METHODS TO EXPRESS DISPERSION OF RESULTS IN FOOD COMPOSITION DATA

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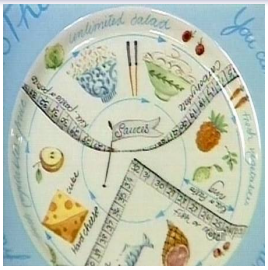
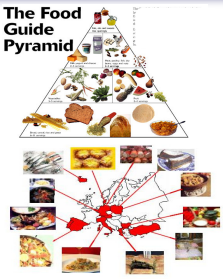
INTRODUCTION

In Europe one feature of National Food Composition Databanks (nFCDBs) is to provide data soundly supported in standardized quality assurance procedures. It is now widely recognized that the evaluation of the degree of dispersion associated with a result is an essential part of any quantitative analysis (1).
According to recent requirements the concept of data quality incorporates the evaluation of the measurement uncertainty (MU) as an indicator of the reliability of the result. The aim of this work is to study the typification of approaches used to estimate measurement uncertainty in food composition analysis in compliance with the criteria established in the "Guide to the expression of uncertainty in measurement (GUM)" (2). The work addressed the approaches founded on the modelling of the measurement process as described in the GUM (chapter 8), and on the experimental approaches, typically precision and bias data, obtained from within-laboratory validation studies, quality controls, inter-laboratory method validation studies or proficiency testing schemes (3).





METHODS

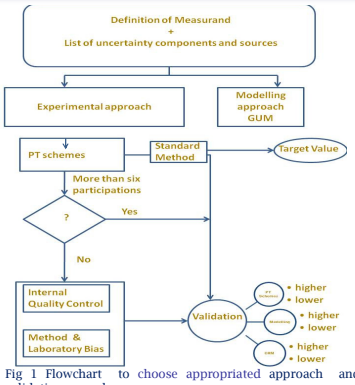


Fig 1 Flowchart to choose appropriated approach and validation procedure

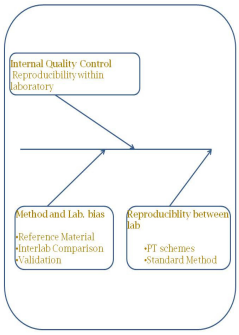


Fig 2 Measureament uncertainty model when reproducibility within-laboratory is combined with the estimates of the method and laboratory bias.

The procedure applied is presented in Figures 1 and 2. The alternative experimental method to modelling is based on distinction between uncertainty evaluation carried out by the laboratory itself (called intra-laboratory approach) and uncertainty evaluation based on collaborative studies (called inter-laboratory approach).

The intra-laboratory approach is subdivided into:
- •Use of data from method validation in a single laboratory
- •Internal day to day Quality Control

The inter-laboratory approach is subdivided into:
- •Use of data from collaborative method performance data (e.g. according to ISO 5725) which is used as target uncertainty
- •Use of data from (inter-laboratory) proficiency tests (PT)

The selected approach is then validated against another experimental approach or modelling approach to guarantee that the probability of including all uncertainty contributions will be maximized.

RESULTS

Case I Determination of β-carotene in edible leaves - measurement uncertainty validated against standard method

- β-carotene in edible leaves is determined by HPLC UV-Vis (3)
- Laboratory has participated in the international study
- The uncertainty is estimated using data from mixed vegetables *uc*, is taken from the S_R from inter-laboratory comparison exercises quoted in the EN method and referred above.

Table 1a): Target uncertainty based on results from the inter-laboratory comparison - β-carotene mixed vegetables by HPLC(3)

Matrix	Number of laboratories	Outliers	Accepted results	Mean value µg/100 g	RSDr	RSDR
Mixed vegetables	14	0	60	2370	6,7%	10,2 %

Table 1b) - Estimation of measureament uncertainty using experimental approach (Internal Quality Control+ Method and laboratory Bias)

Measurand	Combined uncertainty (uc)	Expanded uncertainty U
all-trans-,-carotene	uc=9.9%	2* uc = 18.8%

Comments - Food is similar in the inter-laboratory comparison and β-carotene values in same range, so compiler should accept the laboratory approach.

Case II - Determination of Phosphorus in rice -measurement uncertainty based on data from control sample and PT schemes

- Phosphorus in rice is determined by ICP-OES preceded by microwave digestion
- The laboratory has participated in three PT schemes using the same method and similar matrix.
- So in this case Combined uncertainty, uc is calculated from the control sample limits and bias from inter-laboratory comparisons.

Table 2a)- Summary table of uncertainty calculation

Uncertainty source		Value	Relative u(x)	Comments
Reproducibility within laboratory, Rw				
Control sample X= 200 µg/100 g	Rw	Control limits is set to ± 3.34 %	1.67 %	
Method and laboratory bias				
Inter-laboratory comparisons	bias	$RMSbias$= 2.25 % $u(Cref)$ = 1.5 %	2.71 %	

Table 2b) Calculation of expanded uncertainty

Measurand	Combined Uncertainty u_c	Expanded Uncertainty U
Phosphorus	$\sqrt{1.67^2 + 2.71^2}$ = 3.18	2*3.18 = 6%

Comments – Results agree with target uncertainty and control samples are in the same range of test sample so compiler should accept the approach used by laboratory.

Case III – Determination of cholesterol in lamb meat - Measurement uncertainty calculated from values obtained with SRM 1546 – Meat Homogenate

- Cholesterol in lamb was determined by GLC according to AOAC 994.10
- Uncertainty calculation is based on data from control sample (Rw4%) – certified reference material - bias and reproducibility within laboratory is estimated by analysis of Reference Material (SRM)

Convert the confidence interval to $u(Cref)$	The confidence interval is ± 0.072 expressed in the certificate converting in standard uncertainty: 0.072/1.96 = 0.037
Convert to relative uncertainty $u(Cref)$	100.(0.0072 /0.750) = 9.6 %
Quantify Method and laboratory bias	bias =100*.(0.74-0.750)/0.750 =1.33 % S_{bias} = 2.2 % (n =15) $u(Cref)$ = 9.6 %
Convert components to standard uncertainty $u(x)$	$u\,bias = \sqrt{(bias)^2 + (\frac{S_{bias}}{\sqrt{n}})^2 + u(Cref)^2}$ $= \sqrt{(1.33)^2 + (2.2/\sqrt{15})^2 + 9.6^2}$ = 9,7
Convert in combined uncertainty $u(c)$	$\sqrt{bias^2 + Rw^2}$
	$\sqrt{9.7^2 + 4^2}$
Convert $u(c)$ in U when $k = 2$	10.49 U = 2*10.49= 20.98

Comments - Target uncertainty (u_c)% = 21.3 obtained from RSD_R so measurement uncertainty is below and laboratory described uncertainty budget result should be accepted

Case IV - Defining target uncertainty

Nutrient/Food	Standard Method	RSD (%)
Water in dry foods	Determination of Water in Dry Foods by Karl Fisher Titration	10
	Determination of water in Dry foods by gravimetric determination *Vacuum*	10
Protein in meet	Nitrogen, Determination in foods and feeds according to Kjeldahl. Method No.6. Oslo: NKML, 1976	0,6
Vitamin K in eggs	EN 14148:2003 Foodstuffs - Determination of vitamin K1 by HPLC	10,9
Zinc	AOAC 984.27 - ICP-OES Calcium, Copper, Iron, Magnesium, Manganese, Phosphorus, Potassium, Sodium, and Zinc in Infant Formula	7
	EN 14084:2003 Foodstuffs - Determination of trace elements - Determination of lead, cadmium, zinc, copper and iron by atomic absorption spectrometry (AAS) after microwave digestion	9,3
	EN 14082:2003 Foodstuffs - Determination of trace elements - Determination of lead, cadmium, zinc, copper, iron and chromium by atomic absorption spectrometry (AAS) after dry ashing	12
Iodine in milk	EN 15111:2007 Foodstuffs - Determination of trace elements - Determination of Iodine by ICP-MS (inductively coupled plasma mass spectrometry)	19

Comments : Target uncertainty is defined using data from collaborative studies for standard method or from PT reports choosing similiar matrix under assumption all steps of sample preparation are included

DISCUSSION AND CONCLUSIONS

In this study, the most significant experimental methods, alternatively to modelling, were analyzed. From the overall results, performance of method seems the most simple approach to define target uncertainty. However it involves the following steps: 1) obtaining estimates of the repeatability and reproducibility standard deviations as described in the official method of analysis (CEN; ISO; AOAC; NKML); 2) verifying that the approach is applicable to specific food by assuring that Internal quality Control encompasses all steps of sample preparation; 3) estimating the uncertainty, taking in account any additional effects such as drift of equipment, or operator performance.
When uncertainty is estimated from reproducibility within laboratory associated with method and laboratory bias (obtained from CRM or PT schemes) three situations may occur:

- •The combined uncertainty exceeds the limit meaning the method was not appropriate and validation method should be used
- •The combined uncertainty agrees with the target uncertainty meaning the method was appropriate
- •The combined uncertainty is below the target uncertainty meaning before a final decision of rejection or acceptance of claimed value for expanded uncertainty laboratories are requested to demonstrate their budget uncertainty and main sources of error.

Based on our results systematic uncertainty budgets presented here facilitate the evaluation of data performed by different laboratories and could assist compilers in establishing target uncertainty as a parameter associated to nutrient value that expresses the dispersion (range) of the data.

REFERENCES

1) European Food Information Resource AISBL Network http://www.eurofir.net
2) ISO GUM (1993): Guide to the expression of uncertainty in measurement. ISO, Geneva
3) Eurolab technical report no. 1/2007 (2007) Measurement uncertainty revisited: alternative approaches to uncertainty evaluation. http://www.eurolab.org

ACKNOWLEDGEMENTS

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