Arsenic content in fish and associated measurement uncertainty as a metrological parameter for Total Diet Studies

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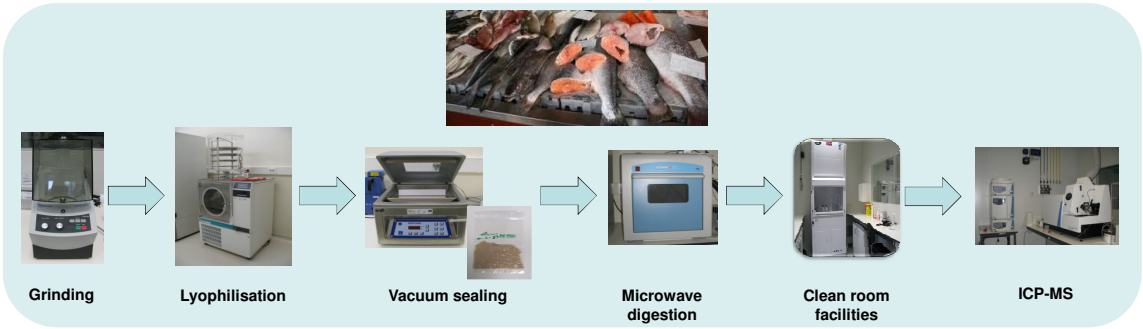
Introduction

Total Diet Studies (TDS) are the most important tools to assure that chemical contaminants presence in foodstuffs remains within safety levels. Reliability of data provided by laboratories to assess the effectiveness of measurements aiming at reducing the risk of exposure to chemical hazards is of paramount importance. Evaluation of measurement uncertainty associated with a result is an important parameter in assessing the sources of analytical data variability. Two methods to estimate uncertainty in analytical measurement of arsenic in fish are discussed.

Materials and Methods

Measurement uncertainty was estimated for the determination of arsenic content in fish samples by Inductively Coupled Mass Spectrometry (ICP-MS). The work addressed both approaches accepted by Eurolab and NIST: modeling (bottom up) and empirical (top down). The Ishikawa diagram was used to identify the most significant sources of uncertainty.



Results and Discussion

Modelling

Table 1 Contributions to uncertainty in the determination of total arsenic in fish by inductive coupled plasma-mass spectrometry (ICP-MS). Type A parameters are determined statistically, while Type B parameters are determined by other means.

Uncertainty Component	Model parameter		Determination
	Type A	Type B	
Analytical signal for analyte in sample	✓		Repeated measurements on the sample (N=5)
Analytical signal for internal std. in sample	✓		Repeated measurements on the sample (N=5)
Internal standard concentration in sample	✓		Control chart
Analytical signal for analyte in calibr. blank	✓		Control chart
Conc. in calibration std. stock solution (new)		✓	Manufacturer's information
Change in stock solution with time		✓	Manufacturer's information
Volume of stock solution	✓		Control chart
		✓	Pipette tolerance
Water volume in dilution to 2nd stock solution	✓		Control chart
		✓	Pipette tolerance
Water volume in dilution to calibration std.	✓		Control chart
		✓	Pipette tolerance
Internal standard concentration in cal. std.	✓		Control chart
Dry matter correction	✓		Control chart
Weight of sample	✓		Control chart
		✓	Tolerance for balance
Pipetting of sample, reagent and water	✓		Control chart
		✓	Tolerance for pipette
Sub-sampling bias	✓		Control chart for duplicate samples
Instrument drift		✓	Tolerance for Drift
Matrix interference			*Neglected (dilute measurement solution)*
Contamination/losses		✓	Estimated from experience
Spectral interferences		✓	Estimated from experience

Estimation of measurement uncertainty from interlaboratory reproducibility information derived from Proficiency Testing Scheme data

Table 2 PT results for arsenic determined by ICP-MS in INSA Laboratory

PT Round (FAPAS)	Element	Assigned Value x_i	Reference Value x_{ref}	Lab. bias $(x_i-x_{ref}) / x_{ref}$
canned crab meat	As	10000	11500	13%
canned fish	As	1131	1354	16%
canned fish	As	856	1079	21%
canned fish	As	2593	2550	2%

The mathematical modeling techniques to assess uncertainty components based on a classical model to account for all recognized significant sources of errors was similar to top down based on the interlaboratory validation data.

Conclusions

The top down approach described is simple and easy to use compared with the mathematical modeling approach and could be used in the future for compilers to assess raw data. This work shows that the top down approach can be used by those involved in TDS studies to establish relative target uncertainty as a parameter associated with component value to describe the range of component values within a food

Acknowledgments

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References

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