Chapter 1

Measurement Uncertainty

- Decisions, Confidence and Measurement Uncertainty
- Comparability and Traceability
- ISO 17025

MANY important decisions are based on measurement results. Some of them are important in their own right, others are important because a lot of money is directly involved. One needs a measurement to estimate the speed of a car on the highway, one needs a measurement of the ore concentration to estimate the yield of a mine... There are uncountable situations where a measurement is the basis of a decision.

A certain level of confidence is necessary in order to come to any decision based on measurement results. In other words *information about the quality* of the measurement is needed. Since nobody can afford to perform every measurement on his own, confidence in foreign measurement results is essential. In many sectors of Analytical Chemistry it is nowadays a formal requirement for laboratories to maintain quality assurance systems in order to ensure that they are capable of and are providing data of required quality. Such quality assurance systems are based amongst others on the use of validated methods of analysis, the use of defined internal quality procedures and the accreditation based on ISO 17025 [4]. It is legally required in some fields to accredit according to international standards such as ISO 17025.

These standards put a focus on comparability and traceability, i.e. it is required that any measurement result is comparable and thus traceable to a well defined reference such as a SI unit, reference material or, where applicable, a defined or empirical method. The Comité International des Poids et des Mesures (CIPM) has defined seven base units to form a *coherent system of units* [16]. It is adopted and recommended by the Conférence Générale des Poids et Mesures (CGPM). All measurement tools are calibrated by comparison to those base units. Hence, each measurement executed with a calibrated measurement tool is ultimatively a comparison to those defined SI units.

As a consequence to the requirement of ISO 17025 laboratories are coming under increasing pressure to document and demonstrate the fitness for purpose by giving a measure of the confidence that can be placed on their results. The *standard uncertainty of a measurement result* is one useful measure for this confidence.

International firms need to compare their results. Therefore, there is an ever growing pressure on Analytical Chemistry and equally on other metrological fields to adhere to international standards such as ISO 17025. The standard ISO 17025 specifies requirements for reporting and for evaluating uncertainty of measurement. The problems presented by these requirements vary in nature and severity depending on the technical field.

National accreditation bodies are responsible for ensuring that accredited laboratories meet the requirements of ISO 17025. The standard requires appropriate methods to be used for estimating uncertainty of measurement. These methods are considered to be those based on the *Guide to the Expression of Uncertainty in Measurement* (GUM) [2] or the standard ISO 5725 [1], endorsed by major international professional bodies. EURACHEM/CITAC along with other bodies have produced more specific guidance for their respective working fields based on GUM.

Accreditation bodies are harmonizing their implementation of requirements for expressing uncertainty of measurement. The International Laboratory Accreditation Cooperation (ILAC) is developing a *mutual recognition arrangement* between recognized accreditation bodies. The goal is to remove technical barriers to trade by putting in place a world network of mutual recognition of accreditation body and laboratory competence which operates transparently and in compliance with international standards such as ISO 17025 and others.

1.1 Historical review

- 1875: Convention du Mètre
- 1970: Realization of the lack of consensus on measurement uncertainty
- 1990: INC-1, Definition and recommendation of the uncertainty concept
- 1993: GUM, Practical realization of the concept
- 1995: Applicable guidelines for Analytical Chemistry

The principal task of the CIPM is to ensure world-wide uniformity in units of measurement based on the *Convention du Mètre* (CM). The CM is a diplomatic treaty between 50 nations which gives authority to the CGPM, the CIPM and the Bureau International des Poids et Mesures (BIPM) to act in matters of world metrology, particularly concerning the demand for measurement standards of ever increasing accuracy, range and diversity, and the need to demonstrate equivalence between national measurement standards. The CM was signed in Paris in 1875 by representatives of seventeen nations. As well as founding the BIPM and laying down the way in which the activities of the BIPM should be financed and managed, the CM established a permanent organizational structure for member governments to act in common accord on all matters relating to units of measurement. The CM, modified slightly in 1921, remains the basis of all international agreement on units of measurement. By now, there are 50 member states, including all major industrialized countries.

In the 70s, the CIPM realized the absence of a globally accepted rule for the estimation and notation of measurement uncertainty. Therefore the CIPM commissioned the BIPM in 1978 to work out a generally acceptable recommendation in collaboration with national metrology laboratories. After intense communications with many national and international metrology laboratories nearly everybody agreed that it was important and desirable to have internationally accepted rules to estimate and express measurement uncertainty. But dissent reigned when it came to the exact procedures to be applied for expressing measurement uncertainty. The BIPM formed a working group of experts from 11 national metrology laboratories who issued the general recommendation INC-1 in 1980. This recommendation was accepted by the CIPM and enacted in 1981. However, this INC-1 recommendation must be viewed as a letter of intent or better a definition of the concept of measurement uncertainty. The development of a guide for the actual calculation of measurement uncertainty was handed over to the International Organization for Standardization (ISO), who knows the needs, wishes and concerns of the industry very well. It is therefore the right institution for formulating practicable and acceptable guidelines and examples. The transformation of the INC-1 recommendations into concretely applicable guidelines took for more than 10 years. This astonishingly long period reflects a fundamental argument between Bayesian and Gaussian statisticians.

In 1993 the ISO issued the *Guide to the Expression of Uncertainty in Measurement* (GUM) [2]. The content of the GUM aims at organizations in the field of standardization, calibration and accreditation of laboratories. Thus it is not directly applicable for analytical chemistry laboratories. EURACHEM however ingested the ideas of the INC-1 recommendation and the GUM and issued the guideline *Quantifying Uncertainty in Analytical Measurement* [18] in 1995. It is now available in second edition and it is being enacted by different organizations such as EURACHEM, CITAC and others.

> This second edition of the EURACHEM guide has been prepared in the light of practical experience of uncertainty estimation in chemistry laboratories and the even greater awareness of the need to introduce formal quality assurance procedures by laboratories. The second edition stresses that the procedures introduced by a laboratory to estimate its measurement uncertainty should be integrated with existing quality assurance measures, since these measures frequently provide much of the information required to evaluate the measurement uncertainty. The guide therefore provides explicitly for the use of validation and related data in the construction of uncertainty estimates in full compliance with formal ISO guide principles. The approach is also consistent with the requirements of ISO 17025 [4][1]

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[1] cited from [18, p. 2]

1.2 Goal of this Work

- Description of the measurement procedure
- Derivation and execution of the mathematics needed for the evaluation of measurement uncertainty

The goal of any *measurement* is to find an estimate of the *measurand*. The measurand is described by a statement about what is intended to be measured, for example the amount of soluble and insoluble sugar in your particular cup of tea. The *result of a measurement* yields numbers representing the estimate for the measurand. The definition of these terms can be found in the GUM and some of them are quoted in Section 2.1.1 on page 10. It may or may not be obvious that the result of a measurement depends on the specific *measurement procedure* performed.

Any analytical chemistry laboratory, in the spirit of quality assurance measures, therefore maintains a catalog of "standard operation procedures (SOP)", "laboratory instructions (LI)" or "measurement procedure", "measurement method" or whatever they may be called. Henceforth we try to restrict ourselves to the term "SOP" in the context of laboratory and quality assurance prescriptions and to the term "measurement procedure" elsewhere. These SOP documents describe the individual steps of how to proceed when performing a particular measurement. Depending on the expected quality and precision of the result these documents vary over a wide range of different levels of detail. They are focused on getting a measurement result as a single number. But according to ISO 17025 [4] a laboratory must be capable of indicating the *measurement uncertainty* of a measurement result. Thus each SOP should indicate how the measurement uncertainty for the particular measurement procedure can be estimated. This can usually be done on the basis of a validation study. A validation study is performed to determine the performance of a particular measurement procedure, i.e. the performance parameters of the particular measurement are evaluated and quantified. Often, these performance parameters are not known rigorously enough for the purpose of evaluation of measurement uncertainty. Therefore, in order to meet the requirements of ISO 17025, such validation studies must be redone.

However, practically all information for estimating the uncertainty can be found in the SOP and the accompanying validation study either explicitly or implicitly. One must thus *just* go through each SOP, extract all information needed for the estimation of uncertainty and gather the possibly missing information from the validation study or other experienced data. Stated the other way round: missing information in the SOP is eliminated by the validation study. Then one can add an additional section to the SOP specifying data and formulae for the evaluation of the uncertainty of measurement for this particular measurement procedure's results.

The difficult and time consuming steps of the described process are the following two: first, to find and to agree on the correct formulae or the model for the particular measurement procedure; second, to locate and to quantify the data relevant for the uncertainty estimation but missing in the SOP documents.

The MUSAC-project is trying to alleviate this issue. The key idea of MUSAC is to describe a measurement procedure based on an SOP and the validation data. The system can help substantially in the process of locating missing data by asking the operator or by consulting databases containing experienced data and other expert knowledge. Once the entire description is known to the system an automatic evaluation of the measurement result can be performed. The MUSAC-project aims at two goals: On one side there's the implementation of a computer program to describe, analyze and to evaluate measurement procedures. On the other side there is the challenge to collect generally accepted and applicable data for implicit general steps of a wide variety of measurement procedures.

Although the general ideas can be applied to any field of metrology, the focus in this work is on Analytical Chemistry. The software system MUSAC is therefore strongly influenced by the needs of Analytical Chemistry.

1.3 What's new

- Automatic generation and subsequent execution of the relevant calculations
- Implementation of a system using C++
- General regression method (not yet used in this context)

It is of course not a new idea to generate a sequence of execution steps from a description of the intended process. In many different areas this idea has come up. Let's review one of special interest: In ancient days people doing linear algebra spent an incredible amount of time writing tedious assembly code which eventually executed their algorithms. It was in those times that people realized that the computer could not only be used to execute the calculations, but it also could assist in the tedious task of writing assembly code very efficiently by translating specific high(er) level descriptions of an algorithm into assembly code. This can be considered the birth of computer languages. Ever since, people perfected the process of developing high level languages and their automatic translation into some other language. These techniques were applied to and tailored for a wide range of applications. Nowadays, we have *macros* to tell an application which commands to execute, there are *shell scripts* to drive the computer system and there are uncountable *programming languages* to tell the computer what to do.

The work presented here introduces one more language. This language is called M. It is specifically adapted to the purposes of describing measurement procedures and subsequently analyzes the description with respect to measurement uncertainty issues. Both the M language as well as the implementation of its interpretation are new. To our knowledge this approach is entirely new in the field of metrology.

Practically all measurements are relative methods, i.e. they compare a known entity to an unknown one. Therefore, in metrology and especially in calibration the mathematical concept of *regression* plays a central role. However the vast majority uses standard linear regression which is basically the solution of a linear least squares problem. This is not appropriate in the presence of uncertainties in x- and y-directions. There are better methods for fitting curves than using the standard least squares method. It remains to specify what "better" really means. But the so called EIV-methods (error in variables methods) generally model the situation of calibration more thoroughly. We present an EIV-method which we have implemented for fitting (almost) arbitrary functions into heteroscedastic data. The method is based on the little known Berkson Model and it allows the specification of covariances between arbitrary data points.