate the mean value *μ* and standard deviation *σ* after a series of repeated measurements or observations D={Di;i=1,2,3,…,N}. Considering the independent measurements, the following model is proposed:

$$Di = \mu + n_i;\ ¥i; \qquad (2)$$

where n_i is the Gaussian noise with zero mean value and standard deviation *σ*.

3. RESULTS AND DISCUSSION

Bayesian approach was applied to estimate the likelihood and uncertainty of analytes at concentrations close to detection levels, in case of primary aromatic amines (PAAs) migrating form polyamide packaging materials in foods. The first a priori probability was considered as concentration of PAAs into food is zero or above zero. It has been proven that at the detection level for *n* independent measurements for the analytes the «true value» *μ* will follow t-distribution for any distribution of the independent measurements e.g. t- or normal distribution. For *Di* independent measurements and *μ* «true value» for each analyte, equations (3) and (4) are applied.

$$\begin{aligned}
\mathrm{P}(D/\mu,\sigma,I) &= \prod_{i=1}^{N} P(D_i/\mu,\sigma,\mathrm{I}) \\
&= \prod_{i=1}^{N} \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{1}{2}(D_i-\mu)^2/\sigma^2\right] \\
&= (2\pi\sigma^2)^{-\mathrm{N}/2} \exp\left[-\frac{1}{2}\sum_{i=1}^{N}(D_i-\mu)^2/\sigma^2\right] \\
&= (2\pi\sigma^2)^{-\mathrm{N}/2} \exp\left[-\frac{Ns^2}{2\sigma^2}\right] \exp\left[-\frac{N(\mu-\overline{D})^2}{2\sigma^2}\right]
\end{aligned} \qquad (3)$$

$$\overline{D} = \sum_{i=1}^{N}(D_i/\mathrm{N}) \text{ και } s^2=1/\mathrm{N}(\sum_{i=1}^{N}(D_i-\overleftarrow{D})^2). \qquad (4)$$

The result is the robust value of the a posteriori distribution and as expanded uncertainty the highest density interval which includes the required percentage of the a posteriori distribution is provided.

For a t-distribution with mean value of measurements *X*, standard uncertainty *u* and degrees of freedom ν_{eff} the highest density interval for confidence level *p* and down limit zero, is calculated as:

$$P_{tot}=1 - P_t\ (-X/u,\ \nu_{eff}) \qquad (5),$$

Where *Pt (q, v)* is the cumulative probability of Student's t. If put:

$$q_1=q_t(1-(1-pP_{tot})/2,\nu_{eff}) \quad (6),$$

where $q_t(P,v)$ the quartile of t distribution, the provided values intervals are $X \pm uq_1$ when $X-uq_1 \geq 0$ and $[0,X+uq_t(P_t(-X/s,\nu_{eff})+pP_{tot}.\nu_{eff})]$ when $X-uq_1<0$.

4. CONCLUSIONS

The present study points out, that probabilities and Bayesian approach can successfully be applied in chemical metrology specifically in measurements at low concentration levels and qualitative observations. Prerequisite is the availability of accurate previous information in the form of a priori distributions which is at initial level.

5. REFERENCES

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