# Application Note 1

# Comparison of a measurement result with the certified value

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*The comparison of a measurement result on a certified reference material with the certified value is explained. The method compares the difference between the certified and measured values with its uncertainty, i.e. the combined uncertainty of certified and measured value. Guidance on how to determine the standard uncertainties of certified values as well as standard uncertainties of measurement results is given.*

## INTRODUCTION

One of the most frequent applications of certified reference materials is validation of measurement procedures. To achieve this, measurements on certified reference materials are performed and the results are compared with the certified values. This comparison is often described in a qualitative manner such as measurement results "agree", "agree well" or even "agree perfectly" with the certified values. However, a structured and quantitative approach exists that allows making a statement on the evidence of any bias.
This approach takes into account the certified value, the measurement result and their respective uncertainties. These uncertainties are subsequently combined and the expanded uncertainty is compared to the difference. This note will explain the procedure of the uncertainty estimation and the comparison of results with a certified value.

## BASIC PRINCIPLES

After the measurement of a CRM the absolute difference between the mean measured value and the certified value can be calculated as

$$\Delta_m = |c_m - c_{CRM}|$$

$\Delta_m$ ........... absolute difference between mean measured value and certified value
$c_m$ ........... mean measured value
$c_{CRM}$ ....... certified value

Each measurement has an uncertainty $u_m$ as described in the ISO Guide to the Expression of Uncertainty in Measurement (GUM) [1] and the Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" [2]. This means, any measurement result is only known within the limits of this uncertainty. Similarly, the certified value of a CRM is only known with a specified uncertainty $u_{CRM}$ stated on the certificate. Uncertainties are usually expressed as standard deviations, but only the variances (the squared standard deviations) are additive. The uncertainty of $\Delta_m$ is $u_\Delta$, that is calculated from the uncertainty of the certified value and the uncertainty of the measurement result according to

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$$

$u_\Delta$......... combined uncertainty of result and certified value (= uncertainty of $\Delta_m$)
$u_m$........ uncertainty of the measurement result
$u_{CRM}$..... uncertainty of the certified value

The expanded uncertainty $U_\Delta$, corresponding to a confidence level of approximately 95 %, is obtained by multiplication of $u_\Delta$ by a coverage factor ($k$), usually equal to 2.

$$U_\Delta = 2 \cdot u_\Delta$$

$U_\Delta$........... expanded uncertainty of difference between result and certified value

**To evaluate method performance, $\Delta_m$ is compared with $U_\Delta$: If $\Delta_m \leq U_\Delta$ then there is no significant difference between the measurement result and the certified value.**

## DETERMINATION OF THE INDIVIDUAL UNCERTAINTIES

### *Uncertainty of the certified value*

The expanded uncertainties $U_{CRM}$ of each certified value are given on the certificate. Each ERM®-certificate also contains in a footnote an explanation of the derivation of the uncertainty (see Figs. 1 and 2). In most cases, the coverage factor is explicitly stated, (an example can be seen in Fig. 1). The standard uncertainty, $u_{CRM}$, of the certified value is obtained by dividing the stated expanded uncertainty by the coverage factor.
In some cases, the uncertainty is the 95 % confidence interval of the mean of laboratory means (for an example see Fig. 2). In this case, the t-factor for a 95 % confidence level

with n-1 degrees of freedom (n being the number of laboratories) needs to be determined from statistical tables. [Alternatively, the factor can be derived in MS Excel® using the function tinv(0.05, n-1)]. The standard uncertainty of the certified value $u_{CRM}$ is then obtained by dividing the stated expanded uncertainty by the t- factor.

### *Uncertainty of the measured value*

According to ISO/IEC 17025 [3], measurement uncertainties must be known for each measurement. In the absence of full uncertainty budgets, several approximations exist (ranked in decreasing usefulness) to estimate measurement uncertainties:

1) The within-laboratory reproducibility standard deviation (intermediate precision) as determined from e.g. quality control charts can be used as (rough) estimation of $u_m$.
2) A reproducibility standard deviation from other sources (e.g. the certification reports available on www.erm-crm.org or an interlaboratory comparison) can be used after it has been proven that the laboratory's performance is equivalent to the performance of the participants in the study in question.
3) The standard deviation of the measurements can be used as very rough estimation. This estimation is typically underestimating the real uncertainty.

**ERM®- BB445**

| PORK FAT | | |
|---|---|---|
| Chlorobiphenyl 1) Ballschmiter No. (Congener name) | Mass fraction | |
| | Certified value 2) [µg/kg] | Uncertainty 3) [µg/kg] |
| **28** (2,4,4'-Trichlorobiphenyl) | 14.8 | 1.3 |
| **52** (2,2',5,5'-Tetrachlorobiphenyl) | 12.9 | 0.9 |

1) As obtained by quantification using GC methods.
2) Unweighted mean value of the means of 8 accepted sets of data, each set being obtained in a different laboratory a with a different method of determination. The certified value and its uncertainty are traceable to the International Syst units (SI).
3) Estimated expanded uncertainty *U* with a coverage factor *k* = 2, corresponding to a level of confidence of about 95 defined in the Guide to the Expression of Uncertainty in Measurement (GUM), ISO, 1995. Uncertainty contributions a

*Figure 1: Certificate with expanded uncertainty. The standard uncertainty of the certified value ($u_{CRM}$) is obtained by dividing the expanded uncertainty by the coverage factor (in this case: 2; marked in red)*

**ERM®- CC580**

| ESTUARINE SEDIMENT | | |
|---|---|---|
| Parameter | Mass fraction (based on dry mass) | |
| | Certified value 1 | Uncertainty 2 |
| Total Hg | 132 mg / kg | 3 mg / kg |
| $CH_3Hg^+$ | 75 µg / kg | 4 µg / kg |

1) Unweighted mean value of the means of 11 to 13 accepted sets of data, each set being obtained in a different laboratory and / or with a different method of determination. Certified value is based on dry mass. The certified values are traceable to SI.

2) The certified uncertainty is the half-width of the 95 % confidence interval of the mean defined in 1). *k*-factors were chosen according to the t-distribution depending of the number of accepted sets of results and were 2.179 for total Hg and 2.228 for MeHg.

*Figure 2: Certificate with a confidence interval. The standard uncertainty of the certified value ($u_{CRM}$) is obtained by dividing the expanded uncertainty (in this case: 4 for $CH_3Hg$) by the coverage factor (in this case: 2.228; marked in red)*

## *EXAMPLE ERM-BB445 (PCBs IN PORK FAT)*

PCB 52: certified value = (12.9 ± 0.9) µg/kg. Footnote 2 of the certificate states that a coverage factor of $k$ = 2 was applied. $u_{CRM}$ is therefore 0.9/2 µg/kg= 0.45 µg/kg.
The laboratory measurements gave an average of (14.3 ± 1.8) µg/kg (single standard deviation of 6 measurements spread over three weeks). The standard deviation is divided by the square root of the number of measurements, as the average of the results is compared with the certified value. $u_m$ is therefore estimated as 1.8/√6 µg/kg = 0.74 µg/kg.

$$\Delta_m = |c_m - c_{MRC}| = |14.3 - 12.9|\ \mu g/kg = 1.4\ \mu g/kg$$

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2} = \sqrt{0.74^2 + 0.45^2}\ \mu g/kg = 0.87\ \mu g/kg$$

The expanded uncertainty $U_\Delta$ is $2 \cdot u_\Delta$ = 1.7 µg/kg. This is larger than the difference $\Delta_m$ between the certified and the measured value. The measured mean value is therefore not significantly different from the certified value.


1 International Standards Organisation (1993) Guide to the expression of uncertainty in measurement. ISO, Geneva. ISBN 92-67-10188-9
2 Ellison SLR, Roesslein M, Williams A (eds) (2000) EURACHEM/CITAC Guide: Quantifying uncertainty in analytical measurement, 2nd edn. EURACHEM. ISBN 0-948926-15-5. Available via http:// www.eurachem.com
3 International Standards Organisation (1999) ISO/IEC 17025: General Requirements for the competence of calibration and testing laboratories. ISO, Geneva