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Measurement uncertainty in Estonian Standard Laboratory for Mass

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LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an overview and the following publications, which are referred to in the text by their Roman numerals. The full texts of the papers are reprinted with the kind permission from the publishers, and included at the end of the thesis.

  I V. Vabson, T. Kübarsepp, R. Vendt, M. Noorma, Traceability of mass measurements in Estonia, Measurement, 43 (2010) 1127–1133.

  II V. Vabson, R. Vendt, T. Kübarsepp, M. Noorma, Method for revealing biases in precision mass measurements, Meas. Sci. Technol., 24 (2013) 025044 (7pp).

  III V. Vabson, R. Vendt, T. Kübarsepp, M. Noorma, Finite Resolution and Serial Correlations in Mass Metrology, submitted to Proceedings of the Estonian Academy of Sciences.

  IV R. Vendt, V. Vabson, T. Kübarsepp, M. Noorma, Traceability of temperature measurements in Estonia, Proc. Est. Acad. Sci., 62 (2013) 116–121.

AUTHOR'S CONTRIBUTION

The research work presented in this thesis has been carried out at the National Standard Laboratory for Mass operated by Metrosert ltd and at the University of Tartu during 1996–2013. The thesis consists of an overview and four publications referred as I to IV. The publications are results of group efforts; in all of them the Author has a clearly distinguished contribution, and in three of them, the Author was fully responsible.

Establishment and development of the NSLM in Estonia has been one of responsibilities of the Author since 1995. This task has been described in publication I; the results are based on the data collected and analysed by the Author during more than ten years. Full text of the article was prepared by the Author.

In publications II and III, the Author proposed the original concept, planned and conducted the experiment, analysed the results, and prepared the manuscript.

The uncertainty analysis presented in publication IV was significantly contributed by the Author.

ABBREVIATIONS AND ACRONYMS

ADEV	Allan deviation (called also the 2-sample standard deviation)
AVAR	Allan variance (called also the 2-sample variance)
BIPM	Bureau International des Poids et Measures
CIPM	Comité International des Poids et Mesures
CIPM MRA	Mutual Recognition Agreement of national measurement standards and of calibration and measurement certificates issued by the National Metrology Institutes
CGPM	Conférence Générale des Poids et Mesures
CMC	Calibration and Measurement Capability
EURAMET	European Association of National Metrology Institutes
GUM	Guide to the expression of uncertainty in measurement
INRIM	Istituto Nazionale di Ricerca Metrologica, formerly IMGC, NMI in Italy
ISO	International Organisation for Standardization
ITS-90	International Temperature Scale of 1990
KCDB	BIPM key comparison database
LNE	Laboratoire national de métrologie et d'essais, NMI in France
METAS	Swiss Federal Office of Metrology and Accreditation, NMI in Switzerland
MIKES	Centre for Metrology and Accreditation, NMI in Finland
mpe	Maximum permissible error
MRA	Mutual Recognition Arrangement
NIST	National Institute of Standards and Technology, NMI in USA
NMI	National Metrology Institute
NSLM	National Standard Laboratory for Mass in Estonia
OIML	Organisation International de Métrologie Légale
PRT	Platinum Resistance Thermometer
PTB	Physikalisch-Technische Bundesanstalt, NMI in Germany
SI	Le Système international d'unîtes, the International System of Units
VIM3	International Vocabulary of Metrology – Basic and General Concepts and Associated Terms, 3rd Edn

1. INTRODUCTION

1.1. Background

A well-developed national measurement infrastructure is strategically important for competitiveness of science [1], technology, industry, and quality of life [2]–[5]. Although this infrastructure is hidden in the background, all industrialized countries – large or small – benefit from the high-level National Metrology Institute (NMI), and from an adequate calibration service [6]. Confidence in the national measurement system is needed before the high quality of products and services offered by an economy can be assumed. The NMI is the most suitable institution to demonstrate the metrological capabilities and competence available in the country; to this end, the Mutual Recognition Arrangement for national measurement standards and for calibration and measurement certificates issued by NMIs (CIPM MRA) was introduced in 1999 [7]. Under the provisions of the MRA, inter-comparative measurements in different subject fields are initiated, regularly repeated, and the degree of equivalence established. The Calibration and Measurement Capabilities (CMCs) of NMIs are validated by international experts based on inter-comparisons and peer evaluations of NMIs, and the collected data are maintained in respective BIPM open-access databases (KCDB) [8], [9]. The MRA helps to ensure the traceability [10] of calibration results to the International System of Units (SI) [11], and helps to validate the traceability and uncertainty claims of laboratories and companies throughout the world [7], [10]. Scientific metrology is engaged in fundamental research needed for primary measurement standards to be maintained at the current state of the art [1], [12], [13]. Scientific metrology helps to establish measurement standards in new technical fields, and reduce measurement uncertainties which might lead to new products or quality improvements [6].

In industrialised countries like the USA, Germany, France, UK, Italy, Korea, Switzerland, Finland, Singapore, etc., at the top of the centralised measurement infrastructure usually stands one NMI realising primary [14] standards according to the definitions of SI units. In small and developing countries like Slovenia, Croatia, Lithuania, etc., the distributed system is often organised whereby national measurement standards are operated by different institutions in order to use the competence and facilities already available in the country as much as possible, thus reducing the costs. In such a distributed systems the level of national standards is usually designed accounting only for the particular needs of a country and for international quality requirements, and will often find themselves below the highest available level for secondary standards [14].

In Estonia the establishment of a national measurement system was initiated at the beginning of the 1990s. Due to limited resources, these national measurement standards were established at the secondary level [14] only for the most important physical quantities [15]. Currently, standards for mass [16],

length, temperature [17] and for some electrical quantities [18] are in operation at the Central Office of Metrology, Metrosert. Mass was one of the two national measurement standards first officially adopted in 2001 [**I**]. Calibration methods and uncertainty estimations needed in the standard laboratory [19] [**II**], [**III**] have been tested and elaborated since its foundation in 1995. Similar basic principles and close inter-relations make cooperation in development of different measurement standards very valuable [**IV**]. Besides these national measurement standards, reference standards are operated in some technical fields, currently for air velocity and humidity. Development is on-going in other measurement fields, e.g. in chemistry [20][21].

Mass is among the most important physical quantities for many different applications in science, technology and economy [22]. The unit of mass the kilogram [23], [24] is one of the base units of the International System of Units (SI) [11]. The kilogram is the last base unit still defined using an artefact standard [25]–[27], and this definition is becoming more and more of an obstacle to progress in science and technology. Therefore in recent years, scientific interest in determining mass to the highest degree of accuracy has greatly increased in order to establish a basis for redefining the kilogram in terms of the fundamental constants of physics [12], [13], [28], such as Planck's constant or the Avogadro constant. Just after redefinition of the Kilogram, the best uncertainty stated for platinum-iridium 1 kg standards will most likely increase about one order of magnitude, but a firm time-constant reference basis is certainly a great advantage. The new kilogram definition will not cause any significant changes for the dissemination of the mass unit. Nevertheless, certain conditions concerning the uncertainty and number of independent experiments realising the new definition are to be met before the redefinition is coming into force [29], [30].

Realization of the mass scale, dissemination of the unit, and mass determinations by weighing traceable to the kilogram are carried out in the 10^{-10} kg to 10^6 kg range [22], [31]. A highest accuracy of about two parts in 10^8 is realised for 1 kg weights, and the calibration of weights better than one part in 10^7 is possible in the 0.1 kg to 10 kg range. For smaller and larger weights uncertainty gradually increases [32] in the direction of minimum and maximum values of the mass scale. The mass standards maintained at the NMIs [31], [33], [34], [**I**] are used for the calibrations of weights of the highest accuracy, and accordingly further down to the dissemination chain [19]. Weights [19], [35], [36] traceable to the international kilogram prototype [37], [38] are mainly used for calibration of balances, which are extensively used in trade [36], industry, testing and analyses, and research and development [39]. Mass as a base quantity is very important for many other technical fields. It serves as a basis for the force, pressure, and density measurements; units of electrical quantities are currently defined through the mass unit. All these technical fields with their immense numbers of applications are extremely important for industry, science and technology [22].

Measurement uncertainty [14], [40], [41] is a key concept for the national measurement standard as, without uncertainty estimates, measurement results are useless. The evaluation of measurement uncertainty [19], [22], [32], [40], [42]–[44], [I], [II], [III] is one of the central tasks in establishing and maintaining national measurement standards. The basis for the estimation of uncertainty is the relevant measurement model, relating all input quantities which contribute to the output quantity of the model to the measurement result. Uncertainty statements are confirmed by results of inter-comparison measurements which are analyzed in terms of the degree of equivalence of each participant against the reference value, including deviation from the reference and its uncertainty.

The published CMCs feature the measurement capabilities of NMIs listing the declared measurement uncertainties for different particular measurands. The difference between the CMC-s of different countries may have also an economic impact. Smaller uncertainties may lead to economic gain, and larger uncertainties could pose additional risks in manufacturing and trade [6].

1.2. Progress in this work

The Estonian standard laboratory for mass (NSLM) was founded in 1995, received its initial accreditation in 2000, and was officially nominated in 2001. In Estonia, traceable mass measurements are needed in the 10^{-7} kg to 10^5 kg range, and realized at the NSLM from 10^{-6} kg to $5 \cdot 10^2$ kg [I]. The reproducibility of mass of the weights from the 1 kg group standard is well below 10^{-8}, but the relative uncertainty available for the mass scale and for the calibration of weights is at a level of 10^{-7} for 1 kg, and for smaller and larger weights it will increase.

This thesis describes further developments in the NSLM [I]. In chapter 2 some fundamental terms of mass measurement are explained. They give the background for how the measurement models are the basis for measurements and calibrations carried out at the NSLM and are described in chapter 3. The models also provide the basis for calculating measurement uncertainty described in chapter 4. In this section there are also some specific problems to be found connected with treating systematic effects in the case of Type B estimation [II], and with handling data samples for Type A estimation [III]. In this chapter the inter-comparisons are reviewed which confirm the stated uncertainty estimates.

Although GUM [40] (the Guide to the Expression of Uncertainty in Measurement) is considered as the major reference document for the evaluation of measurement uncertainty, supported by the international metrology community and standardisation bodies, it has some limitations. GUM assumes that before the combined standard uncertainty is calculated all significant systematic effects possibly present in input estimates are corrected. According

to GUM, bias is usually estimated from a theoretical model if the systematic effect is well known. Methods for the experimental analysis of systematic effects largely remain outside the scope of GUM. Therefore one of the studies for this thesis deals with how such systematic effects affect mass comparisons, which is experimentally revealed by using a simple practical method based on comparison measurements [**II**].

The statistical methods used in this thesis allow separating the data suitable for Type A uncertainty estimation form data sets with significant serial correlations. Applying these methods the relationship between the digital resolution and randomness of data sample is studied [**III**]. These statistical methods are also used for evaluating the uncertainty of weight difference determined using different comparators and for different loads as a function of single values averaged. For some cases significant deviations from results obtained with usual Type A estimation methods have been demonstrated.

Temperature is among the most important influence quantities of all measurement models used at the NSLM which may affect results through different interactions. Therefore, temperature measurement at the mass laboratory, calibration of temperature sensors used at the NSLM, and respective uncertainty estimation is important for both the mass and the temperature laboratories. Calibration procedure established for the temperature sensors of the mass lab is one of the most demanding measurements carried out at the temperature lab for the customers and requires the lowest uncertainties to be issued. This is the natural reason for the close cooperation between the labs [**IV**].

2. IMPORTANT CONCEPTS

2.1. Measurement uncertainty and traceability

In science, uncertainty has been estimated by one means or another for the last two centuries [45]. Measurement uncertainty states that after the result of a measurement is obtained, knowledge about the measurand is still incomplete and is usually represented by a probability distribution over a set of possible values for the measurand. Normally, this distribution is characterized by the standard deviation named *standard measurement uncertainty*. The GUM [40] defines measurement uncertainty as a "parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand'". The VIM [14] defines it as a "non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used'".

In science, ever since the first scientific systems of measurement units were proposed, a close link to specific unit is taken to be self-evident, and traceability is not commonly stated separately. Otherwise, for industrial metrology traceability is a rather new and critical property of measurements that precisely defines the link between a measurement result and the relevant unit. Only a century ago almost all industrial companies operated according to their own measurement systems. The consistency of measurements inside a factory or company was sufficient and the slight difference of units used by other companies was of no major concern. Standardization was strongly promoted with the advent of World Wars I and II, and with subsequent globalization efforts when the world economies became much more closely linked. At present, exchangeability is among the most important requirements as more and more parts and assemblies are manufactured by other companies. Traceability has proven to be an effective means for removing the inconsistencies which formerly existed between countries and companies.

Without well-defined references, an uncertainty statement is meaningless. One source of uncertainty is always any unit realised by a measurement instrument because it might not be exactly the unit stated in the result. For instance, value of the mass $m(X)$ of any object X is expressed as [46]

$$m(X) = \left\{ \frac{m(X)}{m(\text{IPK})} \right\} \text{kg} . \tag{1}$$

Here m(IPK) is the mass of the international prototype of the kilogram (IPK). If the value is measured in kilograms, everybody assumes that the SI kilogram unit has been used, but in the uncertainty budget the actual representation of a kilogram realised by weights and/or balance is to be handled, and linkage to the IPK usually includes more than ten steps of sequent comparisons, each contributing to uncertainty.

2.2. Mass, conventional mass value

Historically, mass is a measure of the amount of material in an object, being directly related to the number and type of elementary entities (atoms, molecules, etc.) present in the object. The mass of the body will change only if material is added or removed.

For determining or estimating the mass in physics, chemistry or astronomy the following relations are used [22]. Mass can be estimated from gravitational potentials

$$\frac{m_{g1}}{m_{g2}} = \frac{F_1}{F_2} \cdot \frac{r_1}{r_2},$$ (2)

with $m_{g1,2}$ being active gravitational masses, $F_{1,2}$ gravitational potentials, and $r_{1,2}$ distances. It can be also determined from weight forces

$$\frac{m_1}{m_2} = \frac{F_{G1}}{F_{G2}},$$ (3)

with $m_{1,2}$ being passive heavy masses, and $F_{G1,2}$ weight forces. Finally, mass can be determined from accelerations

$$\frac{m_{i1}}{m_{i2}} = \frac{a_2}{a_1},$$ (4)

with $m_{i1,2}$ being inert masses, and $a_{1,2}$ weight accelerations. At the NSLM the determination of mass from a comparison of the weight forces equation (3) is applied from three relations only; it is used for determining the mass scale and for dissemination of the unit in the 1 mg to 500 kg range.

In legal metrology [19], instead of mass, the conventional mass of a weight is usually considered. Conventional mass is defined as the conventional value of the result of weighing in air under conventional reference conditions [47]. For a weight taken at a reference temperature of 20 ºC, the conventional mass is the mass of a reference weight of a density $\rho_c = 8000$ kg/m^3, which it balances in air of a reference density $\rho_0 = 1.2$ kg/m^3. Conventional mass is introduced to simplify the calibration of weights. In practice, although reference conditions will not be realized exactly, usually a simple weighing is all that is required for the calibration of weights, and corrections for temperature, material and air density are not applied. If the mass of a weight is known, its conventional mass value can be calculated from the following equation

$$m_{c} = m\frac{1 - \rho_0/\rho}{1 - \rho_0/\rho_c} = m\frac{1 - \left(1.2\,\mathrm{kg\,m^{-3}}/\rho\right)}{0.99985}. \tag{5}$$

Air exerts a buoyancy force on all objects weighed in it. The value of buoyancy depends on the volumes of the objects being weighed and the density of the surrounding air, which itself depends on temperature, pressure, humidity, and the composition of the air. This buoyancy effect will be insignificant in any comparison of similar weights having very close densities. Nevertheless, in practice the densities of the weights being calibrated must be known, either for mass comparisons or for the classification of the weights, if the measurements are carried out in terms of conventional mass.

The majority of mass measurements are carried out in terms of conventional mass and using equation (5) from conventional mass value m_c, the mass m of an object can also be determined. The relative deviation of mass from the conventional mass value in a limited density range relevant for the calibration of weights is shown in Figure 1.
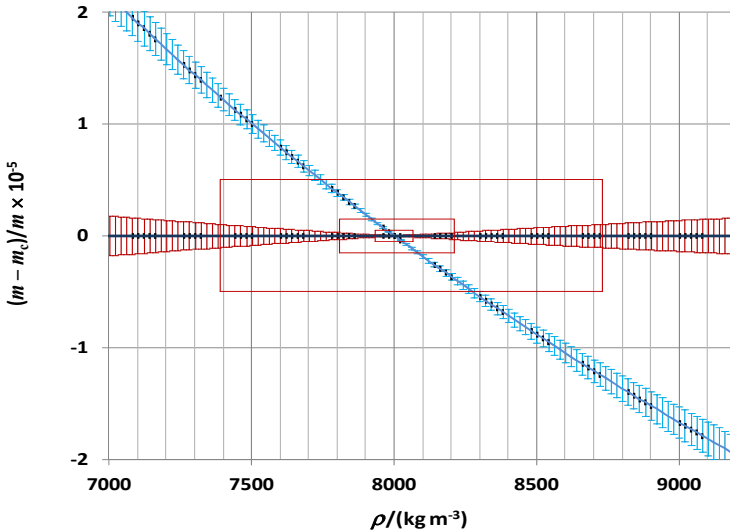
Figure 1. Relative deviation of mass from conventional mass value $(m-m_c)/m$ (blue) as a function of object density. Conventional mass (red) is taken to be constant and not depending on ρ. Uncertainty is due to deviations of $\pm 10\%$ in air density from the reference value $\rho_0 = 1.2\,\mathrm{kg/m^3}$.

The rectangular areas specify the limits for the maximum permissible error and the density of weights in the three classes of accuracy: OIML E1, E2 and F1 (the largest box, see Table 1). The uncertainty of curves is due to the deviation of surrounding air density $\pm 10\%$ from the reference value $1.2\,\mathrm{kg/m^3}$. This deviation considered as an absolute limit can cause error which is still four

times smaller than the maximum permissible error specified for the particular class of weights. The routine calibration of weights can be a simple comparison weighing, if made in terms of conventional mass. The application of air buoyancy correction is indispensable if the comparison is made in terms of physical mass.

2.3. Unit of mass and traceability scheme for the mass measurements

The SI unit of mass is the kilogram (kg) [23], [46]. It is equal to the mass of the International Prototype Kilogram (IPK). The IPK is a cylinder of platinum iridium alloy kept at the International Bureau of Weights and Measures (BIPM) in France. With the present artefact definition, the traceability chain of mass measurements always starts from the IPK. The Estonian primary standard of mass is a stainless steel weight with a mass of 1 kg. For better stability and reliability, a group standard of four 1 kg reference weights is maintained. In Figure 2 the NSLM traceability scheme is shown.

The Estonian primary standard of mass (M001) is a stainless steel weight [**I**], nominally with a mass of 1 kg. Because Estonia is an associate member of the meter convention, the NSLM has no direct access to the IPK at the BIPM. Therefore, every 5 years the two kilogram reference weights are sent for calibration to the Physikalisch-Technische Bundesanstalt (PTB), Germany, which provides traceability to a number of foreign institutes [33]. Upon their return from external calibration, these weights are used to calibrate the weight M001, thus ensuring traceability to the IPK. Such a procedure has been implemented since 1997. For 16 years the instability of the mass of reference weights (M001, M002 and M003) was about 50 µg (see Figure 3). The uncertainty shown with vertical bars represents expanded uncertainties $k = 2$ of the calibrations of the weights at the PTB. Mass changes are similar to data published for the 1 kg stainless steel weights elsewhere [48], [49].
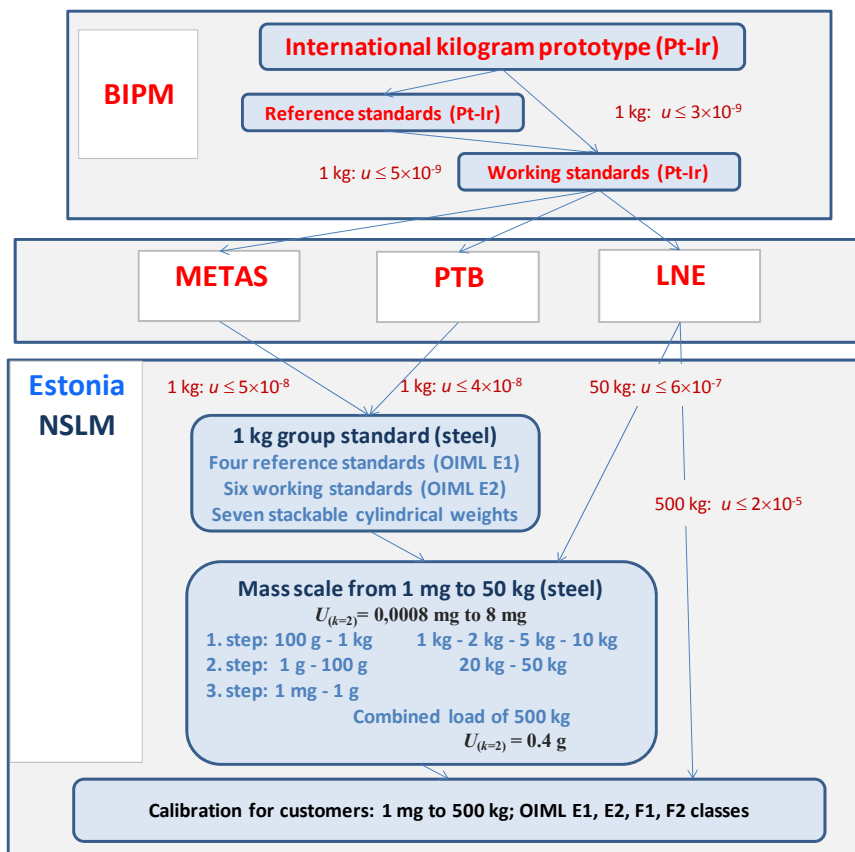
Figure 2. Traceability chart of mass measurements through Estonian NSLM.

In order to be able to measure the mass of an arbitrary object, the mass scale must be realized by subdivision and multiplication and maintained in the relevant measurement range. At the NSLM this is done in the 1 mg to 50 kg range.
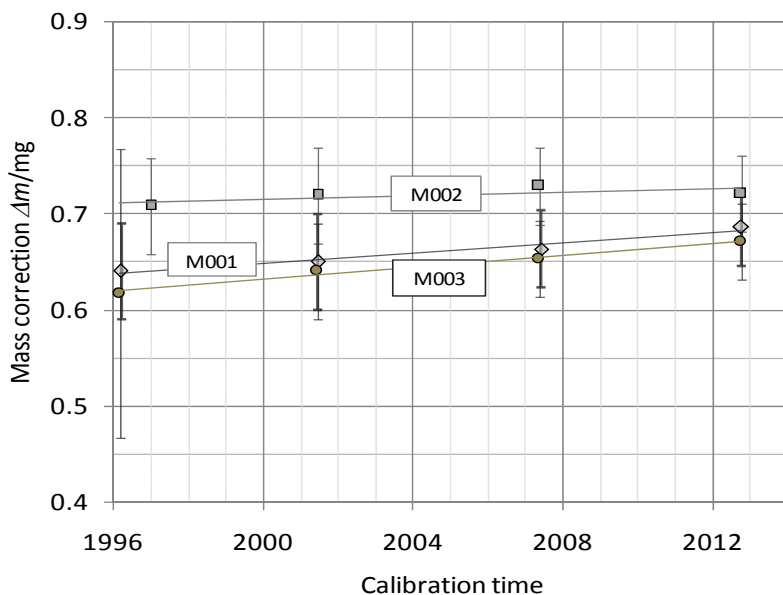
Figure 3. Calibration results of 1 kg reference weights of the NSLM at the PTB demonstrating firm traceability to the IPK.

Mass scale is realised in three steps: first, subdivision from 1 kg down to 100 g, and direct multiplication from 2 kg to 10 kg is performed; second, subdivision from 100 g down to 1 g, and multiplication using five 10 kg weighs from 20 kg to 50 kg is performed; finally, subdivision from 1 g down to 1 mg is performed. Such stepwise realization of scale allows a grouping of comparisons with similar accuracy, and thus simplifies the least square estimation of the results. The traceability chain may include calibrations over a time interval of more than 20 years; therefore, in order to state firm traceability, the stability of standards is of the highest relevance and changes must be carefully recorded and analysed.
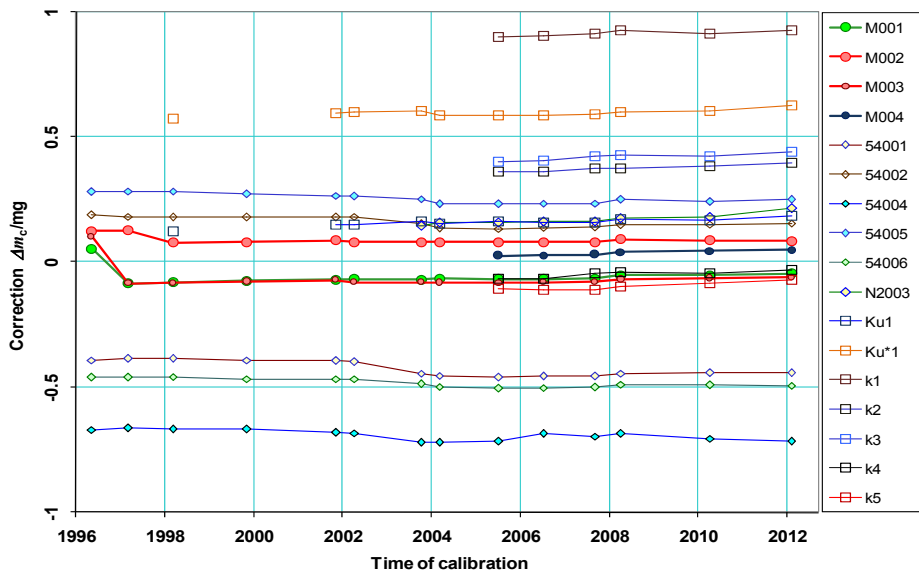
Figure 4. History of the 1 kg group standard based on calibrations at the NSLM.

The stability of stainless steel artefact mass standards depends on the alloy used, construction and manufacturing, environmental conditions, handling and time. The surface of the weights is covered with atomic water and oxide layers, and small scratches, holes and pits left from polishing. Dirt and fine dust particles from the surrounding atmosphere tend to accumulate on the surface, and as a consequence masses often increase with time. The purity of the laboratory air and all equipment in the working space is one of the key factors that affect weight stability. The reduction of masses due to wear and tear through heavy use is also possible. Therefore, the 1 kg group standard additionally includes six OIML shape working standards, and seven stackable cylindrical standards. The stability and reproducibility of the whole 1 kg group is shown in Figure 4. The drift of working standards shown over 15 years is smaller than the stated expanded uncertainty. Typical changes between two sequent calibrations over time are smaller than 10% of expanded uncertainty.

3. NATIONAL STANDARD LABORATORY FOR MASS

3.1. Equipment

3.1.1. Mass comparators

In Table 1 the list of principal mass comparators used at the NSLM for the realization of mass scale is given [**I**]. The main measurement instrument, the Mettler AT1006 1 kg automatic mass comparator is presented in Figure 5. The electronic measurement range of this comparator is from 999.5 g to 1011 g, but in this range it has 1.15×10^7 digital steps, a deviation from linearity of less than ±8 µg, and a standard deviation of less than 1 µg. The effect of non-linearity can be significantly reduced by keeping an actual difference of compared loads to less than ±3 mg. The comparator is used for differential measurements (substitution method). It is equipped with an automatic weight-exchange mechanism with four positions for loads, and mass comparison of these loads can be done fully automatically.
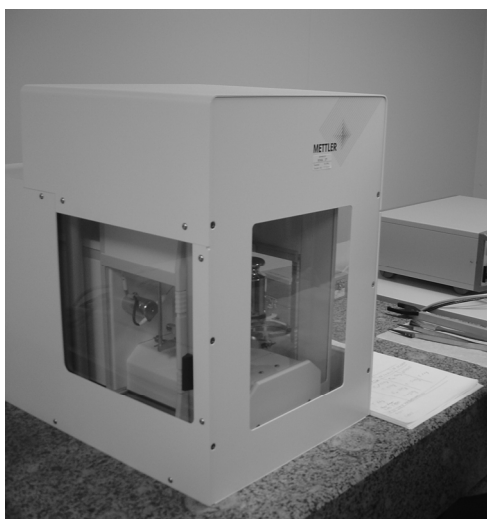
Figure 5. Prototype mass comparator of the NSLM: capability of 1 kg, resolution 1 µg, standard deviation less than 1 µg, automatic weight handler with 4 positions.

By using internal and external dial weights the measurement range of the comparator can be extended to cover loads from zero to 1 kg. In order to use this comparator for the subdivision of mass scale from 1 kg to 100 g, a special set of disc-shaped weights must be used.

The Mettler AT106H 100 g automatic mass comparator has a very similar construction to the 1 kg comparator, except for having a much smaller balance

beam mass and internal dial weighs that are ten times smaller. The electronic measurement range of this comparator is from 99.5 g to 111 g, and by using dial weights it can cover a range of 1 mg to 100 g.

Table 1. Data for principal mass comparators used at NSLM.

Type	Principle	Range of standards	Maximum load	Resolution d	Repeatability
UMT5	Full EMFC	1 mg – 5 g	5.1 g	0.1 μg	0.3 μg
AT106H	Automatic, 4 positions	1 mg – 100 g	111 g	1 μg	0.5 μg
AT1006	Automatic, 4 positions	20 g – 1 kg	1011 g	1 μg	1 μg
AX64004	Automatic, 4 positions	2 kg – 50 kg	64 kg	0.1 mg	0.4 mg

The large-scale mass comparator Mettler AX64004 with a maximum load of 64 kg has an electrical weighing range of 260 g. Its readability is 0.1 mg, and repeatability from the six ABBA type comparison cycles better than 0.4 mg. High repeatability is achieved by using an automatic weight handler with a four-position turntable (loads from P1 to P4), with individual draft shields protecting the loads from air drafts and a self-centering system that reduces the corner load error of the loads. The diameter of the turntable is about 1.1 m. The large weighing pan for diameters of up to 350 mm allows not only single weights but also large composite objects to be measured. The mass of either a single weight or a group of weights can be determined within a range of 1 kg up to 50 kg.

3.1.2. Mass standards and weights

The mass standard is characterised by its mass and the uncertainty of the mass; the most important property of mass standards is stability. Examples of mass standard are: a copy of Pt-Ir prototype, a silicon sphere, a special disc shape weight, a special pair of objects with the same mass and area, but with different volumes used for determination of air density, etc. Weights are special mass standards prepared for use in legal metrology. For the weights detailed regulations apply [19] specifying permissible errors, densities, materials and shapes, markings, surface finishing quality, magnetic properties, and the calibration and testing procedures. The accuracy class E_1 has the smallest maximum permissible errors (*mpe*). For each of the subsequent classes E_2, F_1, F_2, M_1, M_2 and M_3 *mpe* increases approximately by a factor of three, see Table 2. The combined standard uncertainty u_c of the conventional mass must be less than one-sixth of the *mpe* of that class. For calibrations, the reference weight should be of a higher accuracy class than the weight to be calibrated. At

the NSLM, the mass scale in the 1 mg to 20 kg range is presented by weights with specifications meeting the requirements of the OIML E_1 class of accuracy. The second set of weights conforms to the E_2 class of accuracy, and some larger weights to the F_1 class. In Tables 2 and 3 the principal metrological properties of the weights used at the NSLM are given.

Table 2. Data of weights used at NSLM: relative maximum permissible errors (mpe/m_c), standard uncertainties (u_c/m_c), and density limits for weights with $m_c \geq 100$ g.

Accuracy class	mpe/m_c	u_c/m_c	ρ_{min}, ρ_{max} (10^3 kg/m^3)
E_1	5×10^{-7}	$\leq 8.3\times10^{-8}$	7.934–8.067
E_2	1.6×10^{-6}	$\leq 2.7\times10^{-8}$	7.81–8.21
F_1	5×10^{-6}	$\leq 8.3\times10^{-7}$	7.39–8.73

Table 3. Limits for the magnetic susceptibility χ of the weights.

Class\Mass range	$m \geq 20$ g	2 g $\leq m \leq 10$ g	$m \leq 1$ g
E_1	0.02	0.06	0.25
E_2	0.07	0.18	0.9
F_1	0.2	0.7	10

Mostly, the weights used at the NSLM are made of stainless steel with densities in the range (8000 ± 30) kg/m^3 or (7960 ± 30) kg/m^3. Besides the knobbed weights two special sets possessing disc-shape geometry are available for the realization of mass scale. With 12 pieces of OIML F1 class 50 kg weights, a scale up to 600 kg can be realized. The volumes of the weights must be known before mass comparison. The volumes of NSLM reference weights in the range of nominal values from 1 g to 20 kg have been determined by offsite hydrostatic weighing, or onsite at the NSLM. Presently, the NSLM has a procedure to calibrate the volume and density of weights in the 1 g to 2 kg range. Determining density or volume for weights with nominal values smaller than 1 g is not necessary. In order to avoid the magnetic interactions that affect mass determination, limits to the magnetization and susceptibility of the weights are set in [19] (see Table 3) and conformity with these limits must be tested.

3.1.3. Auxiliary equipment

At the NSLM, air density is determined by measuring temperature t, pressure p, and dew-point temperature t_d, using the equations and constants recommended by CIPM [50], [51]. In the measurement of environmental parameters a precision climate instrument Klimet A30 is used. The temperature sensors are thermocouples installed in the 1 kg, and 100 g mass comparators, at a distance of approximately 4 cm from the axis of the measured weight. One set of four

temperature sensors is also installed in the 50 kg comparator, at a distance of 15 cm from the centre of the load receiver. The pressure sensor is set exactly at the reference level of the weights. The dew point sensor is located about 2 m aside of comparators. Relative humidity inside the comparators is calculated from the dew-point and local temperature measured in the comparators. Data can be recorded during mass comparisons or automatically with stand-by comparators.

Magnetic susceptibility and permanent magnetization can be tested by using the attraction method, and/or the susceptometer method [52]–[56]. This method is based on the use of 5.1 g Mettler UMT5 comparator (Table 1), and the Mettler susceptometer. In tests, the weights under study are compared with the same nominal weight from the reference set having known magnetic properties. Weights are placed one after the other on the non-magnetic platform over the comparator at a known distance from a small permanent magnet set on a special pedestal on top of the load receiver. The distance between the magnet and weight subject to testing is determined with callipers. The distance can be changed step-wise by using a special set of gauge blocks. The traceability of magnetic measurements is obtained by using a susceptibility standard calibrated at the PTB.

The density of the weights is determined by hydrostatic weighing in freshly cleaned water. Two balances are available for density measurements. The Mettler AX504 with 510 g capability is equipped for weighing of loads suspended below the balance. It is intended for density determination in the range of weights 1 g to 500 g. The Mettler PM5003 with 5100 g capability has been adapted for weighing below the balance by the addition of a special suspension frame. It is intended for determining the density of weights of 1 kg and 2 kg; the upper limit of 2 kg is due to the difficulty of handling larger weights in water. Density traceability is provided through the known formula for the density of water within a range of 0 ºC to 40 ºC, and through freshly cleaned water meeting grade 2 requirements [57], [58]. The temperature of the water is carefully measured using an Anton Paar CKT-100 thermometer.

3.1.4. Accommodation

Mass comparators are used together with the highest level of mass standards and weights at the top of the dissemination hierarchy of the mass unit [31], [32], [I]. A well-controlled environment is extremely important for a better per-formance of mass comparators, better stability of weights and a reliable determination of influence quantities [19], [31], [32]. Therefore, generally accepted requirements for environmental conditions in mass laboratory measurement rooms are specified, carefully maintained and monitored [19], [59]. Standard equipment – electronic comparators, balances, weights and auxiliary instruments – is housed in three air-conditioned rooms. The main measurement room (41 m^2) is furnished with four granite tables set on special

basements insulated from the floor. One larger insulated base is installed in an adjacent smaller measurement room (19 m^2) for the 64 kg comparator. Access to the measurement rooms is through a small air conditioned corridor (8 m^2). An air handling unit is located at a distance of at least 6 m within a separate technical room. The calibration of weights should be performed in steady ambient conditions under normal atmospheric pressure, at a temperature close to 20 ºC and with a relative humidity between 40% and 60%. Particularly for the OIML E_1 class of accuracy, maximum temperature changes during calibration must be less than 0.5 ºC. In order to ensure the required cleanliness of air in the measurement room, the air conditioning system is equipped with three different air filters. A pre-filter is used in the fresh air channel and for the re-circulated air before the air handling unit. A fine dust filter EU9 is installed in the main air inlet into the clean room. The main measurement room is designed to meet class eight clean room requirements according to standard [60].

3.2. Measurement models

At the NSLM four different measurement models are used [**I**]. The first model is for one-to-one calibration of the mass [19] and/or the conventional mass value [47] of the weights [32]; the second model is for the realisation of the mass scale, starting from the 1 kg, by subdivision and multiplication [19], [22], [24], [31]–[33], [43], [44], [61]; the third model is for determination of the density and/or volume of the weights [19], [62]–[70]; and the forth model is for determining the magnetic properties of the weights [19], [52]–[56]. For each model, all the input quantities and their uncertainties must be estimated for the whole measurement range used at the NSLM.

3.2.1. Measurement model for one-to-one comparison

The determination of mass is carried out according to the substitution method [32], where a single weight or combination thereof is compared with another weight or combination of the same nominal value using the weighing cycle that reduces the effect from the mass comparator zero drift [**I**], [**II**]. From the readings obtained, a drift-corrected difference of the two loads is determined. This difference is corrected for air buoyancy and, if the highest accuracy is needed, it can be corrected for the height of the mass centers over the base, the volumetric expansion of the weights, for scale factor of the balance, etc. In the case of larger differences between the test and reference weights, additional small weights may be added. The mass of the weight m_x subject to calibration is given by

$$m_x = m_r + \Delta m_{rt} + \rho_a(V_x - V_r) + f\Delta m_{x,r} + \Delta s_T, \tag{6}$$

were m_r is mass of the reference weight, $\Delta m_{r t}$ is drift of standard since last calibration, ρ_a is density of air during comparisons, V_r is volume of the reference weight, V_x is volume of the weight subject to calibration, f is a scale factor converting balance readings to mass units, Δm_{xr} is measured difference corrected for zero drift of the weighing instrument, and Δs_T is systematic error due to residual temperature differences between compared weights.

The unknown conventional mass m_{xc} is given by

$$m_{xc} = m_{rc} + \Delta m_{r c t} + C(\rho_a - \rho_{a0})(V_x - V_r) + f_c \Delta m_{x,r} + \Delta s_T, \qquad (7)$$

were m_{rc} is conventional mass of the reference weight, $\Delta m_{r c t}$ is drift of standard since last calibration, f_c is a scale factor converting balance readings to mass units. After electrical adjustment of the balance its expectation value is $f_c = 1$ for prevailing conditions during adjustment.

For the measurement of scale factor f, converting the differences Δm_{xr} indicated by balance into mass values, an additional special comparison cycle is required whereby adding sensitivity weight of known mass m_d and volume V_d to the test weight, the difference $\Delta m_{x+d,r}$ of $(m_x + m_d) - m_r$ is measured. From these two comparisons the scale factor f is given by

$$f = \frac{m_d - \rho_a V_d}{\Delta m_{x+d,r} - \Delta m_{x,r}}, \qquad (8)$$

were Δm_{xr} is drift-corrected difference of calibrated and reference weights, and $\Delta m_{x+d,r}$ is the same difference with the sensitivity weight added. Similarly to the situation in mass measurement, the scale factor f_c is evaluated using the difference of the two comparisons with and without sensitivity weight

$$f_c = Cf = \frac{m_{dc} - C(\rho_a - \rho_{a0})V_d}{\Delta m_{x+d,r} - \Delta m_{x,r}}, \qquad (9)$$

For practical purposes the following simplified expression is often sufficient:

$$f_c \approx \frac{m_{dc}}{\Delta m_{x+d,r} - \Delta m_{x,r}}. \qquad (10)$$

3.2.2. Measurement model for subdivision and multiplication

Mass determinations are in general carried out as differential weighing between nominally equal masses [**I**]. For calibration of the weight set with weights of different nominal values, using only one reference, much more complex calibration by subdivision or multiplication is needed [42], [44], [71]. This requires the involvement of a certain minimum number of weights that are suitable for determination in itself. Several mass differences between properly selected weight combinations of equal nominal masses are determined, and from these differences a suitable (over determined) system of weighing equations is established. The measurement result – estimates of masses or conventional masses for involved weights – is obtained by using the least square analysis, which besides estimates gives the uncertainties (variance-covariance matrix) resulting from the whole set of comparisons.

A system of weighing equations, called the design matrix, is the matrix of constants $X^*(n,l)$ representing the coefficients of a linear system of equations. In matrix notation this is described as

$$Y^* = X^* m + \varepsilon^*, \tag{11}$$

where vector m counts l mass values of weights to be determined, vector Y^* gives n mass differences obtained by comparison and corrected for air buoyancy, and the random vector ε^* stands for n unknown observation errors.

The elements of X^* are either $+1$ or -1, depending on which side of the comparison a given mass appears, or 0 if in this comparison the mass is not included. Assume that vector Y^* has a variance-covariance matrix $V_Y(n,n)$ known up to the constant factor. Then, by using the matrix $W = V_Y^{-1}$ referred to as weighting matrix, and defined as matrix product $W = (W^{1/2})^T W^{1/2}$, the system (2) may be transformed. By re-defining the terms in (7) as follows $X = W^{1/2} X^*$; $Y = W^{1/2} Y^*$ and $\varepsilon = W^{1/2} \varepsilon^*$, a generalized weighted system is obtained

$$Y = X m + \varepsilon. \tag{12}$$

The weighted least-square estimate $\hat{m}$ of parameters m in (7) can be written as

$$\hat{m} = (X^T X)^{-1} X^T Y. \tag{13}$$

The air buoyancy correction included in the measurement models can be obtained with sufficient accuracy only if ambient conditions are stable and in equilibrium with the balance and weights. If the weight has a temperature different from the surrounding air, convection effects occur [72], [73], because air density changes at the weight's surface due to heating or cooling. This air

movement causes friction on the vertical surfaces of the weight and pressure forces on horizontal surfaces, leading to errors in the balance reading. Due to the temperature gradients inside the balance chamber, changes in convective forces between load receiver and different positions of the weight handler may be revealed even in the case of an unloaded comparator. Special care is required in the case of multiplication or subdivision when loads of different shapes and/or compositions are to be compared.

3.3. Uncertainty of mass measurement

3.3.1. General terms and concepts

Uncertainty in mass calibrations at NSML is expressed based on the GUM [40], EA-4/02 [74], and in accordance with [32], [42], [44], [71]. Evaluation is based on the measurement model, which gives the output quantity y as a function f of input quantities x_i: $y = f(x_1, x_2, x_3...)$. For every input quantity standard uncertainty is separately evaluated. There are two types of standard uncertainties: Type A and Type B. Type A is of statistical origin; Type B is determined by means other than statistical analysis (usually based on *a priori* knowledge). Both types of uncertainties are indicated as standard deviations, denoted correspondingly by the letters s and u.

The combined standard uncertainty u_c is the uncertainty of output quantity y, and it is calculated from the standard uncertainties s and u of all input quantities according to the rules of error propagation. The combined standard uncertainty corresponds to simple standard deviation. The expanded uncertainty U is obtained by multiplying the combined standard uncertainty u_c by a coverage factor k as follows: $U = k \cdot u_c$. The coverage factor $k=2$ is generally used by calibration laboratories, representing in the final result a confidence level of approximately 95%.

3.3.2. Uncertainties of input quantities

In the determination of mass, as a minimum the following standard uncertainty contributions of input quantities are individually considered [**I**; **II**; **III**]:
1. Uncertainty of reference weight(s);
2. Uncertainty of air buoyancy correction;
    2.1 Uncertainty of air density;
    2.2 Uncertainty of the volumes of reference and test weights;
3. Uncertainty of the balance;
    3.1 Uncertainty due to the sensitivity constant;
    3.2 Uncertainty due to digital resolution;
    3.3 Uncertainty due to eccentric loading;
    3.4 Uncertainty due to magnetism;
4. Uncertainty of the weighing difference.

The uncertainty contribution arising from the mean value of weighing differences is considered as Type A. Contributions from mass of reference standards, air density, volumes of reference and test standards, and the residual temperature difference of compared weights are considered to be of Type B. In the realized range of mass scale from 1 mg to 50 kg, the significance of uncertainty contributions will change considerably in different parts of the scale, and the dominant contributions always should be treated with special care.

According to the measurement model (6), the combined standard uncertainty for a determined mass m_x is calculated as

$$u_c^2(m_x) = u^2(m_r) + u^2(\Delta m_{rt}) + (V_x - V_r)^2 u^2(\rho_a) + \rho_a^2 u^2(V_x) + \rho_a^2 u^2(V_r)$$
$$+ f^2 u^2(\Delta m_{xr}) + \Delta m_{xr}^2 u^2(f) + u^2(\Delta s_S) . \tag{14}$$

The variance-covariance matrix $V_{\hat{m}}$ for the least-square estimate $\hat{m}$ of parameters m of (12;13) can be written as

$$V_{\hat{m}} = \sigma^2 (X^T X)^{-1}. \tag{15}$$

In the determination of least-square estimate $\hat{m}$ covariance V_Y must be known up to the constant factor σ^2. To determine the variance of estimate $\hat{m}$, the constant σ^2 must also be known. In the case that only one comparator with limited range of only one decade is involved, the same accuracy and independence for all corrected mass differences is often assumed and V_Y will take the simple form of the identity matrix.

The constant σ^2 can be estimated from the minimum value of the residual sum of squares Q^2, calculated using the obtained least squares estimates $\hat{m}$ as

$$Q_{min}^2 = [Y - X\hat{m}]^T [Y - X\hat{m}] . \tag{16}$$

The estimate s^2 of the constant σ^2 is

$$s^2 = \frac{Q_{min}^2}{n - l}, \tag{17}$$

where $v = n - l$ is the number of degrees of freedom. In the un-weighted case $V_Y = \sigma^2 I_n$ where I_n is the identity matrix the equation (17) gives an unbiased estimate of the common variance of all observations Y. The variance-covariance matrix of the solution $\hat{m}$ of (13) is

$$V_{\hat{m}} = s^2 (X^T X)^{-1}. \tag{18}$$

The diagonal elements of $V_{\hat{m}}$ are the variances of determined values of standards, the non-diagonal elements the covariance's.

3.4. Statistical tools for correlated measurements

Specially designed statistical methods are recommended for the uncertainty analysis of randomly-varying repeated measurements that may be correlated [40]. Such special methods include Allan variance, autocorrelation function, power spectral density, etc., and are well developed in the time and frequency domain [75]–[77]. They are commonly used for electrical and radiation standard measurements [78]–[82], but in well-established methods such as mass measurement [83], [84] they are still rather rare. Nevertheless, in all metrology areas the influence of correlations on the uncertainty evaluation of repeated measurements can be important [40], [75], [78].

Random processes peculiar to the time series measured at uniform intervals can be of many different types [75], [76]. The random processes in the time and frequency field are modelled by five integer power law spectrums $S_y(f) \sim f^{\alpha}$, where the appropriate exponent α varies from -2 to $+2$ depending on the instrument used and the region of Fourier frequency f or the averaging time τ under consideration. For electrical quantities two spectrums are considered [78], with $\alpha = -1$ and $\alpha = 0$. However, in some other fields, usually only a white noise process with $\alpha = 0$ (uncorrelated measured quantity values) is assumed. Although at first glance the measurement sequences may imply different types of random process, clearly distinguishing a white noise process from a $1/f$ noise process purely by looking at a plot of a time series or at its histogram is impossible [78]. These distinctions are important, because the uncertainty associated with these processes will be much different: the variance of the sample mean of the white noise process is inversely proportional to the number of values in the sample, whereas for the $1/f$ noise process, the variance of the sample mean is independent of sample size.

One of the central tasks in time-frequency metrology is frequency stability analysis in the time domain based on an array of data points y_i with constant time intervals between successive measurements. The statistical noise characteristics of a frequency source are usually analyzed only after eliminating factors like drift and environmental effects. Data sampling or measurement is carried out during time interval τ_0, and the analysis or averaging during a multiple of τ_0 time τ, which is given by

$$\tau = m\tau_0 , \qquad (19)$$

where m is usually the integer averaging factor.

More than ten different statistical variances have been used for frequency stability analysis in time-frequency metrology [76], [77]. Amongst others, the most widely used are Allan variance and its later overlapping version which, for the same data set, can provide the extension to longer averaging times and better confidence than for the original version. The stability and uncertainty of a

frequency signal have rather similar meanings as both are measures of frequency fluctuation.

The stability of a frequency source in the time domain is usually shown by using a so-called logarithmic $\sigma - \tau$ plot that presents some variance σ^2 (or standard deviation σ) of data y_i as a function of the time τ over which the points y_i are averaged. At the same time, the $\sigma - \tau$ plot shows the stability of the signal and the type of statistical noise. The slope of the curve μ is characteristic for a particular power law noise. The most relevant types of noise related to the frequency and time domain exponents α and μ are given in Table 4. In the frequency domain, white noise is a random signal with a constant power spectral density $S_y(f)$ independent of frequency; thus $\alpha = 0$ means that $S_y(f) \sim f^0$. In the time domain, the well-known law for white noise is valid, stating that the variance of the mean is adversely proportional to the number of averaged values N: $\sigma_y^2(\tau) \sim N^{-1}$, where the respective exponent $\mu = -1$. For the data set with frequency modulation (FM), the relation between α and μ is

$$\alpha = -\mu - 1. \tag{20}$$

Table 4. Frequency and time domain exponents for some statistical power-law noises.

Type of noise	Exponent α	Exponent μ
White (WFM)	0	−1
Flicker (FFM)	−1	0
Random walk (RWFM)	−2	1

One important application of the $\sigma - \tau$ plot is determining the flicker floor of the frequency signal or standard [76], [85]. This is the point where white FM noise with $\mu = -1$ will turn to flicker FM noise with $\mu = 0$. This point defines the principal stability and/or uncertainty limit achievable with this particular signal source. Determining of this point requires a lengthy measurement series which may take several months and also depends on the analytical method (type of variance) used for analysis. Further improving uncertainty by averaging after achieving the flicker floor is impossible.

3.4.1. Variances suitable for correlated data

The estimated variance for N independent random variables y following [40] is calculated as

$$s^2 = \frac{1}{N-1} \sum_{i=1}^{N} (y_i - \bar{y})^2, \tag{21}$$

where y_i are the N values of the data set and $\bar{y}$ is their arithmetic average.

In the case of auto-correlated and therefore non-independent random data, s^2 is not applicable because it is non-convergent but (21) shows that s depends on N. This problem of adequate estimation will arise if the average value of measurements is not stationary. But with Allan variance this sample-dependent unstable behaviour is normally avoided. The Allan variance AVAR (also called 2-sample variance) is calculated from the data set y_i as [75]

$$\sigma_y^2(\tau) = \frac{1}{2(M-1)} \sum_{i=1}^{M-1} (y_{i+1} - y_i)^2 , \qquad (22)$$

where y_i is the ith of M values averaged over sampling interval, τ.

Stability is often expressed as the square root of variance $\sigma_y(\tau)$, the Allan deviation ADEV. For white FM noise the Allan variance is the same as ordinary standard variance s^2. For more divergent noise types such as flicker noise, Allan variance, as distinct from s^2, converges to a value that is independent of the size of averaged samples.

   At present, the most common choice in time-frequency metrology is overlapping Allan variance defined as [76], [77]

$$\sigma_y^2(\tau) = \frac{1}{2m^2(M-2m+1)} \sum_{j=1}^{M-2m+1} \left[\sum_{i=j}^{j+m-1} (y_{i+m} - y_i) \right]^2 , \qquad (23)$$

where according to (19), m is the averaging factor, τ averaging time, and M is the full sample size. In comparison with the original Allan variance, the overlapping version possesses much better reproducibility and allows for larger averaging times τ being used for the same data set M. The original and overlapping versions of Allan variance will give exactly the same result for the smallest time τ_0 during which a single value is measured, and for longer averaging times the expectations of both versions are the same. The estimated sample variance s^2 (or standard deviation) and the overlapping Allan variance (or Allan deviation) are mostly used for analysis in the present thesis [**III**].

3.4.2. Power law noise identification

Knowing the power law noise type can considerably improve the planning of measurements; for example, deciding on the optimal averaging time, determining the uncertainty intervals and the equivalent number of degrees of freedom, and correcting for different biases. The well-developed practice of time and frequency metrology can be applied in other fields of measurement as well. Three methods can be found for power law noise identification:

1. Barnes B_1 bias function [75], [76], [86], which is the ratio of s^2 to the Allan variance;
2. Slope on the logarithmic $\sigma^2 - \tau$ plot [75], [76];
3. Using the Lag 1 autocorrelation coefficient [76], [87] as a basis, including differencing and recalculation of autocorrelation for those noises with more divergent data.

For Method 1, the Barnes B_1 bias function shows the non-convergence of standard variance and is defined as

$$B_1 = \frac{s^2(\tau)}{\sigma_y^2(\tau)}. \tag{24}$$

Here, $s^2(\tau)$ is the estimated sample variance for points with averaging time τ, $\sigma_y^2(\tau)$, the Allan variance for averaging time τ.

Method 2 for power law noise identification is based on the slope of the line fitted through the logarithmic plot of Allan variance and averaging factor or time. For this method, obviously at least two different averaging factors are needed, and estimation is valid for all points used. For practical purposes, a single point estimate of method 1 or 3 is preferable.

Method 3 makes use of the lag 1 auto-correlation coefficient calculated from

$$r_1 = \frac{\sum_{i=1}^{N-1}(y_i - \bar{y})(y_{i+1} - \bar{y})}{\sum_{i=1}^{N}(y_i - \bar{y})^2}, \tag{25}$$

where y_i are the sequent results of the recorded data set.

According to the Method 3 algorithm, exponent α can be calculated from the expression

$$\alpha = -2(\delta + d), \tag{26}$$

where d is the order of differencing of data y_i ($d = 0$; 1; 2), and δ is defined as

$$\delta = \frac{r_1}{1 + r_1}. \tag{27}$$

If $\delta < 0.25$, we assume that the result calculated from (26) is valid and final. Otherwise, the lag 1 auto-correlation coefficient is calculated anew from the first differences $y_{i+1} - y_i$ of the data, and (26) with $d = 1$ is applied. Method 3 can give reliable results for samples starting with $N \geq 64$ where, for $\alpha = 0$, the expanded uncertainty covering 94% is approximately from -0.4 to $+0.7$. For samples with 128 points the expanded uncertainty covering 99% will be from -0.3 to $+0.5$. [87].

4. UNCERTAINTY EVALUATIONS

4.1. Uncertainty of reference mass standards

The standard uncertainty $u_{ref}(m_r)$ of the reference mass m_r is taken from the calibration certificate dividing the expanded uncertainty $U(m_r)$ with stated coverage factor k, and including the allowance for the post-calibration instability of the standard

$$u_{ref}(m_r) = \sqrt{\left(\frac{U(m_r)}{k}\right)^2 + u^2(\Delta m_{rt})} \; . \tag{28}$$

The contribution due to instability $u(\Delta m_{rt})$ can be estimated from data of the calibration history (see Fig. 3, 4, and 6). If the combination method (multiplication or subdivision of mass) is used, the standard uncertainty of combination $u_{comb}(m_i)$ is calculated as

$$u_{comb}(m_i) = \frac{m_i}{m_r} \cdot u_{ref}(m_r). \tag{29}$$

Here, m_i/m_r is the ratio of the relevant nominal values of the compared loads.

Figure 6 presents the instability data of working standards in the 1 g to 500 g range determined over a period of 15 years at the NSLM. Similar data are available for all reference and working standards covering the whole mass scale represented at the NSLM, and these collected and slightly modified data are shown in Figure 7.
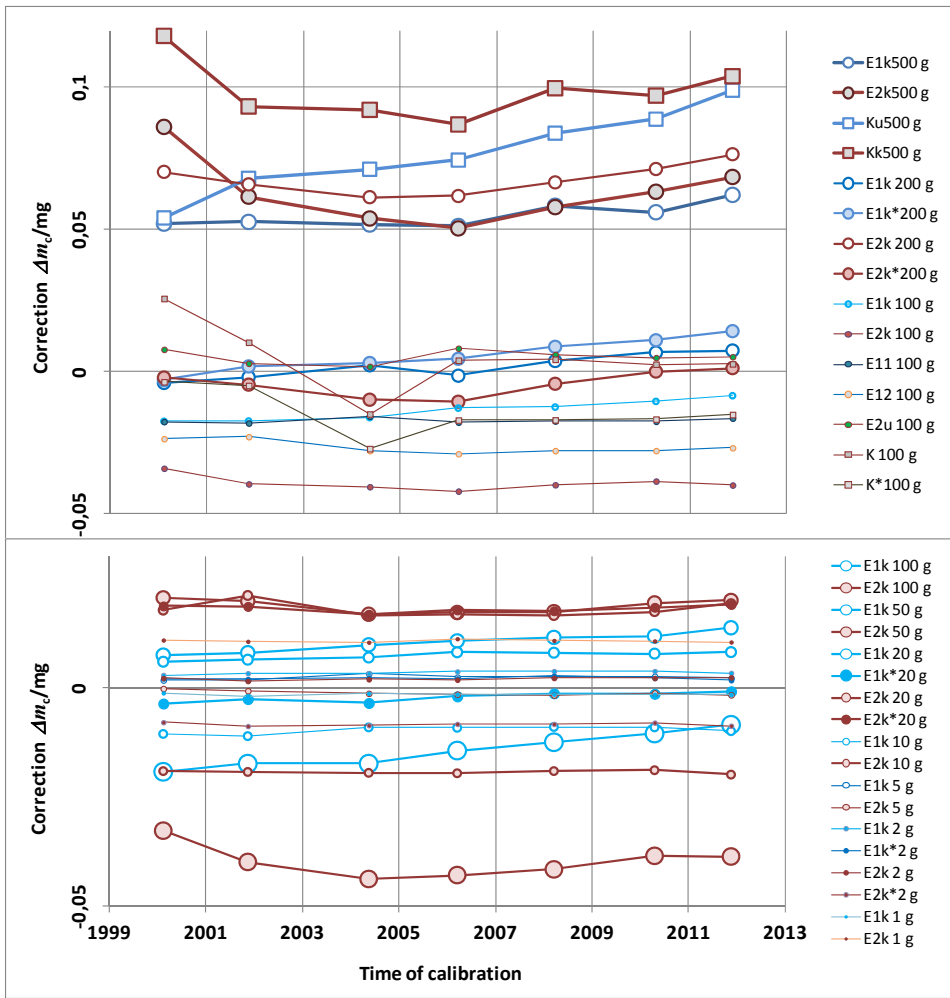
Figure 6. Stability of working standards in the 1 g to 500 g range determined at the NSLM.
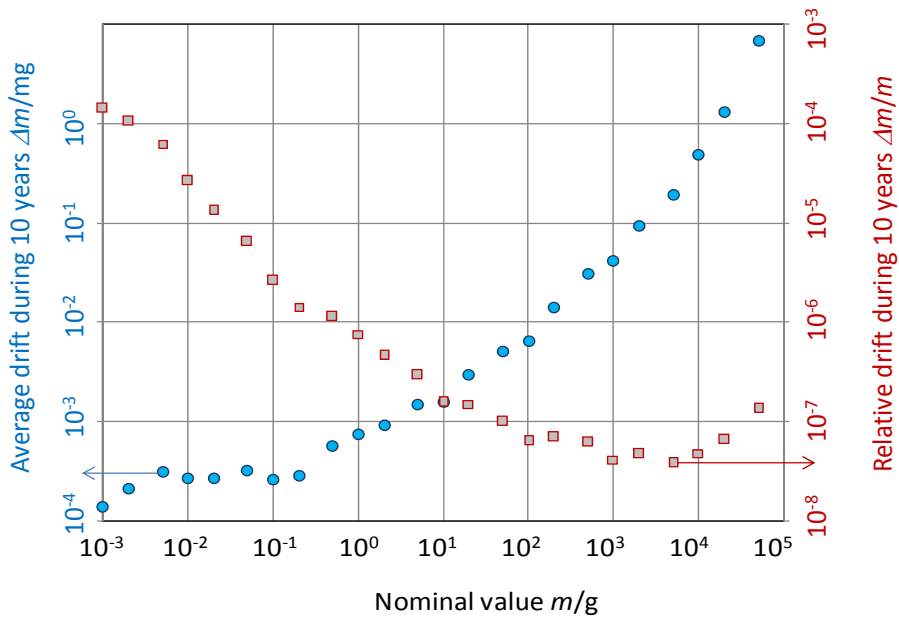
Figure 7. Average drift of the mass standards used for the realization and representation of the mass scale from 1 mg to 50 kg at the NSLM based on data monitored over ten years.
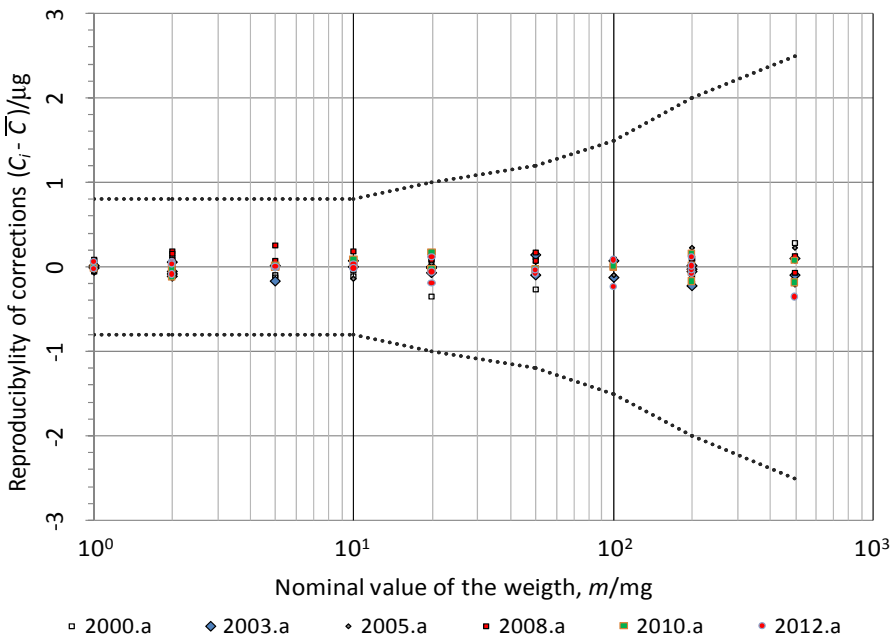
Figure 8. Reproducibility of mass corrections for the 23 weights of 1 mg to 500 mg determined six times over 12 years. Expanded uncertainty for the E_1 class is shown with dotted lines.

As can be seen in Figure 7, in the 500 mg to 50 kg range a rather steady and predictable drift is evident. The mass of the weights increases over time and the average drift rate is roughly proportional to the surface area of the weights, implying that air cleanliness can be a major source of drift in sequent calibration values of mass. The major cause of weight instability in the 1 mg to 500 mg range seems to be the reproducibility of sequent calibrations (see Figures 7 and 8).

4.2. Uncertainty of air buoyancy correction

Air density ρ_a is calculated using the well-known CIPM formula [51]. The calculation of the uncertainty contribution due to air density $u(\rho_a)$ is given by

$$u^2(\rho_a) = u^2(\mathrm{M}) + \left(\frac{\partial \rho_a}{\partial p} u(p)\right)^2 + \left(\frac{\partial \rho_a}{\partial t} u(t)\right)^2 + \left(\frac{\partial \rho_a}{\partial t_d} u(t_d)\right)^2 + \left(\frac{\partial \rho_a}{\partial x} u(x)\right)^2, \quad (30)$$

where $u(\mathrm{M})$ is standard uncertainty of the model, $u(p)$ is measurement uncertainty of air pressure, $u(t)$ is measurement uncertainty of air temperature, $u(t_d)$ is measurement uncertainty of dew point temperature and $u(x)$ is uncertainty of CO_2-content estimates in the air.

Table 5. Uncertainty budget for measurement of air density in comparator chamber.

Quantity X_i	Uncertainty $u(X_i)$	Sensitivity coefficient	Uncertainty $u_i(Y)$
P	10 Pa	$1.2 \cdot 10^{-5}$ kg/(m^{3}Pa)	$12 \cdot 10^{-5}$ kg/m^3
T	0.02 K	$4.4 \cdot 10^{-3}$ kg/(m^{3}K)	$9.6 \cdot 10^{-5}$ kg/m^3
t_d	0.05 K	$3.6 \cdot 10^{-4}$ kg/(m^{3}K)	$2 \cdot 10^{-5}$ kg/m^3
x_{CO_2}	145 ppm	0.5 kg/m^3	$7 \cdot 10^{-5}$ kg/m^3
BIPM model	$9 \cdot 10^{-5}$ kg/m^3	1	$9 \cdot 10^{-5}$ kg/m^3
Combined uncertainty $u(\rho_a)$			$1.92 \cdot 10^{-4}$ kg/m^3
Expanded uncertainty $U(\rho_a)$			$4.0 \cdot 10^{-4}$ kg/m^3

The standard uncertainty of the air buoyancy correction u_b is calculated as follows

$$u_b^2 = (V_x - V_r)^2 u^2(\rho_a) + \rho_a^2 u^2(V_x) + \rho_a^2 u^2(V_r). \quad (31)$$

Here V_x and V_r are the volumes of the test and reference weights. In the case of subdivision in terms of conventional mass, the second and third terms to the right of (18) are usually small and can be omitted.

4.3. Uncertainty of comparison difference

For high accuracy mass comparisons [40] RTTR type measurement cycles are commonly used; for each cycle a mass difference between the test weight T and reference R is calculated from two readings for W_T and from two readings for W_R

$$\Delta m_{x,R,1} = (W_{T1} - W_{R1} - W_{R2} + W_{T2})/2. \tag{32}$$

The average weighing difference is calculated from n repeated comparison cycles, and associated standard uncertainty is calculated from

$$u_A^2 = s_n^2 = \frac{s^2}{n}, \tag{33}$$

where s^2 is the experimentally estimated sample variance from equation (21) and s_n^2 is the estimated variance of the average of n values. Normally, this estimated variance of the average is considered as a Type A uncertainty contribution.

In order to test the validity of the usual Type A estimation procedure given in (33) for different comparators, loads and averaging factors [**III**], data obtained over several days containing from 120 to more than a thousand values of mass differences in total were analysed together. The Allan variance $\sigma_y^2(\tau)$ (23) of the mass differences as a function of averaging factor m corresponding to averaging time τ (19) is presented as logarithmic $\sigma^2 - \tau$ plots (Allan variance versus factor m) in Figure 9. Here, factor $m = 1$ means that variance is calculated from all successive values and corresponds to measurement time τ_0; factor $m = 2$ means that groups of two successive values are averaged and variance calculated from them corresponds to measurement time $2\tau_0$; factor $m = 3$ means that groups of three values with measurement time $3\tau_0$ are used; and so on. More than ten $\sigma^2 - \tau$ results each based on a set of 120 values are presented for the AT106H comparator with 20 g loads in Figure 9.a, and similarly for the AT1006 comparator with 1 kg loads in Figure 9.b. Both graphs show the deviation of experimental curves from white noise $1/n$ dependence given with a dashed straight line. As can be seen, these deviations are different: for the AT106H comparator with 20 g loads, the slope of the variance dependent on the number of averaged values is significantly stronger than proportionality to the $1/n$ predicted in [40] for random independent series, and for the AT1006 comparator with 1 kg loads it is much weaker.
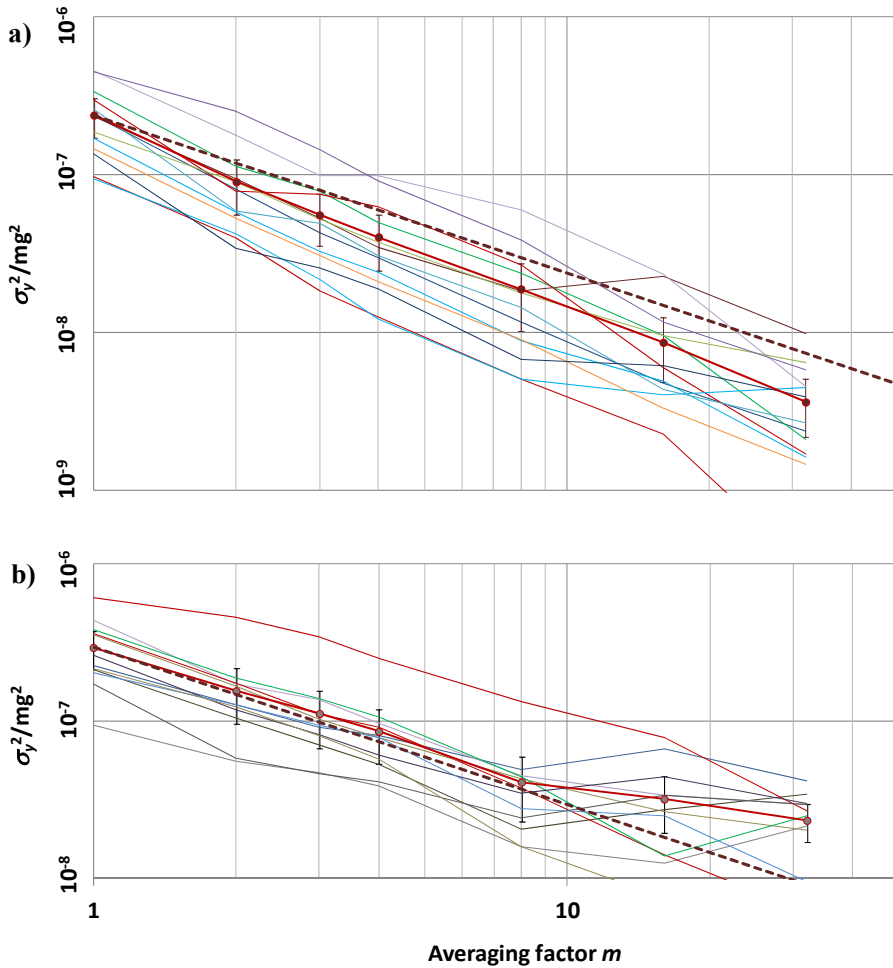
Figure 9. Group of σ^2–τ results with a set of 120 values in each, showing deviation from white noise $1/n$ dependence (dashed straight line); a) AT106H with 20 g loads; b) AT1006 with 1 kg loads.

The same data sets presented for both comparators are analysed together as single series; Allan deviation as a function of averaging factor m is presented in Figure 10. For the AT106H comparator, data obtained with 100 g loads is additionally shown. Data series with 20 g loads is added for the AT1006 comparator. From these σ – τ plots, the lowest limit of comparison uncertainty achievable for the particular comparator, load, and averaging factor m can be determined. The lower curve in Fig. 10 shows the performance of the AT106H comparator with 20 g loads, the upper curve performance of the AT1006 with 1 kg loads, and between them lie the AT106H with 100 g and the AT1006 with 20 g loads; white noise $\sim 1/\sqrt{n}$ dependences for both comparators are presented with dashed straight lines.

The slopes of the curves in Fig. 10 also specify the respective random noise type as a function of averaging factor m. For data measured with the AT106H comparator and using 20 g loads, the dominant power law noise process was identified for τ_0: $\alpha = 0.45 \pm 0.23$ and $\mu = -1.45 \pm 0.23$. The values are peculiar for the few first points in the curve; the slope for the central part of the curve is $\mu = -1.05$, implying the presence of a white noise process and, starting from $m = 64$, the curve gradually turns from white to flicker noise with a significantly smaller slope. For the AT1006 comparator with 1 kg loads and τ_0: $\alpha = -0.32 \pm 0.20$ and $\mu = -0.68 \pm 0.2$, the slope for the central part of the curve is $\mu = -0.93$ and, starting already from $m = 8$, the curve turns to flicker noise mode and further improvement of uncertainty using averaging becomes unfeasible.
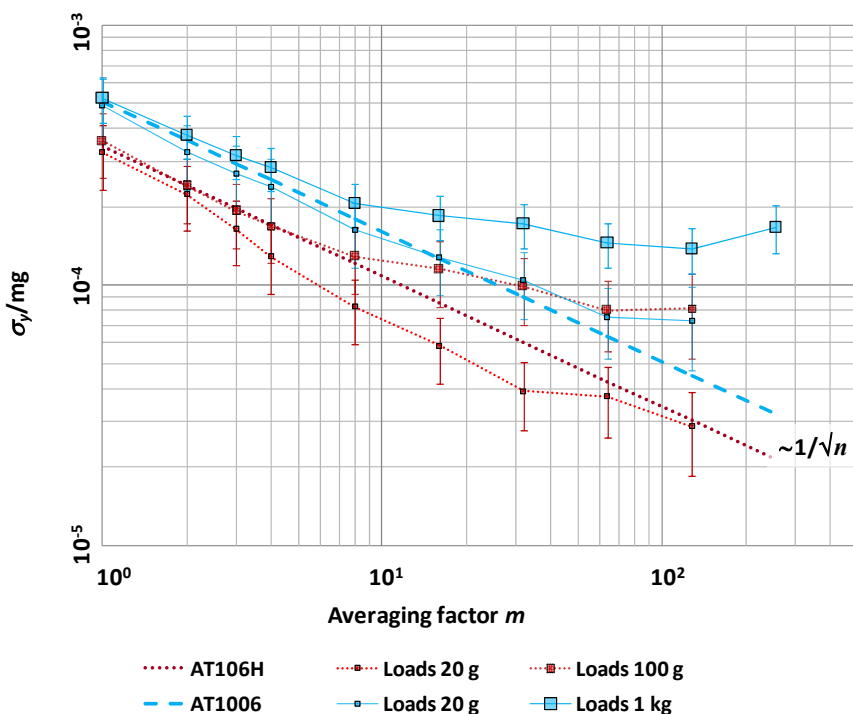
Figure 10. Determination of the lowest limit for comparison uncertainty from the $\sigma - \tau$ plots; performance of AT106H comparator with 20 g and 100 g – lower curves, performance of AT1006 with 1 kg and 20 g – upper curves; white noise $\sim 1/\sqrt{n}$ dependence – dashed straight lines.

For the AT1006 with 1 kg loads after averaging ten values the flicker floor is already reached; but, in contrast, for the AT106H with 20 g the flicker floor is not completely reached even after averaging one hundred values. The uncertainty of difference determined by using the AT106H comparator can

easily be reduced more than ten times if the sample with $N \approx 100$ is averaged. At the same time, if the sample with $N \approx 100$ is averaged for the AT1006 comparator with 1 kg loads, uncertainty is reduced less than three times. Thus Fig. 10 clearly shows that, for samples measured with the AT1006 comparator that include more than ten values, the usual averaging and uncertainty evaluation according to the Type A procedure for uncorrelated values following [40] is not justified.
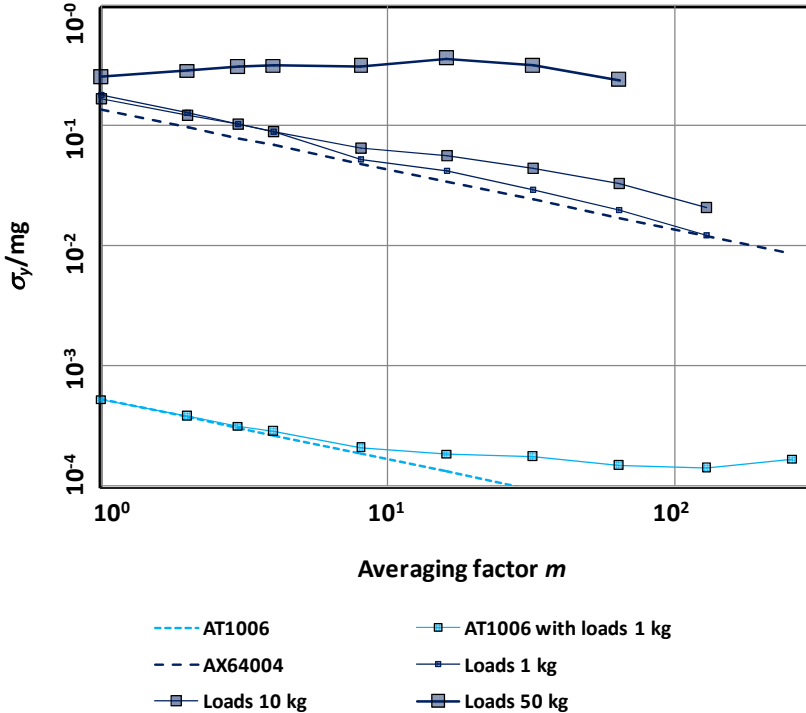

Figure 11. Determination of the lowest limit for comparison uncertainty from the $\sigma - \tau$ plots; performance of AT1006 comparator with 1 kg – lower curve, performance of AX64004 with 1 kg, 10 kg and 50 kg – upper curves; white noise $\sim 1/\sqrt{n}$ dependence – dashed straight lines.

Similar $\sigma - \tau$ results for the large scale comparator AX64004 tested with 1 kg, 10 kg and 50 kg loads are presented in Figure 11. The common Type A evaluation procedure is rather suitable for smaller loads in the 1 kg to 10 kg range, but is obviously inappropriate for 50 kg loads because the slope of the $\sigma - \tau$ curve is close to zero. This implies a random process with dominant flicker noise which is not suitable for improving uncertainty by averaging. Data from the AT1006 comparator are shown in Fig. 11 in order to demonstrate that they can be used as reference values for detecting systematic effects of the AX64004 comparator.

4.4. Uncertainty due to systematic effects affecting the performance of comparator

4.4.1. Uncertainty arising from equilibrium

Laboratory temperature, temperature gradients and variations are among the most important influence quantities in mass metrology and must be carefully monitored during mass measurement. For temperature measurements we used thermocouple sensors featuring an absence of internal heating, small contact gradients, a very small area and mass, and a high-precision readout device. Attaching sensors directly to weights, to moving weight platforms or to the load receiver can affect measurement results and/or damage the weights; therefore air temperature inside the balance chamber is usually recorded [**II**; **IV**].

For the AT1006 comparator, two temperature sensors are mounted inside the balance chamber but temperature differences between weights cannot be measured directly. An estimate of the temperature gradient between the compared 1 kg weights can be obtained from recorded mass differences. A stationary equilibrium condition is established during one day after having installed the weights into the comparator which is kept in its stand-by state. Six hours after measurement begins the measured mass difference will gradually stabilize, implying that a new dynamic equilibrium appears. Thus, changes of mass difference during stabilisation can allow an estimate of temperature difference in the stationary equilibrium condition (see Figure 12). This gradient between the compared 1 kg weights is around 20 mK [72].
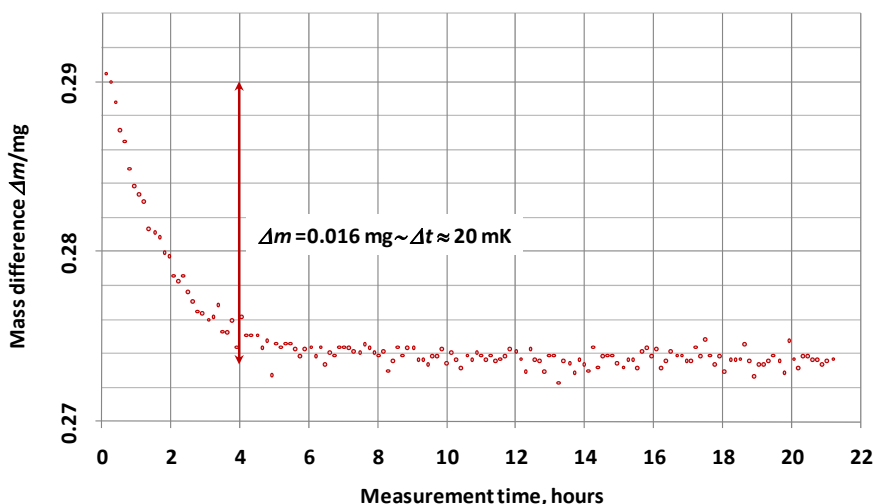
Figure 12. Stabilisation of measured mass difference of 1 kg weights after starting the AT1006 comparator: during transfer from the stationary to the dynamic equilibrium condition $\Delta m = 0.016$ mg.

In order to obtain the best estimate for the weights' temperature differences inside the AX64004 comparator, four special brass cylindrical blocks simulating the shape of 1 kg weights were prepared. The blocks had deep vertical holes to accommodate the temperature sensors.
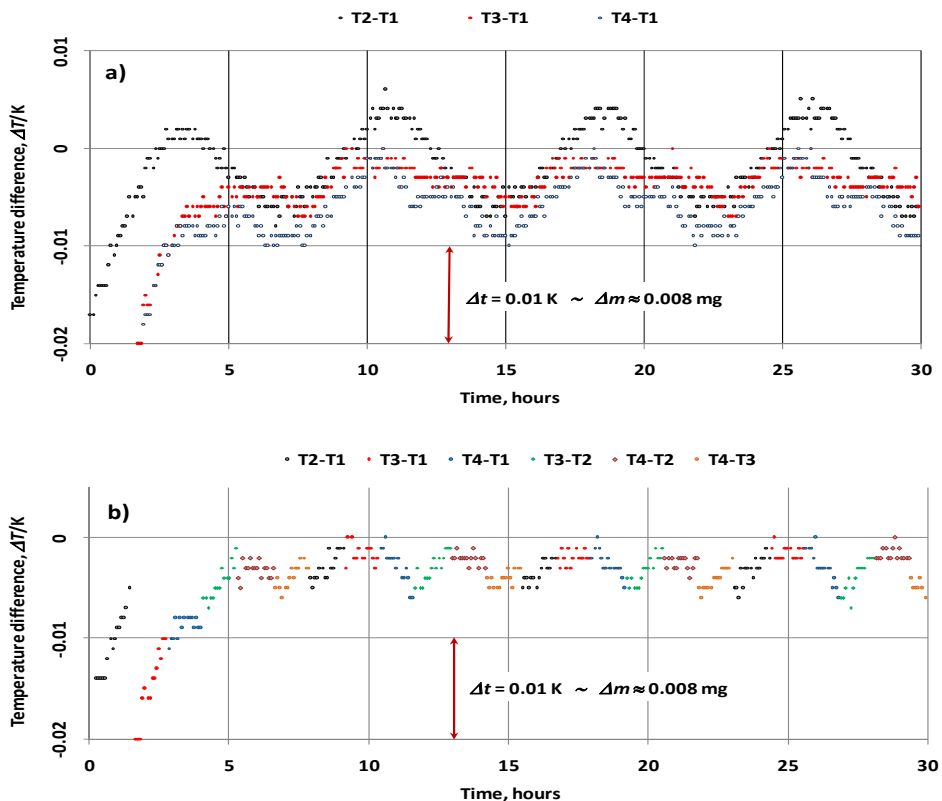
Figure 13. Dynamic equilibrium inside the AX64004 comparator for dark condition: a) continuous records between T2 – T1, T3 – T1, and T4 – T1; b) only the temperature difference between positions is shown where mass comparison is concurrently performed.

Temperature sensors inserted into the blocks were mounted in the comparator under glass covers. It was possible to measure the weights' temperatures concurrently with mass comparisons because the AX64004 comparator's turntable that carries the weights does not turn only in one direction but rotates half a turn one way and then back again. The prepared blocks permitted a fairly close imitation of real measurement conditions.
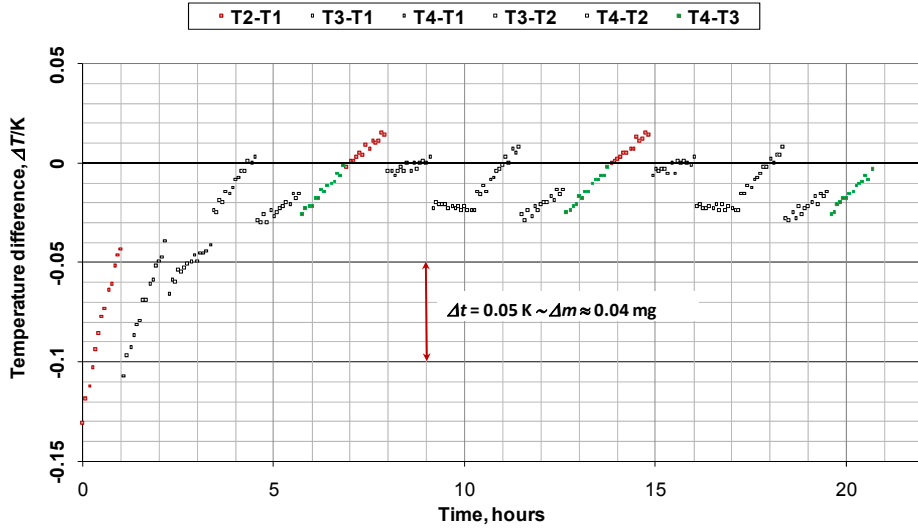
Figure 14. Dynamic equilibrium inside the AX64004 comparator for normal illumination.

Temperature differences between loads from P1 to P4 for dark conditions are presented in Figure 13. Continuous records between T2–T1, T3–T1, T4–T1 are shown in Fig. 13.a. Fig. 13.b shows only measurements concurrent with mass measured temperature differences. Measurements concurrent with mass measured temperature differences for normal illumination are shown in Figure 14.

Temperature differences inside the AX64004 comparator fluctuate around zero, but full equilibrium evidently does not appear. Although not seen from the record in Fig. 12, one may assume similar temperature behaviour inside the AT1006 comparator. After reaching dynamic equilibrium inside the AT1006, some temperature differences between the weights of at least around ±1 mK may most likely still exist, and it is also likely that such differences will slightly vary each day. It is probable that this variability of the detected mass difference represents one of the major causes for the flicker floor in the case of 1 kg loads, seen in Fig. 10.

4.4.2. Uncertainty from asymmetry of the weight-exchange mechanism

Results obtained by using automatic comparators with weight handlers are highly reproducible; ideally, the repeatability of a comparator will be a sufficient basis for estimating comparison uncertainty [19]. However, comparison uncertainty is not always limited by experimentally-determined repeatability as the asymmetry sometimes observed between weighing positions of the weight exchange mechanism implies the presence of systematic effects [88], [89]. The

application of conventional statistics to produce realistic uncertainty estimates is limited if such systematic effects bias the series of measurements [40]. Bias may be estimated from other information, mostly by using a theoretical model if the systematic effect is already known. Detecting unrecognized biases in results is extremely difficult [**II**] and only can be done using comparison measurements [90].

The asymmetry effect of the AX64004 comparator is evident from convergence data of the mass differences measured between 10 kg loads that are otherwise the same but are set at different positions in the weight exchange mechanism. In Figure 15 five series of 60 differences in each are measured between positions 3 and 1. The reference line is the average of all measured differences; the uncertainty corridor in Fig. 15 is shown as expanded uncertainty calculated from the Allan deviation of 10 kg differences, obtained from the lower curve of Fig. 17.
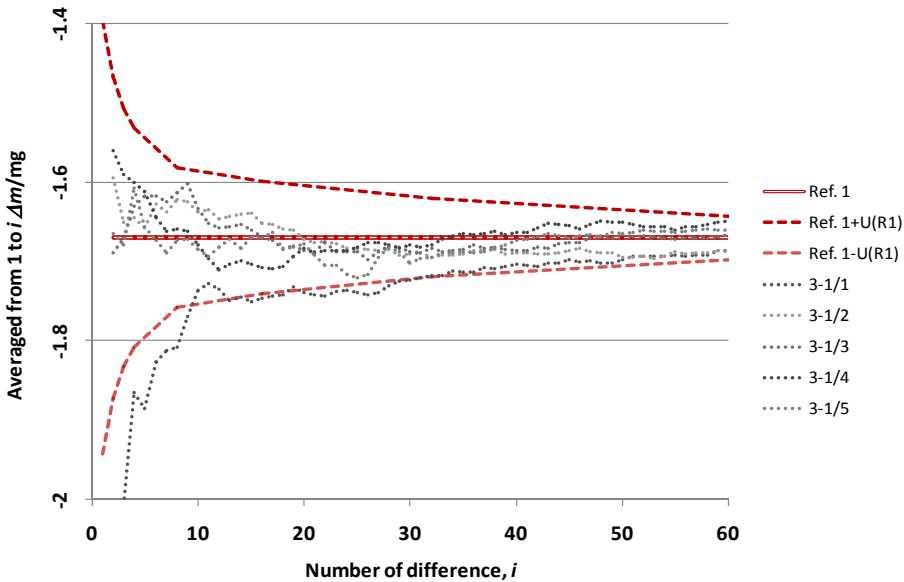
Figure 15. Convergence of sample mean as a function of sample size *n*; five series of 60 differences in each are measured by using the AX64004 comparator with 10 kg loads between P3 – P1. Reference line is average of all values; expanded uncertainty ($k = 2$) is shown calculated from Allan deviation of Fig 17.

In Figure 16 between the same 10 kg loads the difference between positions P2 – P1, P4 – P1, P1 – P3, P4 – P2, and P1 – P2 is additionally measured. New reference line is the average of all differences; expanded uncertainty ($k = 2$) is shown calculated from Allan deviations (upper curve for the 10 kg loads in Fig 17).
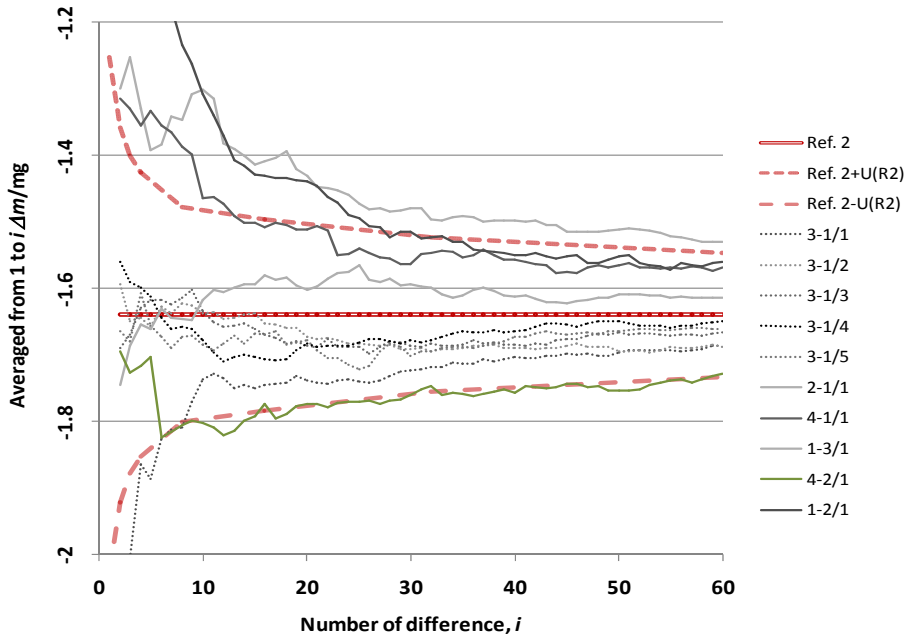
Figure 16. Asymmetry of AX64004 comparator with 10 kg loads; additionally to P3–P1 difference of the same 10 kg loads is measured between positions P2 – P1, P4 – P1, P1 – P3, P4 – P2, and P1 – P2.

The same data set for 10 kg is used for calculation of the $\sigma - \tau$ plots and is given in Figure 17, together with results for 1 kg and 50 kg. The asymmetry effect of the 10 kg loads is much larger than that of the 1 kg loads. As seen in Figures 15 and 16, Allan deviation describes the reproducibility of the results rather satisfactorily, and the increase of uncertainty due to asymmetry is significant. Unfortunately, this procedure is insufficient for fully revealing systematic effects. Much more reliable is the method described in [**II**] whereby the reference values for the determination of systematic effects are obtained by using other procedures with a much higher accuracy of measurement.

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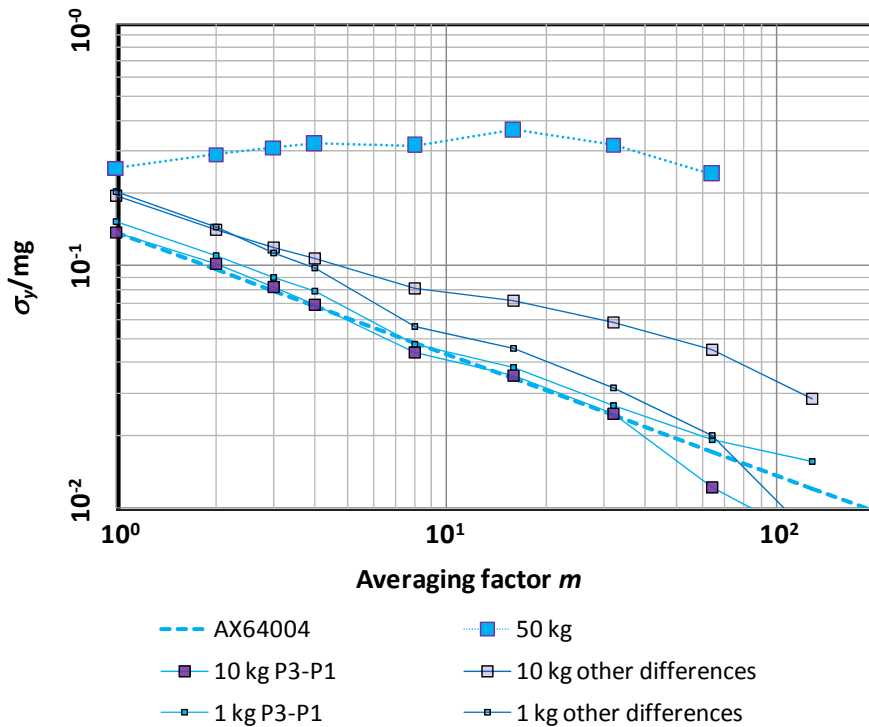
Figure 17. Performance of AX64004 comparator with 1 kg, 10 kg and 50 kg loads. Measurement between positions P3–P1 is first shown for 1 kg and 10 kg loads; the comparator's asymmetry effect is evident from results between the same loads set at other positions P2–P1, P4–P1 and P4–P2, shown by the second curve.

In [**II**], for the quantification of systematic errors in the large scale AX64004 comparator, sixteen suitably grouped 1 kg stainless steel weights with known mass differences were used. These mass differences were also determined using another mass comparator with a 1 kg maximum load and much higher accuracy as can be seen in Fig 11. All possible independent mass differences were measured and biases for 0 kg, 1 kg, 2 kg, and 4 kg loads were determined with concurrent temperature measurements under the individual draft shields covering each of the handler's positions. The biases for 1 kg loads were monitored as a function of environmental conditions and seasonal effects over a period of 16 months.

The distribution of biases in the AX64004 for the four 1 kg loads from P1 to P4, determined against known reference values and describing the behaviour of six combinations of the weight exchange mechanism (P2 – P1, P4 – P1, P1 – P3, P4 – P2, P1 – P2), are shown in Figure 18. The pattern of bias distribution for the 1 kg loads recorded over 16 months was rather stable. The biases of the three differences 2 – 1, 4 – 1 and 4 – 2 were close to zero; three other biases 3 – 1, 3 – 2 and 4 – 3 with significant negative or positive shifts can

be clearly distinguished. The pattern in Fig.18 was rather typical. Room illumination does not significantly influence the pattern; measurements made with and without illumination in the measurement room were similar. At the same time, the temperature pattern inside the comparator does significantly depend on illumination (see Figures 13 and 14).

After adjusting the AX64004 in September 2012, the pattern of biases for differences between P3 – P1, P3 – P2, and P4 – P3 greatly improved: now all biases for 1 kg loads fall inside ±0.05 mg. This is also confirmed by the Allan deviations presented in Fig 17.
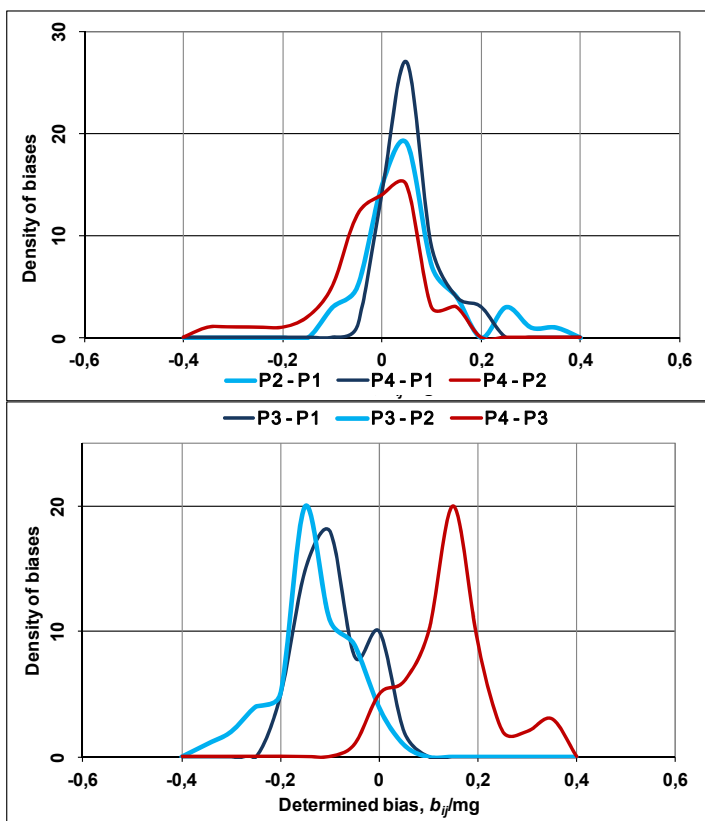
Figure 18. Distribution of systematic errors of the AX64004 comparator with 1 kg loads as a function of positions compared measured before adjustment in 2010.

The biases detected for the large-scale mass comparator with loads of up to 4 kg were found to remain within ±0.4 mg. Most of the 0.02 mg change to the biases' standard uncertainty is due to the repeatability of the tested comparator. The large-scale mass comparator's measured biases are much larger than corrections to known estimated systematic effects.

4.4.3. Uncertainty due to digital resolution of comparator

Ref [40] in section F.2.2.1 identifies the resolution of the digital instrument's indicating device as contributing to measurement uncertainty and suggests that a Type B estimation method should be used for that effect. Contribution from digital rounding should be evaluated using a uniform distribution with a full width of one resolution unit q, resulting in a standard uncertainty of $0.29q$ for any given indication. Example H.6 in [40] suggests that this uncertainty component is independent and should be added in a root-sum-of-squares manner to the uncertainty of repeated observations

$$u(y) = \sqrt{s^2(\bar{y}_i) + q^2/12} \quad . \qquad (34)$$

A similar model for repeated observations using a digital instrument is proposed in [91] where random effects are revealed by using a Type A uncertainty estimate from a series of independent observations, and digital rounding is treated as an independent additive systematic effect. In [19] digital rounding is treated in the same way as in expression (34).

Section 8.4.4 in [92] suggests that the resolution of the analogue or digital measurement equipment, or the step in the last digit or decimal of a measured value, or rounded mean value – whichever is largest – creates an uncertainty component with a standard uncertainty of $0.29q$ where q is the resolution or the step in the last digit or decimal. Ref. [92] treats the resolution quite similarly to [40], but it better covers all situations where resolution contributes to uncertainty. It further suggests, quite correctly, that resolution is already included in the standard deviation of repeated measurements because the rounding effect obviously affects any of the recorded indications. It therefore recommends only using the larger of the two in the uncertainty evaluation if the repeatability-based component is smaller than the Type B component derived from the resolution. The repeatability component referred to is not unique: a standard deviation s_{x}, or a standard deviation of the mean value $s_{\bar{x}}$ of the sample based on n indications calculated according to 8.2.2 in [92][1]. As $s_{\bar{x}}$ is proportional to $1/\sqrt{n}$, the type B uncertainty component is consequently applied as it is usually the larger.

The influence of the digital resolution on the statistical properties of the data sample was experimentally studied in [**III**]. Different resolution settings of the automatic mass comparator were applied and the same mass difference was extensively measured under repeatability conditions. A digital resolution interval was the sole parameter intentionally changed during the experiment process. The resolution was changed from 0.001 mg up to 0.2 mg, up to a factor of 200. From 600 up to 1600 indications were recorded at uniform time

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[1] Unfortunately in the choice of s_x, or $s_{\bar{x}}$ there is an ambiguity.

intervals with every resolution setting and, thus, large data sets from 150 to 400 mass differences sufficient for statistical analysis were obtained. Data sets with different statistical properties were recorded and, as recommended in [40], [75], [78], special methods of accounting for possible correlations were used for the statistical analysis.

In Figure 19 the experimental standard deviation s and Allan deviation $\sigma_y(\tau)$ are presented as functions of the digital resolution q applied. As stated in [92]–[95] resolution q will not affect the conventional statistical inference if $s \geq 0.5q$; and conventional statistical inference cannot be applied if $s \leq 0.3q$ [94]. These limits are depicted as straight, solid lines in Figure 5. The major part of all experimental standard deviations determined over a month fit within the range specified by those limits; only one deviation for resolution $q = 0.2$ mg is smaller, implying that conventional statistical inference cannot be applied. At the same time, as confirmed by power law exponents in Fig 20, data sets with dominating white noise suitable for conventional analysis are obtained only for the first three points with resolutions from $q = 0.001$ mg to $q = 0.005$ mg; for data with resolutions of 0.01 mg to 0.2 mg, more advanced tools suitable for correlated data are apparently required. The minimum value of experimental standard deviation observed with $q = 0.001$ mg was $s = 0.00029$ mg, and $\sigma_y(\tau_0) = 0.0003$ mg. Nevertheless, these data are still suitable for conventional analysis, as the determined exponents ($\alpha = 0.54$, and $\mu = -1.54$) surpass white noise values. As a consequence, the process of determining the distinction between data sets which are suitable for conventional analysis and data that requires more advanced tools cannot be based on the ratio of standard deviation to resolution unit q. The respective Allan deviation is a significantly better choice, but still less reliable than identifying power law noise.
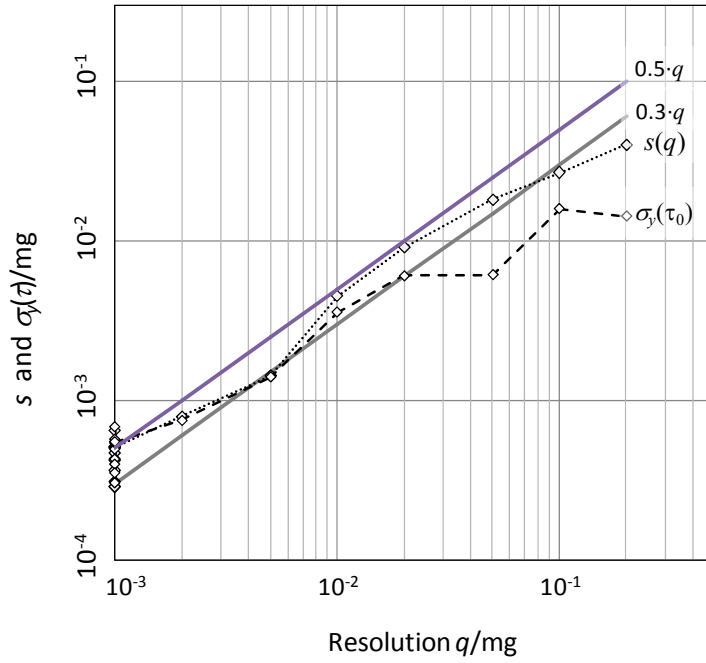
Figure 19. Standard deviation and Allan deviation as a function of digital resolution unit q. Solid lines show the range from $0.3q$ to $0.5q$ of the respective resolution unit.
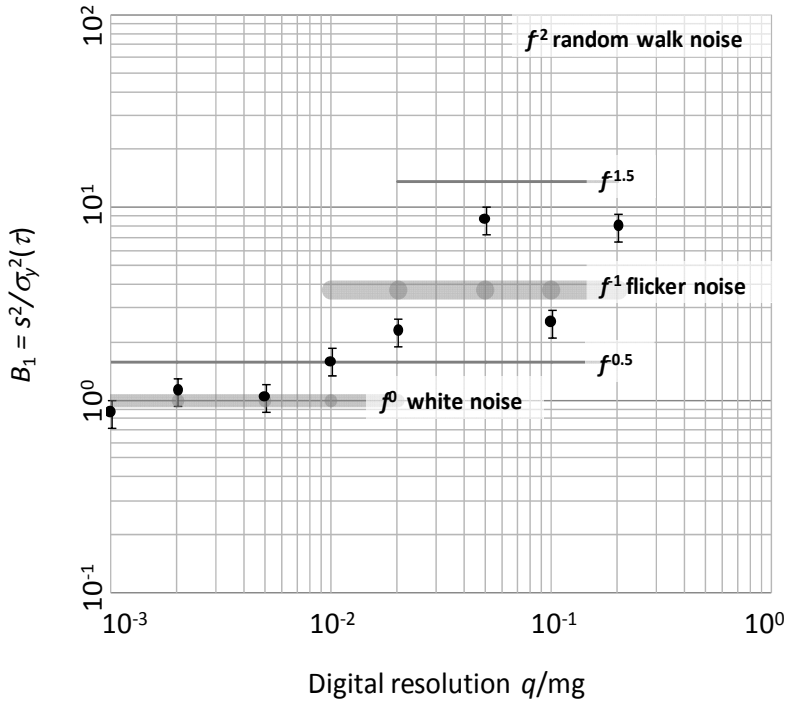
Figure 20. Random noise identification in dependence on digital resolution unit by using the ratio of standard variance to the Allan variance.

In Method 1, the Barnes B1 bias function was applied to data sets measured with different digital resolutions q, and the results are shown in Figure 20. Comparing the actual value of the B1 with the values expected for the various noise types [75], [86] allows identification of the dominating noise type. It is clearly evident that dominant random noise types depend on the resolution used and change from the white noise process for 0.001 mg – 0.005 mg to the combined $1/f$ and $1/f^2$ noise processes for 0.02 mg – 0.2 mg.

4.4.4. Uncertainty due to non-conformance of a weight

For determining the mass scale in the 1 mg to 500 mg range, a system including 62 equations (61 mass comparisons and one for traceability) for two weight sets with a total of 24 weights was solved. Residues of the least square estimation with one magnetically non-conforming 20 mg weight, and after its replacement with a conforming weight, are shown in Figure 21. The standard deviation of residues calculated from (17) is $s^2 = 0.00026$ mg for the system including a non-conforming 20 mg weight, and this reduces to $s^2 = 0.00013$ mg with a new weight conforming to class requirements.
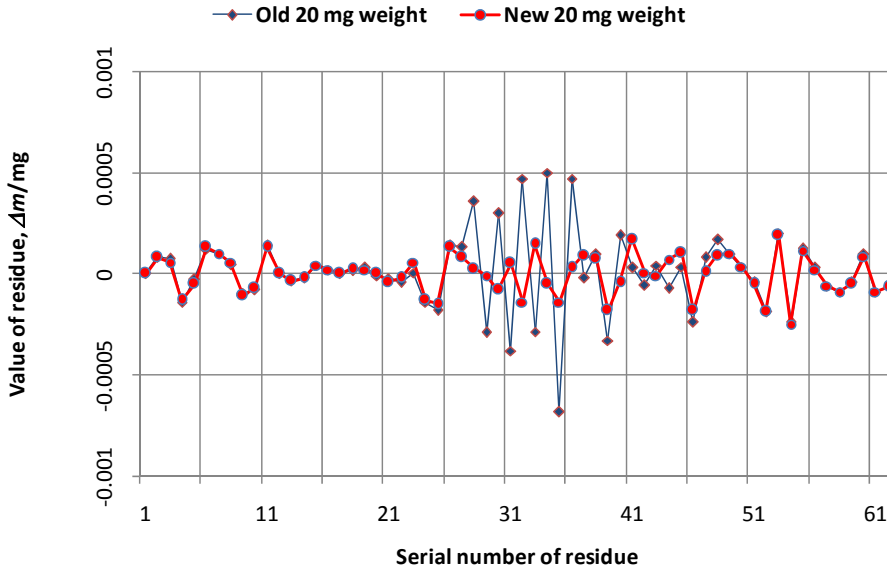
Figure 21. Residues of the least square estimation for 24 milligram weights with a non-conforming 20 mg weight, and after its replacement with a weight conforming to requirements.

This difference in s^2 looks not very large, but errors caused in mass comparisons with a non-conforming weight are around 0.0005 mg, which is of the same order as the expanded uncertainty stated in Table 7. And these errors affect all of the weights included in comparisons together with the non-conforming item. Therefore testing all weights representing the mass scale on order to safely meet the relevant requirements of [19] is important.

4.5. Expression of combined uncertainty

4.5.1. Uncertainty budgets

The uncertainty budget [**I**] for the determination of mass using the AT1006 comparator and a M001 1 kg reference standard is presented in Table 6. The data given in this table are taken from the relevant calibration certificates and the contributions described in chapter 4 above. To improve reliability, the limits for the instability of the reference standard are set at least twice as large as is evident from the calibration history. For the uncertainty of volume of the test standard it is assumed that $u(V_x)/V_x \approx 10^{-4}$. As can be seen, the highest uncertainty components arise from the reference standard, from the volume of the test standard, and from possible systematic effects. It is therefore important to apply measurement methods which allow one to reveal or avoid systematic effects as far as possible.

Table 6. Uncertainty budget for determination of mass using M001 reference standard.

Quantity X_i	Estimate x_i	Uncertainty $u(X_i)$	Sensitivity coefficient	Uncertainty $u_i(Y)$
m_r	1.00000064 kg	0.020 mg	1.0	0.020 mg
Δm_r	±0.012 mg	0.009 mg	1.0	0.009 mg
V_r	$1.255965 \cdot 10^{-4}$ m^3	$3 \cdot 10^{-10}$ m^3	$-\rho_a$ (-1.2 kg/m^3)	0.0004 mg
V_x		$1 \cdot 10^{-8}$ m^3	ρ_a	0.012 mg
f	0.99985 mg/mg	$2 \cdot 10^{-6}$ mg/mg	Less than 10 mg	0.00002 mg
$\Delta m_{x,r}$		0.002 mg	1	0.002 mg
Δs_s		0.005 mg	1	0.005 mg
ρ_a	(1.2 ± 0.06) kg/m^3	$1.6 \cdot 10^{-4}$ kg/m^3	ΔV ($\pm 5 \cdot 10^{-6}$ m^3)	0.0008 mg
Combined standard uncertainty $u_C(Y)$				0.026 mg
Expanded uncertainty $U_C(Y)$				0.052 mg

The uncertainty budget for conventional mass according to [19] using a 1 kg working standard, and determination by subdivision in the 1mg to 1kg range using the AT1006 and AT106H comparators, is given in Table 7. The test object is a class E1 weight set. Calibration is carried out in a step-by-step three-stage procedure, starting with highest decade (500-200-200-100). The determination of conventional mass is mostly required by customers of the NSLM. The measurement procedure is less demanding from the point of view of systematic effects, but the requirements for material, construction, density, magnetic properties and surface finishing of the weights tested must be verified to meet the limits set in [19].

In Table 8 is given the uncertainty budget for conventional mass according to [19] in the 2 kg to 500 kg range using ten 1 kg working standards, determination by multiplication and the AX64004 comparator. The test object subject to calibration is a class E1 weight set. For 500 kg the Mettler KC500-1 comparator and ten class F1 weights were used.

Table 7. Uncertainty budget for conventional mass values using 1 kg working standard in the 1 mg to 1kg range. Dominant uncertainty contribution is printed in boldface.

Nominal value	Reference $u_{\text{ref}}(m_r)$/µg	Air buoyancy u_b/µg	Temperature difference $u_{\Delta t}$/µg	Weighing u_A/µg	Combined u_c/µg	Expanded U_c/µg
Reference for calibration of 1 kg weight has standard uncertainty of 25 µg (normal distribution) and a contribution due to instability of ±15 µg, (rectangular distribution)						
1 kg	**26.5**	10.8	5	0.5	29	58
500 g	**13.25**	5.4	3	0.5	14.6	29.3
200 g	**5.3**	2.2	1	0.5	5.9	11.7
100 g	**2.65**	1.1	0.5	0.5	2.96	5.92
Reference for 100 g of the next decade has a standard uncertainty 3 µg (normal distribution)						
50 g	**1.5**	0.54	0.3	0.2	1.63	3.26
20 g	**0.6**	0.22	0.1	0.2	0.68	1.36
10 g	**0.3**	0.11	0.05	0.2	0.38	0.76
5 g	0.15	0.05	0.05	**0.2**	0.26	0.52
2 g	0.06	0.02	0.05	**0.2**	0.22	0.44
1 g	0.03	0.011	0.05	**0.2**	0.21	0.42
Reference for 1 g of the next decade has a standard uncertainty 0.21 µg (normal distribution)						
500 mg	0.11	0.005	0.05	**0.2**	0.23	0.46
200 mg	0.042	0.002	0.05	**0.2**	0.21	0.42
100 mg	0.021	0.001	0.05	**0.2**	0.21	0.42
50 mg	0.0105	0.0005	0.05	**0.2**	0.21	0.42
20 mg	0.0042	0.0002	0.05	**0.2**	0.21	0.42
10 mg	0.0021	0.0001	0.05	**0.2**	0.21	0.42
5 mg	0.00105	0	0.05	**0.2**	0.21	0.42
2 mg	0.00042	0	0.05	**0.2**	0.21	0.42
1 mg	0.00021	0	0.05	**0.2**	0.21	0.42

Table 8. Uncertainty budget for conventional mass values in the 2 kg to 500 kg range, calibrated using ten 1 kg working standards. Dominant uncertainty contributions are printed in boldface.

Nominal value	Reference $u_{ref}(m_r)$/mg	Air convection u_b/mg	Eccentric loading $u_{\Delta l}$/mg	Weighing u_A/mg	Combined u_c/mg	Expanded U_c/mg
For the calibration of 2 kg weights two 1 kg weights were used as a reference, for 5 kg five 1 kg weights, etc.						
2 kg	0.067	0.005	**0.15**	0.1	0.19	0.38
5 kg	0.16	0.016	**0.24**	0.16	0.33	0.66
10 kg	0.31	0.032	**0.33**	0.2	0.5	1
For the calibration of 20 kg weights two 10 kg weights were used as a reference, for 50 kg three 10 kg and one 20 kg weight.						
20 kg	**1.0**	0.066	0.4	0.3	1.12	2.24
50 kg	**2.5**	0.53	0.5	0.5	2.65	5.3
For the calibration of 500 kg weights nine 50 kg weights and a fifty-kilogram platform were used as a reference.						
500 kg	180	500	**710**	500	1020	2100

Expanded uncertainty of the reference standards ($k = 2$), evaluated according to [40], [74] and always provided with the weights representing the mass scale, is shown in Figure 22. The uncertainty of weights combines contributions from the mass, stability and volumes of the standards used, from air buoyancy corrections and from the weightings. It includes contributions due to convection, asymmetrical performance of the weight exchange mechanism and different shapes of the compared loads [**I**].
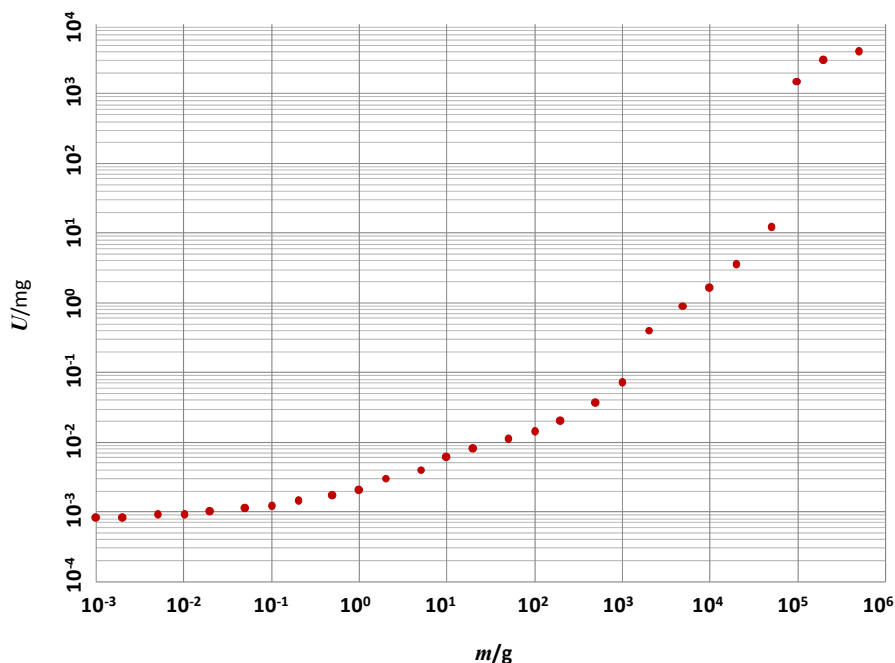
Figure 22. Expanded uncertainty of routine calibrations available at the NSLM.

The reference and working weights that represent the mass scale are used in calibrations of weights for the accredited metrology and analytical labs and for industry in Estonia. Although the number of calibrations provided annually for customers of the NSLM is not very high (around 200), demand for high accuracy calibrations is gradually growing. The present uncertainties available for calibrating weights in the 1 mg to 50 kg range are adequate for the majority of customers. The calibration of larger weights in the 500 kg up to 2000 kg range needs further improvement.

4.5.2. Conformation of uncertainties by inter-comparison measurements

The European Association of National Metrology Institutes (EURAMET) is a regional metrology organisation in Europe that helps metrology institutes to develop and receive international recognition for regional measurement com-petence. Regular participation in suitable regional measurement comparisons is used to achieve this aim. In the field of mass measurement, Estonia has participated in three key comparisons and in a number of additional regional or bilateral comparisons [**I**], as listed in Table 9.

Comparison EUROMET.M.M-K4: This comparison of 1 kg mass standards was carried out in 2002–2004 between twenty-five laboratories [96]. Four

stainless steel 1 kg transfer standards were used, two of which were circulated in each of two separate loops. The results of the NSLM are consistent both with other participants and with the key comparison reference value of comparison CCM.M-K1 to which this comparison was linked [97]. The equivalences between the NSLM results, EUROMET 510 reference values and associated k=2 uncertainties are given in Table 10.

Comparison EUROMET.M.M-K2.1: Following completion of the measurements for project 445 [98]–[100], an additional comparison was conducted from 2005 to 2008 over the same range for 11 NMIs: six new and five repeating participants. The NSLM also repeated the measurements in 2007 because of a significant improvement in the calibration method for 10 kg, and also due to confusion with the results for 20 g weights. SP again provided the transfer standards, INRIM (Italy) provided links between loops and reference values, whilst NPL (UK) collated and analyzed the results. One set of transfer standards was circulated in three sequent loops. INRIM determined the masses of each of the transfer standards at the beginning and end of each loop, in this way giving the stability estimate of the transfer standards. The equivalences between NSLM and EUROMET M.M-K2 comparison reference values providing link to the comparison CCM.M-K2 are given in Table 11.

Table 9. Comparisons with participation of NSLM.

Comparison Project	Description
Pro. **445**: EUROMET.M.M-K2	Submultiples and multiples of the kilogram
Pro. **510**: EUROMET.M.M-K4	Stainless steel 1 kg mass standard
Pro. **675**: Additional	Bilateral comparison of density/volume (VSL, The Netherlands; NSLM)
Pro. **832**: Additional	Sub-regional 50 kg comparison
Pro. **786**: EUROMET.M.M-K2.1	Follow-project of the 445
Additional comparison	Sub-regional comparison of 500 kg with MIKES , Finland as pilot laboratory
Pro. **1110**: Additional	Comparison of the magnetic properties of the weights

Table 10. Equivalence between NSLM and reference values, and associated $k = 2$ uncertainties.

	NSLM – pro 510	NSLM – CCM.M-K1
Δm/mg	9	13
$U(\Delta m)$/mg	77	67

Table 11. Equivalence between NSLM and EUROMET M.M-K2 comparison reference values providing link to the comparison CCM.M-K2, and between NSLM and M.M-K2.1. Associated expanded uncertainties are given with coverage factor $k = 2$.

Nominal values	Results of EUROMET M.M-K2				Results of EUROMET M.M-K2.1			
	In reference to M.M-K2		Linked with CCM.M-K2		In reference to M.M-K2.1		Linked with CCM.M-K2	
	Δm/µg	$U(\Delta m)$/µg	Δm/µg	$U(\Delta m)$/µg	Δm/µg	$U(\Delta m)$/µg	Δm/µg	$U(\Delta m)$/µg
10 kg	−840	6370	−800	6450	0	1360	40	1470
500 g	0	38	2	50	−6	46	31	43
20 g	−9	10	−5	7	0.2	7.1	−0.4	9
2 g	−1.4	4.4	−1	2.7	−0.7	2.8	−2.3	4.2
0.1 g	−0.1	1.3	0.1	1.6	−0.6	1.3	−0.6	1.9

EUROMET project 832: A 50 kg mass comparison [101] between five national laboratories (Metrosert, MIKES, EIM, LNMC, JV) was carried out in 2004–2006. MIKES acted as pilot, provided transfer standards, evaluated stability and analysed the results. After the comparison, a link to PTB and to CCM.M-K3 [102] was established. The equivalences between NSLM, Metrosert and EUROMET 832 reference values, and associated $k = 2$ uncertainties are given in Table 12.

Table 12. Equivalence between NSLM and EUROMET 832 reference values, and associated $k = 2$ uncertainties.

	NSLM − pro 832	NSLM − PTB	NSLM − CCM.M-K3
Δm/mg	3.2	0	−2
$U(\Delta m)$/mg	11.3	15	16

A 500 kg bilateral conventional mass comparison between Metrosert and Lahti Precision was carried out in 2006; a similar comparison between Metrosert and MIKES was repeated in 2012. Finnish laboratories acted as pilots, providing transfer standards and reference values. Results are given in Table 13.

Table 13. Equivalence between NSLM and Finish Laboratories providing 500 kg conventional mass reference value, and associated $k = 2$ uncertainty.

	NSLM − Lahti Precision, 2006	NSLM − MIKES, 2012
Δm/g	2.04	0.96
$U(\Delta m)$/g	4.1	2.2
E_n	0.50	0.43

All comparison results determined by the NSLM show satisfactory agreement with the relevant reference values and thus confirm the reliability of the stated uncertainty estimates [**I**].

5. DISCUSSION AND CONCLUSIONS

The Estonian national standard laboratory for mass NSLM has been established. It was one of the two first national measurement standards officially adopted at the Central Office of Metrology, Metrosert in 2001. At the NSLM traceable mass measurements are realized from 10^{-6} kg to $5 \cdot 10^2$ kg. The relative uncertainty available for the mass scale and for the calibration of weights has an order of magnitude of 10^{-7} for 1 kg, but for smaller and larger weights it considerably increases. The accuracy currently offered by the NSLM that allows the highest accuracy OIML E1 class weights to be calibrated is sufficient for the majority of customers.

In this study, the uncertainty of mass scale regularly realised at the NSLM in the 1 mg to 50 kg range is extensively tested, evaluated, and the international equivalence of calibration services demonstrated. Mass scale is realised by multiplication and subdivision processes from 1 kg at least once every two years; scale is represented at least by two weights for each nominal value. The traceability of mass measurements to the IPK is provided by using a group of 1 kg stainless steel standard weights of which two are calibrated at the PTB every five years.

The uncertainty of the weights representing mass scale at the NSLM is estimated following GUM standard procedures. In general, mass scale uncertainty is suitably small to allow calibration of the highest accuracy OIML E1 class weights in the whole realised range. Although GUM, as the major reference document for measurement uncertainty, performs satisfactorily in most cases, some improvement in uncertainty evaluation is still possible if sufficient measurement data are available.

The Type A estimation method is easily and reliably applicable only if uncorrelated data sequences are analysed. Except some references, testing for the randomness and independence of data stays outside the GUM approach. In this study some statistical methods are described which are also suitable for data samples with correlated data. They allow the detection of the type of dominant statistical power law noise, and the selection of suitable approaches for further data handling. Noise identification is important, as the uncertainty associated with these noises will be much different. These statistical tools are applied to data samples measured with limited digital resolution; further they are applied in evaluating the performance of different mass comparators operated with different loads. These methods are also suitable for a partial accounting of systematic effects present in automatic mass comparators. The reliable and justified application of a particular estimation method is especially important if the uncertainty component under consideration is dominant in the uncertainty budget (Tables 7 and 8).

The logarithmic $\sigma^2 - \tau$ plot with Allan variance or Allan deviation as a function of averaging factor m or averaging time τ is one of the most effective means for describing the uncertainty of the comparison result or for detecting

the principal uncertainty limit which can be achieved with the particular comparator and loads by increasing the averaging time. In the case of dominant white noise sequences, Allan variance and usual sample variance s^2 will give the same results, but in the case of correlated data Allan variance is much preferable. As distinct from standard variance it does not depend on the sample size. The slope of the logarithmic $\sigma^2 - \tau$ plot with Allan variance shows the type of dominant statistical noise. Drawbacks related to Allan variance are the relatively large sample size required for reliable analysis, and the more complicated calculation procedure.

Limited digital resolution may cause a strong autocorrelation of sequent results, rendering the averaging of large data samples senseless. Checking the type of dominant statistical noise is strongly advisable if there exists any doubt that results in the sample may be correlated. A similar situation can occur when evaluating the performance of mass comparators. Most noticeably different from usual white noise behaviour is the performance of the AX64004 comparator with 50 kg loads (see Figures 11 and 14). But the applicability of the Type A estimation method is also limited when using the AT1006 comparator with 1 kg loads (Fig. 10). At the same time, for all three NSLM comparators operated with small loads, applying the Type A estimation method is justified; the best resolution achievable using data averaging obtained from these comparators will usually be significantly smaller than the particular digital resolution q.

Knowing the systematic effects and biases which may affect mass comparison is important. Otherwise, considerable underestimation of uncertainty in mass measurements may occur. Reducing systematic errors involves two interconnected techniques: adjusting the comparator and decreasing disturbing environmental effects. The comparator will only perform well in a good environment and after adequate adjustment. If the environment is not well suited, correct adjustment may also be hindered. The standard uncertainty of the mass differences determined for 1 kg weights using the AX64004 comparator following only the Type A estimation procedure is 0.02 mg, and can range up to more than 0.1 mg if possible biases are correctly revealed and/or accounted for.

The services developed at the NSLM are accredited by the Estonian Accreditation Centre. Nevertheless, important evidence of the laboratory's correct performance can be obtained from regional or bilateral inter-comparisons. The NSLM has participated in a number of EUROMET comparisons and the agreement demonstrated between presented results and comparison reference values to date has been good. This shows that the measurement methods, calibration procedures and respective uncertainty estimates developed and tested at the NSLM can be reliably applied in practice.

SUMMARY

A high-level, well-working national measurement infrastructure is essential for the competitiveness of a country, for the advancement of science and technology, and for the quality of life. Since 2001 in Estonia, at the Central Office of Metrology, Metrosert, the national standards for mass, length, temperature and electric quantities have been established at the international secondary level. The national measurement standard usually represents the top level of competence of the country in the respective scientific-technical field. However, in order to use its capabilities effectively, confidence in the measurement uncertainty and international equivalence of the services on offer is needed. The technical level and international equivalence of the standard are validated by international experts based on inter-comparisons and peer evaluations in which measurement uncertainty is a key element for the meaningful determination of the degree of equivalence between the standards and measurement results. In chapter 1 the background and aims of this thesis are given; the important concepts are treated in chapter 2.

In chapter 3 the Estonian standard laboratory for mass (NSLM) is described. NSLM realizes and represents mass scale from 1 mg to 50 kg, being able to calibrate the mass and conventional mass values of the weights in the highest OIML E1 accuracy class. NSLM can test the conformity of magnetic properties of the weights according to all requirements of the respective accuracy class. NSLM can calibrate the density of the weights in the 1 g to 2 kg range. The mass laboratory is equipped with three automatic mass comparators, more than 100 weights, and with many auxiliary instruments; the laboratory is housed in air-conditioned measurement rooms with temperature and humidity control, and filtered air. At the NSLM four measurement models are preferably used; these models are carefully validated for the whole relevant measurement range. For the evaluation of uncertainty in measurements, extensive calibration histories are available for most of the instruments. Additionally, special studies are conducted in order to improve the database for uncertainty estimation as provided by routine measurements.

Uncertainty estimation for the weights representing the mass scale at the NSLM is described in chapter 4. Uncertainty is estimated following GUM standard procedures. In general, uncertainty evaluated according to GUM performs satisfactorily for the majority of applications. Nevertheless, there are some situations in practice that allow for improvement if sufficient measurement information is available. The effect of nonzero serial correlation is, for example, not easy to handle. Another similarly complicated problem is revealing the possible systematic effects in comparator readings in order to eliminate them or at least to take them into account in measurement results and uncertainty estimates. If these problems are not considered then substantial underestimation of uncertainty may occur.

In this study, in order to evaluate the uncertainty of series of results which may be correlated, some special statistical tools were applied, including Allan variance and statistical power law noise identification. These statistical tools are effective in revealing data sets with significant serial correlations, and thus elaborate the planning of experiments. To reveal possible systematic effects in comparator readings, a simple practical method was proposed and extensively tested. This method is based on comparing the performance of two different comparators. First, the differences of a number of test loads are measured with a high-resolution mass comparator featuring insignificant bias. At the second stage, a large-scale comparator is tested by combining these loads and measuring the combined loads with known mass differences. After comparing the different results, the biases of any comparator can easily be revealed.

The methods proposed in this study will reduce the risks of underestimating measurement uncertainty; they solve such problems at least partially, and these methods are applicable in many other measurement fields. The agreement between the inter-comparison results presented by the NSLM and comparison reference values demonstrated to date shows that the measurement methods, calibration procedures and respective uncertainty estimates developed and tested at the NSLM can be reliably applied in practice.

SUMMARY IN ESTONIAN

Mõõtemääramatuse hindamine
Eesti massi riigietaloni laboratooriumis

Riigi mõõteinfrastruktuuri kõrge tase ja sujuv toimimine on väga oluline element riigi konkurentsivõime, teaduslik-tehnoloogilise suutlikkuse ja elukeskkonna turvalisuse tagamisel. Alates 2001.a on Eestis Metroloogia keskasutuses Metrosert sisse seatud massi, pikkuse, temperatuuri ja elektriliste suuruste riigietalonid rahvusvahelisel sekundaartasemel. Reeglina kehastab mõõteetalon riigi tipptaset vastavas teaduslik-tehnilises valdkonnas, kuid selle võimalusi saab täielikult ära kasutada vaid siis, kui on kindlustatud etaloni ja nende abil osutatud mõõtetenuste mõõtemääramatuse usaldusväärne hindamine ja rahvusvaheline ekvivalentsus. Etalonide tase ja rahvusvaheline ekvivalentsus ilmneb rahvusvahelise koostöös, eelkõige hea kooskõla kaudu sobiva taseme võrdlusmõõtmistel. Mõõtemäätamatus on tulemuste kooskõla hindamisel võtmekohal. Paetükk 1 esitab uurimistöö tausta ja eesmärgid, peatükk 2 selgitab tähtsaimaid mõisteid.

Peatükis 3 kirjeldatakse Eesti massi riigietaloni laboratooriumi seadmeid, keskkonatingimusi ja mõõtemeetodeid. Laboratoorium realiseerib ja esitab massiskaala piirtkonnas 1 mg kuni 50 kg, on võimeline kalibreerima rahvusvahelise klassifikatsiooni järgi kõige täpsemate OIML E1 klassi vihtide massi ja leppelist massi. Võimalik on määrata vihtide magnetiliste omaduste vastavust täpsusklassi nõuetele ja piirkonnas 1 g kuni 2 kg vihtide tihedust. Laboratooriumi käsutuses on kolm automaatset massikomparaatorit, rohkem kui sada vihti ja mitmeid abimõõtevahendeid. Laboratoorium asub konditsioneeritud filtreeritud õhuga mõõteruumis, milles kontrollitakse temperatuuri ja suhtelist niiskust. Mõõtmised põhinevad neljale kogu mõõtepiirkonnas hoolikalt kontrollitud mõõtemudelile. Mõõtemääramatuse hindamiseks on viieteist aasta jooksul kogunenud ulatuslik mõõtevahendite kalibreerimiste ajalugu. Lisaks sellele on läbi viidud ka mitu spetsiaalset uurimust, mis lubavad hinnata mõõtemääramatust paremini kui rutiintöös saadavad üsna napid andmed.

Massiskaalat esitavate vihtide mõõtemääramatuse hindamist kirjeldatakse peatükis 4. Määramatuse hindamise aluseks massi riigietaloni laboratooriumis on rahvusvaheline juhend GUM. Üldiselt vastavad selle alusel saadud määramatuse hinnangud enamiku rakenduste nõuetele, kuid praktikas esineb olukordi, mille korral GUM ei anna optimaalset lahendust. Üheks keerulisemaks küsimuseks on mõõteseeria keskmise alusel määratud mõõtetulemuse määramatuse hindamine, kui seeria tulemused omavahel korreleeruvad. Teiseks mitte vähem keeruliseks probleemiks komparaatori tulemuste hindamisel on süstemaatiliste efektide kindlakstegemine ja elimineerimine või siis vähemalt nende panuse arvessevõtmine mõõtemääramatuses. Mõlemad probleemid võivad tähelepanuta jätmisel viia mõõtemääramatuse ekslikule hindamisele.

Antud uurimistöös kasutatkse korreleeruvate mõõteseeriate hindmisel Allani dispersiooni ja statistilise müra võimsusspekterit iseloomutava astmefuntsiooni astme määramist (f^0 – valge müra, f^{-1} – madalsageduslik flikkermüre e $1/f$ müra jne). Müra dominantspektri määramine lubab eristada nn valge müra tüüpi mõõteseeriaid, mis sobivad tavapärseks A-tüüpi määramatuse hindamiseks vastavalt GUM juhistele neist, mille korral tuleks arvesse võtta tulemuste vahelist korrelatsiooni. Mõõteseeria statistilise iseloomu alusel on võimalik mõõtmiste otstarbekam kavandamine. Võimalike süstemaatiliste vigade avastamiseks komparaatori lugemite seerias on välja töötatud lihtne meetod, mis põhineb kahe erineva komparaatori tulemuste võrdlusel. Esmalt määratakse suure arvu katseobjektide erinevused täpsema komparaatoriga, mille korral on tõestatud, et süstemaatilised efektid on väiksed ja kindlais piires. Neist koormustest moodustatakse sobivad liitkoormused, mille enrinevus on arvutatud täpsema komparaatori mõõtetulemuste alusel. Teise komparaatori süstemaatilise vea hinnangu saame võrreldes selle mõõtetulemust eelnevalt hinnatud väärtusega.

Antud uurimistöös väljatöötatud meetodid võimaldavad vähendada mõlemat ohtu määramatuse alahindamiseks ja neid saab rakendada ka paljudes teistes mõõtevaldkondades. Massi riigietaloni laboratooriumi mõõtetulemuste ja määramatuse hinnangute usaldusväärsust kinnitab hea kooskõla, mida on näidatud arvukatel rahvusvahelistel võrdlustel.

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