Sampling - validation, quality control and uncertainty estimation

Christian Grøn, DHI, Denmark, chg@dhigroup.com

Method validation and quality control have been implemented in analytical laboratories since the late 1970es, e.g.: /1/. With the publication of guidance documents for uncertainty estimation, e.g.: /2/, implementation of uncertainty estimation in analytical laboratories has been well under way since the mid 1990es. Still, the use of concepts such as validation, quality control and uncertainty estimation has been confined to the analytical processes. A recent inquiry to the 20 major Danish operators of groundwater investigations demonstrated the all used laboratories accredited according to ISO 17025 /3/ for analysis, an accreditation that requires validation and quality control of applied analytical methods. Most operators specified quality requirements to the analysis, although only half of them actually verify the analytical quality obtained. On the other hand, only 1/3 of the operators applied quality control procedures of sampling and only 10% required accredited sampling.

As sampling uncertainty may be considerably larger than analytical uncertainty (examples in /4/), estimation and reduction of sampling uncertainty are easily identified as the next important targets in controlling measurement uncertainty.

With the guidance of the recently published Eurachem/EUROLAB/ CITAC/Nordtest/AMC Guide: *Measurement uncertainty arising from sampling: a guide to methods and approaches* (available at http://www.eurachem.org), the first steps towards making this practicable have been taken. Accordingly, quality control of sampling is recommended in the guidance document on groundwater monitoring published by the European Commission /5/.

The Nordtest handbook on uncertainty from sampling

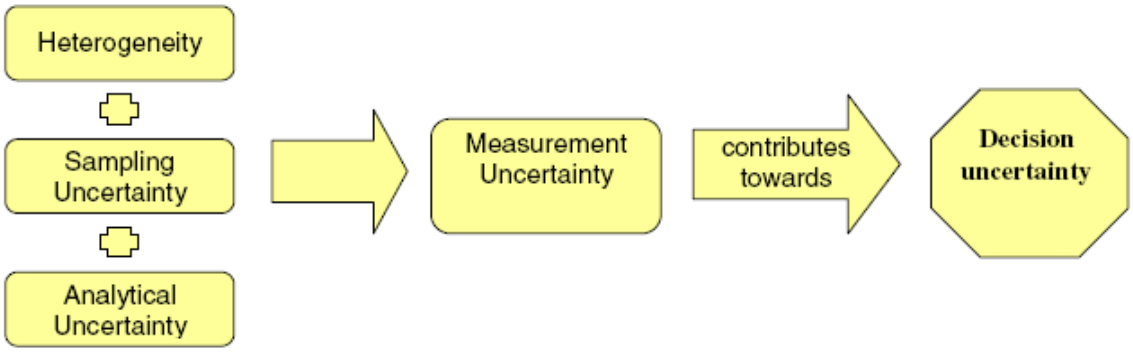
A handbook has now been prepared supported by Nordtest under the Nordic Innovation Centre on uncertainty from sampling /4/. The Nordtest handbook is an extract of and based upon the principles, methods and text of the Eurachem guide on uncertainty from sampling /6/. The handbook provides practical guidance on sampling uncertainty estimation in the Nordtest handbook format and will be freely available at the Nordtest web site at http://www.nordicinnovation.net/nordtest.cfm, under NT technical reports, report number NT tec 604. Until the final report is available on the Nordtest web site, a final draft of the Nordtest handbook is available at http://www.samplersguide.com..

Sampling purpose and quality requirements

The first part of the handbook emphasizes the fact that all measurements are done for a purpose and that sampling in most cases is an integrated part of the measurement process. Therefore the target of the sampling and the required sampling quality depends upon the purpose. The role of sampling in the uncertainty and decision chain can be seen from Figure 1.

In the handbook, examples are given on how to quantify the required sampling uncertainty, e.g.: on setting sampling quality objectives.

Figure 1 Sampling in the uncertainty and decision chain



Sources of uncertainty
To support efforts to control sampling uncertainty, the contributions to sampling uncertainty are discussed and divided into the well know concepts of random and systematic errors. A range of tools are presented for the estimation of different types of uncertainty, see e.g.: Table 1, including equations for calculating sampling uncertainty.

Table 1 Uncertainty contributions from random and systematic effects

	***Random** (precision)*	***Systematic** (bias)*
Analysis	Analytical variability - including sample splitting/preparation and handling (combined contribution of random effects)	Analytical bias (combined effect of bias sources)
Sampling	Sampling variability (dominated by heterogeneity and operator variations)	Sampling bias (combined effect of selection bias, operator bias etc.)

Validation and quality control of sampling
The concepts of method validation and quality control familiar from analysis are then explained as tools that can be used for sampling as well. A major barrier is here, that sampling may appear either as one or a few samples taken at each occasion, or as large sampling campaigns at one site. The use of validation and quality control is described in order to accommodate to different types of sampling without requiring an excessive number of quality control samples (and derived costs) compared to the samples required anyway for the measurements.

The methods presented are the replicate method for both validation and quality control, in addition to a time series based control chart type of quality control.

Furthermore, the requirements for competence of both samplers and samplings planners are discussed and the required documentation of sampling is described in details. The minimum documentation stipulated is:

- Written sampling procedures based upon defined sampling methods

- Sampling field report
- Sampling report stating uncertainty of sampling

Whereas this may seem trivial as seen from the world of analytical chemistry, these requirements are not commonly met for sampling. The Danish inquiry mentioned above demonstrated that ¼ of the major Danish operators of groundwater investigations did not apply a written procedure and even when a written procedure existed, only 15% of the procedures were based upon a standard method. Less than 1/3 of the operators would be able to provide estimates of sampling uncertainty.

Uncertainty estimation
The major part of the Nordtest handbook describes the methods that can be used for estimating the sampling uncertainty. The methods are based upon the replicate design, and the statistical methods are range statistics and two types of ANOVA. The methods are described in details showing all calculations in order to facilitate implementation. Guidance is given with respect to selecting the most appropriate statistical methods for the purpose, although the differences caused by using different statistical approaches in some case may seem very minor, see Table 2.

Table 2 Example of calculation of uncertainty contributions using different statistical methods, data from sampling vitamin A in baby food

	$s_{analysis}$	$RSD_{analysis}$	$s_{sampling}$	$RSD_{sampling}$	$s_{measurement}$
	µg/100 g	%	µg/100 g	%	
Range – single split	-	-	-	-	42
Range – double split	30	8.6	19	5.5	35
ANOVA	29	8.3	17	5.0	34
Robust ANOVA	31	8.8	21	6.1	37

Finally, the use of variography as an alternative tool is described in principles.

Practical examples
Perhaps the most important part of the Nordtest handbook is a series of worked examples demonstrating in details the use of the methods presented for different sectors: groundwater (environmental monitoring), iron ore (production control), baby porridge (product quality control) and wastewater (environmental/process control). The examples are given showing all data used and all steps of the calculations in order to facilitate understanding of the principles and methods.

Perspectives
The main message of the handbook is that uncertainty from sampling can be estimated with reasonable efforts and following steps that are comparable to those used in quality assurance of laboratory analysis: method validation and quality control. Still, the main emphasis has until now been upon the uncertainty contributions from random effects.

We urgently need practical tools for controlling the uncertainty contributions to sampling from systematic errors comparable to those available in analytical chemistry: proficiency tests and certified reference materials. Examples of such methods that are still only very sparsely available are:

- Sampling method studies
- Sampler proficiency tests
- Sampling reference sites

Among the efforts currently in progress in order to further enhance implementation of uncertainty control in sampling are:

- Preparation of horizontal sampling standards for sampling of dynamic and stationary systems irrespective of sector supported by Nordtest/Nordic Innovation Centre
- Implementation of personnel certification of environmental samplers, also in a Nordtest scheme
- Preparation of textbooks and exams for education of sampling staff supported by the European Leonardo program for the implementation of a European Community vocational training policy

Although the process of understanding and controlling sampling uncertainty to the same extent as analytical uncertainty has thus been started at the technical level, implementation and enforcement will not be realized until required by regulations and by the customers.

Acknowledgements
The contributions of my co-authors of the Nordtest handbook: Jette B. Hansen, DHI, Bertil Magnusson, SP Technical Research Institute of Sweden, Mikael Krysell, Ulla O. Lund and Kirsten J. Andersen, Eurofins A/S, Denmark and Astrid Norbotten, Food Safety Authority, Norway are gratefully acknowledged. The inquiry to Danish operators of groundwater investigations was initiated and performed by Mogens Wium, GEO, a contribution that was essential for describing the importance and the perspectives of the Nordtest handbook.

The Nordtest handbook and the workshop were supported by Nordic Innovation Centre/Nordtest under contract 04130. The sampler education textbook preparation is supported by the Leonardo program under contract DK/06/B/F/PP-145.622, see also www.sampler-education.dhi.eu.

References

1. Water Research Centre. Manual on Analytical Quality Control for the Water Industry. 1978.
2. ISO. Guide to the expression of uncertainty from sampling. 1993.
3. ISO. General requirements for the competence of testing and calibration laboratories. ISO 17025. 2005.

4. Grøn, C., Hansen, J B, Magnusson, B., Nordbotten, A., Krysell, M., and Lund, U. Uncertainty from sampling - A Nordtest Handbook for Sampling Planners on Sampling Quality Assurance and Uncertainty Estimation. 2007. Nordtest.

5. European Commission. Guidance on groundwater monitoring. WFD CIS Guidance Document no. 15, Technical report 002-2007. 2007. European Commission.

6. Eurachem, EUROLAB, CITAC, and Nordtest. Measurement uncertainty arising from sampling - A guide to methods and approaches. 2007.