Examples of applications for the estimation of uncertainty of chemical tests on milk and dairy products

Summary of the talk presented by Ph. TROSSAT (CECALAIT) at CECALAIT's AGM 2004

Amongst the different methods of estimation possible, 3 lines of approach are frequently encountered in testing laboratories:
- **Analysis of the measuring process and application of a principle of propagation on the sources of uncertainty**
- **Use of accuracy values of the method**
- **Use of performance criteria obtained during participation in proficiency testing**

1) Using the application of a principle of propagation:

The different stages of this approach are:
- *Characterisation of the test process, which defines the means necessary for carrying out the test considered (object, tools, environment, method and competencies).*
- *Creation of an uncertainty budget using the principle of propagation for the estimation of each uncertainty component.*
- *An inventory of causes of error and the possibility of applying a correction to cancel these errors.*

Example: determination of fat content using the Rose Gottlieb method.

CHARACTERISATION OF THE TEST PROCESS

Method : Determination of fat content using the Rose Gottlieb method

1 - OBJECT Milk samples
2 - TOOLS - Water bath at 40°C - Class I balance - 150 ml Tubes + balls - Rotary evaporator - Oven at 102°C
3 - ENVIRONMENT Temperature regulated chemistry laboratory
4 – METHODE Ammoniacal attack of a milk test sample, fat extraction using a mixture of solvents. Elimination of the ether phase by evaporation and oven drying and weighing of the residue.
5 - COMPETENCIES Qualified operator

PREVISIONNAL BUDGET OF UNCERTAINTY

Method: Determination of fat content using the Rose Gottlieb method (g/kg)

Origin	Uncertainty component
A : REPEATABILITY (Sr/√n)	0.067/√2 = 0.047
B : IDENTIFIED CAUSES - B1 : Balance accuracy → B11 : sample weight ± 2 mg : that is 0.018 % for a weight of 11 g. For a milk with 40 g/kg of fat : ± 0.0072 g/kg	Rectangle principle 0.0072/√3 = 0.042
→ B12 : final weight ± 2 mg: that is 0.5 % for 400 mg of residue. For a milk with 40 g/kg of fat : ± 0.20 g/kg	Rectangle principle 0.20/√3 = 0.115
- B2 : Numerical indication of final weight 0.1 mg / 400 g → ± 0.01 g/kg	0.01/2√3* = 0.0289
- B3 : Constant weight tolerance 0.5 mg → ± 0.025 g/kg	Rectangle principle 0.025/√3 = 0.0144
COMPOSED STANDARD UNCERTAINTY	0.135 g/kg

* special case of standard uncertainty for numerical indications, where standard uncertainty = a/2√3

INVENTORY OF CAUSES OF ERROR

Method: Determination of fat content using the Rose Gottlieb method

Identified cause of error	Correction yes/no
1 – MESURAND Representativity of test sample	no
2 – MEASURING INSTRUMENTS - Balance → accuracy → numerical indication - Oven at 102 °C	no no no
3 – MEASURING METHOD - Extraction yield - Stirring method - Tolerance of constant weight	no no no
4 – MAGNITUDE OF INFLUENCE Laboratory temperature	no

The broadened uncertainty U(y) is equal to the composite uncertainty Uc (y) x k (broadening coefficient)

U(y) = 2 x 0.135 = 0.27 g/kg

2) Using the accuracy values of the method:

The principal of this approach is to assimilate the standard deviation of reproducibility of the method used to the standard composite uncertainty [Uc(y)].
Therefore, the broadened uncertainty is U (y) = k x SR (k = 2)

Examples :

- Determination of fat content using the Rose Gottlieb method: SR = 0.144 g/kg → **U(y) = 0.29 g/kg**

- Determination of dry matter by oven drying: SR = 0.072 g/100 g → **U(y) = 0.14 g/100 g**

3) Using performance results obtained during proficiency testing:

The principal of this approach is to use the information relative to the repeatability of the method (Sr), the precision (mean bias) and the dispersion (standard deviation), observed whilst participating in proficiency testing, in order to estimate the standard composite uncertainty.

- $\mathbf{U^2(x) = Sr^2/n}$

- calculation of the superior and inferior maximum limit values = $\bar{d} \pm 2$ Sd. The standard uncertainty is calculated with the help of the rectangle principle: $\mathbf{u^2(y) = [(a^2/3)]}$, a being the biggest limit value (superior or inferior, absolute value).

$$U^2c(y) = U^2(x) + U^2(y)$$

To increase the pertinence of the estimation, this approach can be carried out using the "mean" performance values, taking into account the results of participation in several proficiency tests.

Example: determination of fat content using the Rose Gottlieb method

FAT EXTRACTION

Name	d	Sd	SL	Lim sup	Lim inf
1	0.02	0.07	0.05	0.16	-0.12
2	0.07	0.11	0.07	0.29	-0.15
3	0.15	0.06	0.08	0.27	0.03
4	0.04	0.10	0.05	0.24	-0.16
Mean	**0.07**	**0.09**	**0.06**	**0.24**	**-0.10**

$\mathbf{U^2c(y) = 0.06^2/2 + 0.24^2/3 = 0.0210}$ **and Uc(y) = 0.15**
U(y) = 2 x 0.15 = 0.30 g/kg.

CONCLUSION

Although the approach using the propagation principle is described in the GUM, it is certainly the most difficult to set up in a testing laboratory. Furthermore, certain error components (matter reagent interactions, for example) are impossible to quantify.

Using accuracy results can be a simple method. However, laboratories should apply the method such as it is described and verify that the limits used to estimate uncertainty are prescribed to (as far as accuracy is concerned). In any case, the calculated uncertainty will not be totally specific to the laboratory.

The use of proficiency testing results, although they necessitate a rather large amount of data, will enable obtainment of a realistic estimation of laboratory performance.