RADWAG BALANCES AND SCALES
ADVANCED WEIGHING TECHNOLOGIES

Metrology in laboratory

MEASUREMENT OF MASS AND DERIVED VALUES

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Contents

‘Science requires doing measurements for several reasons. One of them is an justified need of separating our observations from our convictions; using impersonal machines is one of options. Another reason is an obvious wish of carrying out more accurate measurements than our bare senses can afford. The third reason is usefulness of measurements which can be repeated in different places by different people.

If we say that science can measure, we bear in mind the effort of acquiring accurate and coherent knowledge, so that people all over the world are able to recreate it in appropriate conditions.’

Professor L. N. Cooper ‘The core and structure of physics’

FROM THE AUTHOR

This publication presents several processes, basis of which is weighing operation. This quite simple process can be analysed from different perspectives, either purely metrological or personal, i.e. ability of a particular person to carry out repeatable measurements. While describing certain processes I did not mean to show all the possible relations that can occur, I focused mainly on essential issues.

It is probable that wide circle of balance users is already familiar with part of presented here information, but I am sure that some of the readers shall find it as an introduction to a lively, in-depth discussion on subjects of their interest. I hope that at least some chapters will be of great value for you. This release of "Metrology in Laboratory", in comparison to the previous one, provides some supplementary material being an effect of newly gained experience and new insight into the previous release.

Sławomir Janas

Research Laboratory Manager
RADWAG Electronic Balances

1. Introduction

Mass measurement is seemingly the most basic measurement process in laboratory. Usually the sample mass is not known before the analysis, therefore the measurement result is intuitively accepted as accurate. And we can optimistically assume it is true. A seemingly simple process of measurement like weighing implies quite complicated mechanisms. Understanding their meaning and mechanisms allows not only to improve the work, but also use balances optimally.

It is impossible to conduct the analysis of all elements and situations connected with mass measurement. Solutions presented in the publication are the outcome of research and knowledge and they are usable.

Metrology is a science of measuring methods and the rules of results interpretation. Generally, it can be divided into industrial, scientific and legal metrology (concerning the regulations). The basis of metrology are units of measurement grouped in systems (the most widely used International System of Units SI). A part of metrology related to a practical acquiring measuring results is measuring. Metrology also includes the measuring instruments. The results interpretation requires being familiar with the calculus of errors. All those fields are tightly connected.

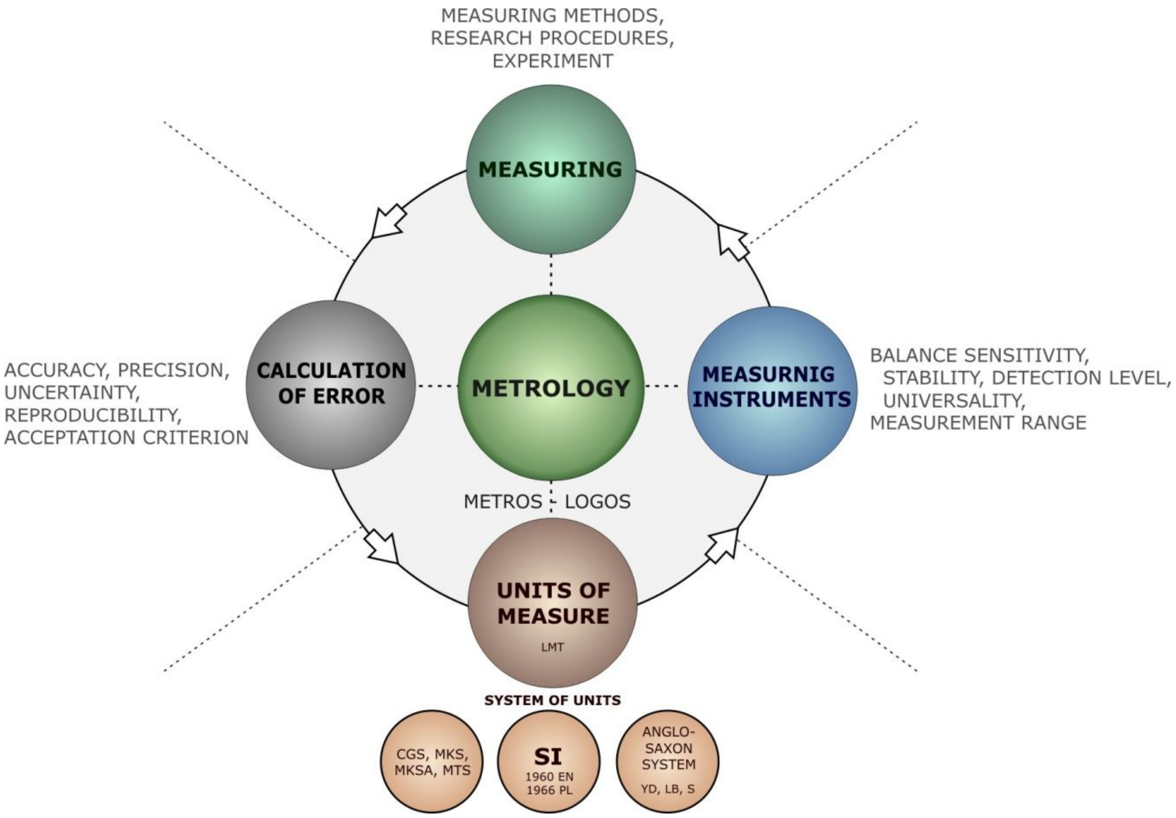


Fig 1. Key issues related to metrology

There are three different branches of metrology:

- Legal Metrology – branch of metrology referring to actions that are connected with legal requirements and concern measurements, units of measure, measuring instruments and measuring methods. These actions are taken by adequate state authorities.
- Industrial Metrology – branch of metrology dealing with measurements in different fields of science and industry excluding law regulated sphere (Legal Metrology)
- Scientific Metrology - branch of metrology dealing with maintaining and development of measurements standards and related values.

General globalization that has been growing for more than a decade, brought about a quality change in perception of metrology. It is expected to acquire more accurate measurements, exchange information quickly and verify the results. Digitization is common, especially in a technologically advanced societies. Living up to those expectations is possible, but it usually implies high cost. A cooperation between metrology research centers and industry seems to be the right direction; it might be beneficial for both sides.

2. Metrological infrastructure

The idea of metrology involving a vast area requires proper infrastructure. Globally, there are two organizations connected with metrology:

- BIMP (Bureau International des Poids et Mesures - The International Bureau of Weights and Measures) deals with scientific metrology
- OIML (International Organization of Legal Metrology) deals with legal metrology

Scientific metrology creates and develops different fields connected with improving international standards, measurements, units of measurement. Legal metrology makes guidelines related to measuring instruments. as they are 'only' guidelines, they do not have to be respected by all countries. Practically speaking, however, they are adopted to legislation of most member countries. Thanks to that we can use the same requirements regarding weighing instruments all over the world.

On regional level, in particular regions there are several organizations dealing with scientific metrology:

- European Association of National Metrology Institutes (Euramet);
- Euro-Asian Cooperation of National Metrological Institutions (Coomet);
- Intra-Africa Metrology System (Afrimets);
- Asia Pacific Metrology Programme (APMP);
- Inter-American Metrology System (SIM).

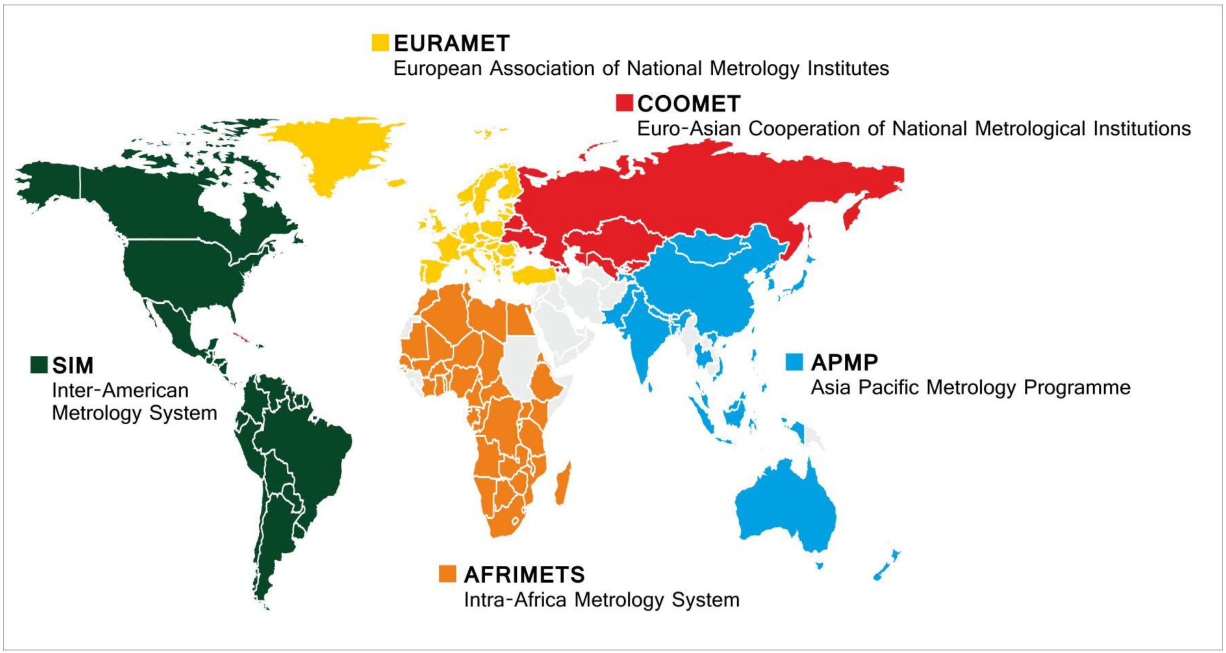


Fig. 2. Regional Metrological Organizations

Obviously, in every member country, regardless the region, there are national institutions responsible for scientific and legal metrology. This system provides the flow of information as well as coherence regarding basic requirements.

Despite the apparent equality of national metrological institutions, what matters in Europe is mainly tradition, reputability, achievements, the level of knowledge and researches. Some of the notified units carry out big research on new technological solutions, mainly for the industry. It is also one of the ways of raising funds for development, which contributes to the development of brand name as well as metrological institution.

It should be emphasized that within the scope of legal metrology national metrological institutions monitor **only fields essential for the state functioning**. They also make categories of instruments which are monitored (subject to conformity assessment). Regarding on-automatic balances (NAWI directive – see lexicon), they are mechanisms used to define mass:

- In trade;
- Which is the basis for calculation of fair fees, tolls, taxes, bonuses, discounts, penalties, awards, compensations and similar types of fees;
- At executing legal regulations and giving experts opinions in trials;
- Of a patient during a medical treatment in order to monitor, diagnose and treat;
- At prescription medicines production;
- At analyses carried out in medical and pharmaceutical laboratories;
- At products packing.

Automatic balances for single loads, batching scales, checkweighers scales, conveyor scales and rail weighbridges are included in MID directive – see lexicon.

On the one hand, the national system of measuring instruments monitoring is problematic for a common user (also for economic reasons). On the other hand, it guarantees safety and high quality (buying products, sales, diagnosis, fees, etc.). Regardless of the complexity of metrological system, maintaining measuring coherence by matching the mass standards is the basic requirement and measurement reliability guarantee. Nowadays, the basic competence is also quality and reliability of measurements. It only supports the old saying '**time is money**'.

It should be clearly stated that not every scale is subject to legal control; it is decided by its purpose. It is generally assumed that if a scale is legalized (it has M sign on green background) it will be more accurate than the one which is not. It is not true. All scales are produced in the same production and control process, so they meet the same quality criteria.

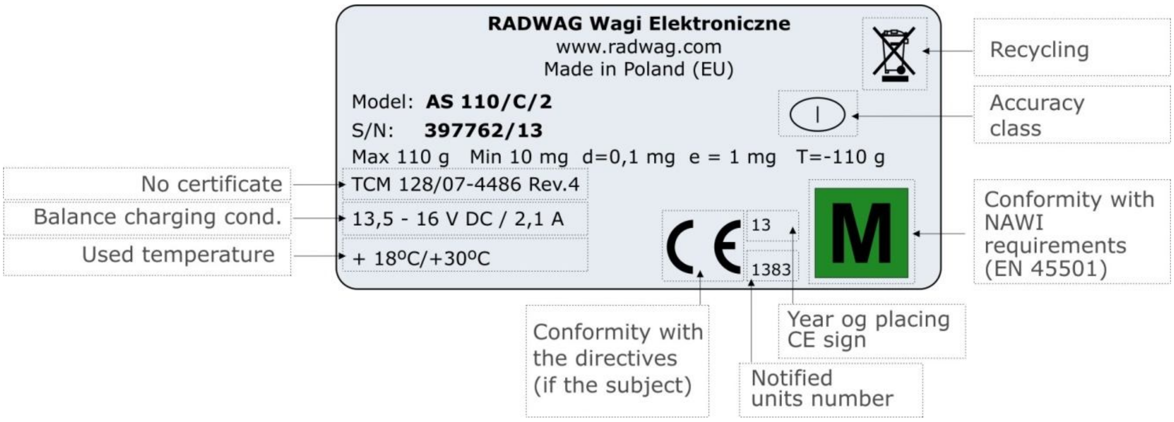


Fig. 3. Rating plate of a legalized scale - general view

It is the producer's quality system, not a green sticker, that guarantees a balance quality. In case of RADWAG products, their quality is the result of introduced and certified ISO 9001:2008 quality system. It is additionally monitored by a notified unit of CMI concerning the basic directives NAWI and MID. This system allows RADWAG company to carry out the conformity assessment of their products.

Like in every production plant the product quality is constantly monitored not only by the final product control, but also by improving other fields connected with balances production. First, production planning or new construction solutions. The key element here are our customers' opinions and requirements. The production process implies combining accuracy and technological and IT processes.

In case of technologically advanced products, a constant production process monitoring is an essential requirement for achieving efficiency. Production process monitoring implies not only the scale control, but it is a complex process. It begins with the reception of construction elements in Supply Control Department and finishes with the scale's metrological parameters check. A constant improvement of all processes in the company is an obvious thing for innovative companies like RADWAG. Our activity implies not only technological processes, but also marketing; the customer is most important for us.

Improving processes in RADWAG is introduced according to W. E. Deming's model ((W. J. Latzko, D. M. Saunders: 'Modern theory of management', WNT 1998)

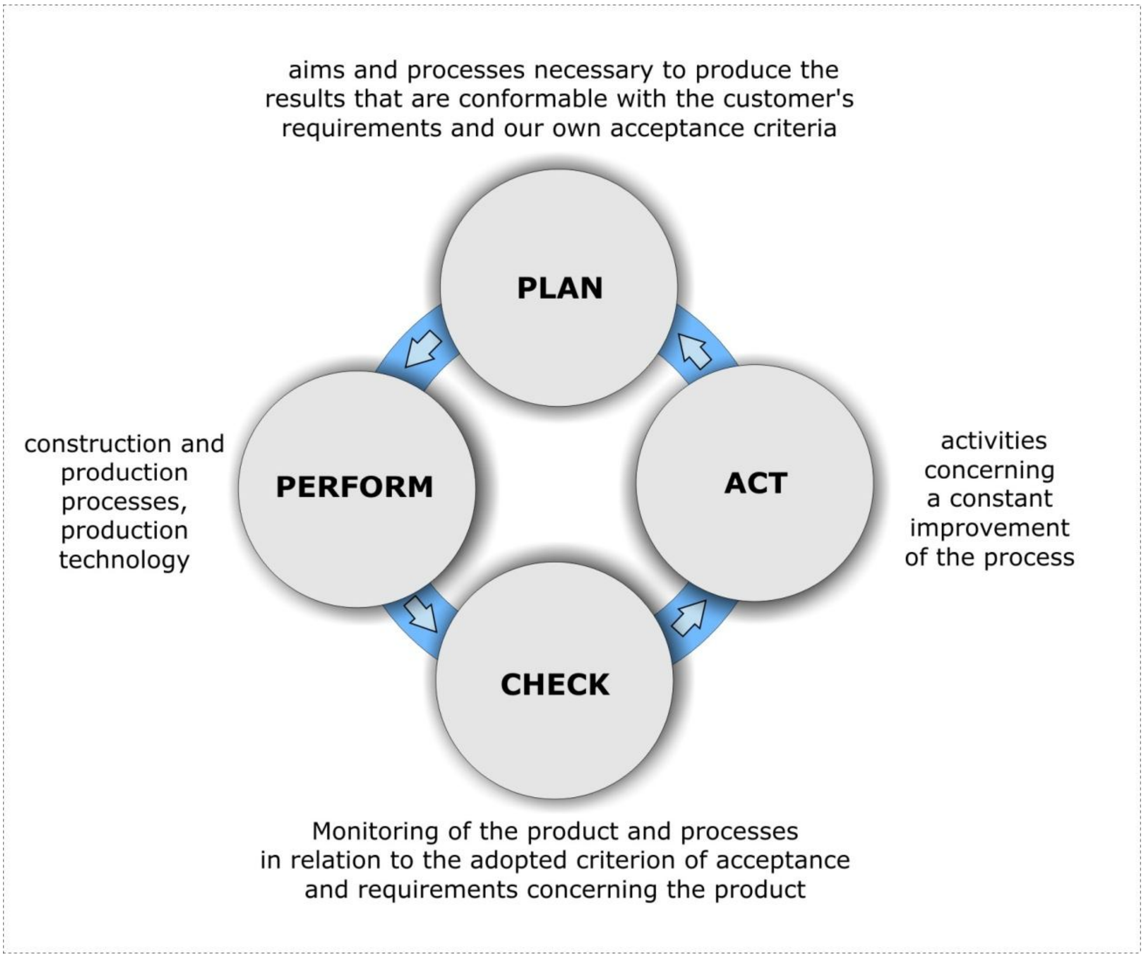


Fig. 4. Improving quality processes according to W. E. Deming's advice

Quality control systems and production processes in RADWAG are connected by a computer system. It is particularly important for registering, correction, archiving the production process for particular products and the final product control.

In our practice we use defined procedures from the project beginning to its implementation. The production process is defined and controlled on every stage in details. The introduced system of electronic verification allows us to reproduce the production and monitoring history of practically every scale which is produced in our company. Therefore, it can be said that RADWAG has its own infrastructure whose key element is Quality Control Department.

Guarantee control of mass measurements carried out in RADWAG is matching mass standards we use with standards of the higher hierarchy. The chart below presents a diagram of measurement traceability.

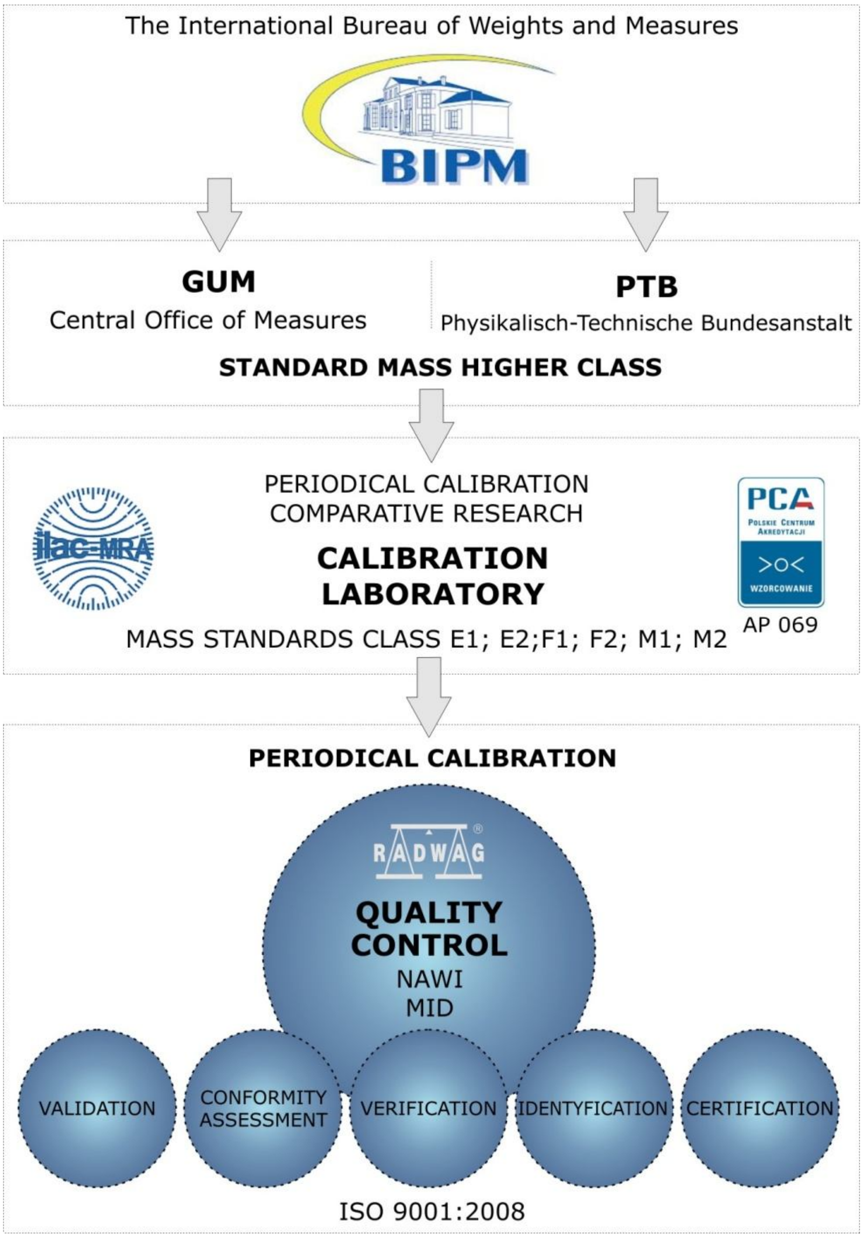


Fig. 5. Traceable to the mass standards of the higher hierarchy

The introduced quality control is subject to annual audits. They include ISC Quality Control System as management process as well as those branches which concern conformity assessment (mainly production and control process).

3. Basic meteorological concepts for mass measurement

Practically every area of operations in laboratory has a specific terminology. Sometimes so called technical slang is used, which might be incorrect but generally understood. Regarding mass measurement, this terminology concerns legal regulations and technical parameters of balances. Most useful concepts included in Index (attachment A). Below you can find definitions of the most important ideas.

Certification
Process of balances parameters control which checks their indications comparing them with maximum permissible errors (PN-EN 45501). Tests are believed to be correct when all the tests give a positive result, namely indication errors are not bigger than maximum permissible errors (MPE). It is the basis for issuing a certificate (EC type approval) for a given balance producer (series).

Declaration of Conformity
Declaration of Conformity is a written statement issued by the producer, which says that balances are conformable with the approved type and they live up to all directives requirements.

Re-legalization
The procedure concerning balances in use which checks their basic parameters comparing them with maximum permissible errors values. Error values are listed in norm PN-EN 45501. Re-legalization is done seasonally in accordance with the abiding law. The duty of subjecting a balance to re-legalization is on the user's side. It is essential that during re-legalization a balance errors are related to maximum permissible errors (MPE). Therefore, before re-legalization it is essential to check if a balance errors are smaller than MPE. It is a guarantee of the procedure success. During the usage a balance is said to be efficient when its errors do not exceed 2xMPE.

Interval
Expressed in mass units, the value of difference between values of two neighboring interval indications at an analog indication, or a difference between values of two consecutive indications at a digital indication. Electronic balances usually have following intervals:

- 1,2,3,4,5,6,7,8,9,0
- 0,2,4,6,8,
- 0,5

The interval value of legalized balances is described by procedures. The interval value of balances without legalization is selected by the producer. Usually, every balance has ONE interval. Multi-range and multi-interval balances make an exception: they have more than one interval. Those balances are not common and they are used in some industry branches.

Minimum load

Value of the load below which the weighment result can be subject to an excessive relative error (PN-EN 45501). As definition goes, weighing below the minimum load is not forbidden, although the weighing range according to PN-EN 45501 is defined from minimum to maximum load.

Note:

Absolute error – a difference between the measured value x and the real value x_0.

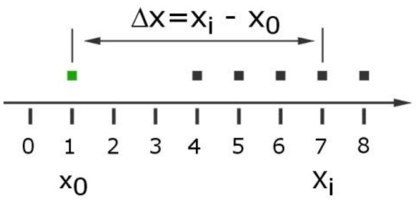


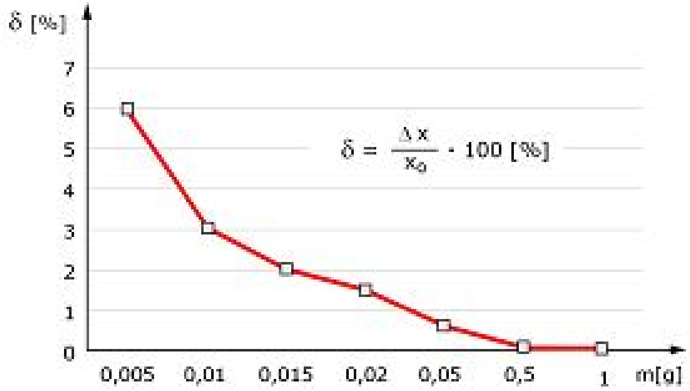
Fig. 6. Absolute error – graphic interpretation

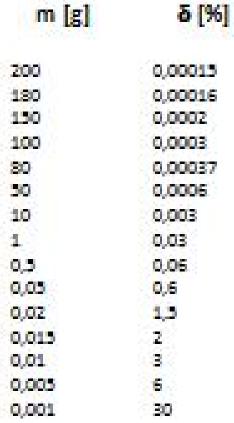
For small loads absolute error results from two factors. The first on is the repeatability of indications for small mass. Weighing the same mass several times, we achieve a certain difference of results which can be assumed as an absolute error. During testing zero indications of the balance between weighments should be observed: it is important to start every weighment with so called ‘real’ zero. It is the other factor.

Relative error – the ratio of an absolute error to the real value

$$\delta = \Delta x / x_0$$

Knowing the value of an absolute error we can calculate a relative error for a given sample mas. In this way we will define the accuracy of weighing process, it can be expressed in mass units as well as in percentages. The below dependence is true: the smaller sample mass, the bigger relative measurement error.





m [g]	δ [%]
200	0,00015
180	0,00016
150	0,0002
100	0,0003
80	0,00037
50	0,0006
10	0,003
1	0,03
0,5	0,06
0,05	0,6
0,02	1,5
0,015	2
0,01	3
0,005	6
0,001	30

Dependence of relative error (%) on the used load (Δx = 0,3mg)

As you can see on the chart above, for mass 10 mg the relative error is 3%. For a 1mg mass sample it will be 30%.

Measurement accuracy

Closeness of agreement between a measured quantity value and a true quantity value of a measurand, VIM 2010 (International Vocabulary of Metrology, Basic and General Concepts). Generally speaking, we can say that the measurement is precise when the difference between the measurand and real value is very small.

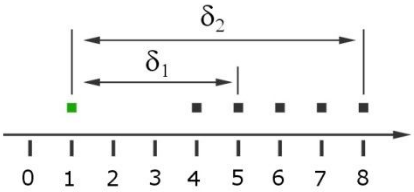
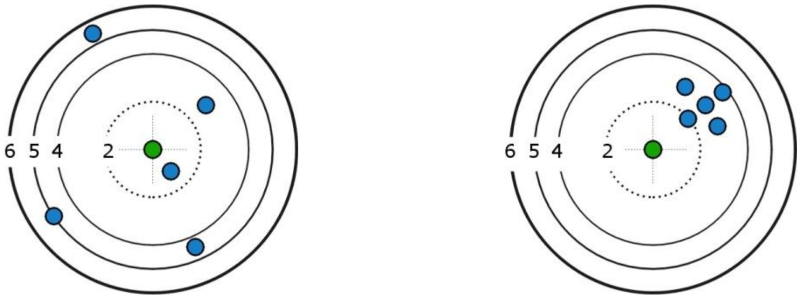


Fig. 7. Measurement precision – graphic chart

Calculation of error value requires a comparison of the measurement result and the expected value, so it can be carried out only on the basis of a standard. Measurement precision cannot be defined by means of the weighed sample.

Measurement precision

Closeness of agreement between indication and measurand values obtained by replicate measurements on the same or similar objects under specified conditions, VIM 2010. A significant precision is achieved when the measurands are close to one another.



Imprecise
values are far away
and not accurate

Precise
Values are close
But not accurate

Fig.8. Precision in measurements.

As the above descriptions show, accuracy can be referred to a single measurement, but precision requires a series of measurements. A precise measurement (e.g. average) might not be accurate. While precision can be defined by several weighments of a given sample, accuracy implies a comparison of a mass standard weighing result and the real value. It is a nominal mass of a mass standard after taking into consideration its error. Calibration certificate contains information about the error of a mass sample.

$$Mass_{NOM} = mass_{wz} - \delta_{wz} \qquad (1)$$

Uncertainty of measurement (u)

The value determining a number interval where the real value is with a certain, quite big probability. This approach is a result of measuring instruments imperfection and the used methods; it is impossible to define the measured value clearly.

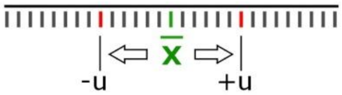


Fig. 9. Uncertainty of measurement

Note:

There is a significant difference between uncertainty of measure and measurement error. Error is a difference between the achieved value and the real value, e.g. an ideal mass standard 50 g during measurement shows 50,0020 g, so error equals 0,0020 g. Therefore, measurement of every mass sample 50 g will be afflicted with an error of 0,0020 g.

However, determined complex uncertainty of measurement is an interval range in which the expected value can take place with certain probability. Therefore, determined uncertainty cannot be used for the achieved result correction.

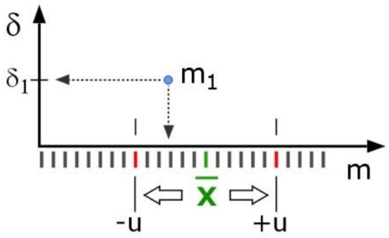


Fig. 10 Uncertainty of measurement and accuracy

Uncertainty issue is elaborated in the further parts of the book.

Measurement traceability

It is a feature of measurement or reference measurement unit which you can link to certain references, usually with state or international reference mass standards, with an unbroken comparison traceability chain, all of which are afflicted with some uncertainty.

Keeping measurement traceability is the condition of uniqueness of the measurement results enabling their comparison. Measurement traceability feature the following elements:

- Unbroken traceability chain comparable with state or international reference mass standards,
- Registered uncertainty of measurement,
- Registered measuring procedure,
- Technical competence,
- References to the SI system of units, measurement reference standards or measuring procedures including a measurement unit,
- Time intervals between calibration processes.

Adjustment

A chain of activities which make a weighing instrument work according to its purpose. In case of electronic balances, adjustment corrects the balance sensitivity by comparing the standard weighing result (usually inside the balance) with its reference mass value. Those comparisons are carried out in automatic cycles (controlled by temperature and time changes) or semi-automatic cycles (controlled by an operator).

Calibration

A number of operations determining in certain conditions relations between the measured values indicated by the measuring instrument or measuring system or values represented by measure standard or by reference material and certain values represented by measurement units.

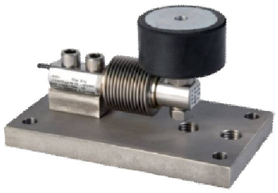
To make it simple, the process implies testing the balance characteristics with mass standards, which determines mass measurement errors for measuring points. In this way we achieve the information of what kind of error we can expect when we weigh a sample with similar mass. This approach does not imply specific features of a sample (e.g. electrostatics), it is the user’s role. As you can see, during calibration process you do not regulate any parameters of the balance. Calibration is usually registered in the calibration certificate.

4. Metrology of mass measurements

4.1. Measuring systems of electronic balances

Our perception of a balance gets down to the balance look. So we have the housing shape, a display type, the outfit aesthetics: all that our eyes can perceive. However, this object implies certain construction solutions which determine the following parameters: repeatability, linearity and measurement speed. Acquiring the demanded parameters requires using the appropriate measuring system. There is no need to discuss all the possible solutions. Therefore this publication will discuss only two of them: the cheapest and the most accurate ones.

Tensometric converters



They are produced worldwide so their price is relatively low.
They measure the measuring (extensometer) deviations.
A change of a extensometre's resistance is proportional to mechanical stress.

$$\Delta R = kR\Delta e = kR\frac{\Delta\sigma}{E} \tag{2}$$

where: R –extensometre's resistance without the stresses
k – tensometric constant of a sensor
e – relative elongation;
σ - stress;
E – Young elasticity module.

A big advantage of this solution (apart from the price) is a possibility of making balances with large max loads. Its disadvantage (not necessarily though) is a low measuring uncertainty. Selection and optimization can ensure quite high resolutions of 60 000 divisions like for WLC balances. The figure shows a tensometric converter in WLC 6/A2 balance construction. Tensometric converters are also used ten in industrial scales construction up to more than tons. The converter's construction is a bit different in this case, but the operating principle is the same. Converter fixed to the ground with a pan bracket

Magneto-electric converters

In balances using this converter type, force does not bend the mechanical system of the straight-line mechanism, which enables to achieve big resolutions at low indications errors. This is how they work:

When the balance is not loaded and the system is in its initial stage, the balance display shows zero stage. After loading the pan we register (F_G) force with which the Earth attracts the load. You achieve it by deflection of an element placed in the position sensor's reach. This deflection is balanced by (F_c) force powered by the coil installed in the magnetic field. As a result, the pan position does not change. Having the balancing force values we can determine the measuring result.

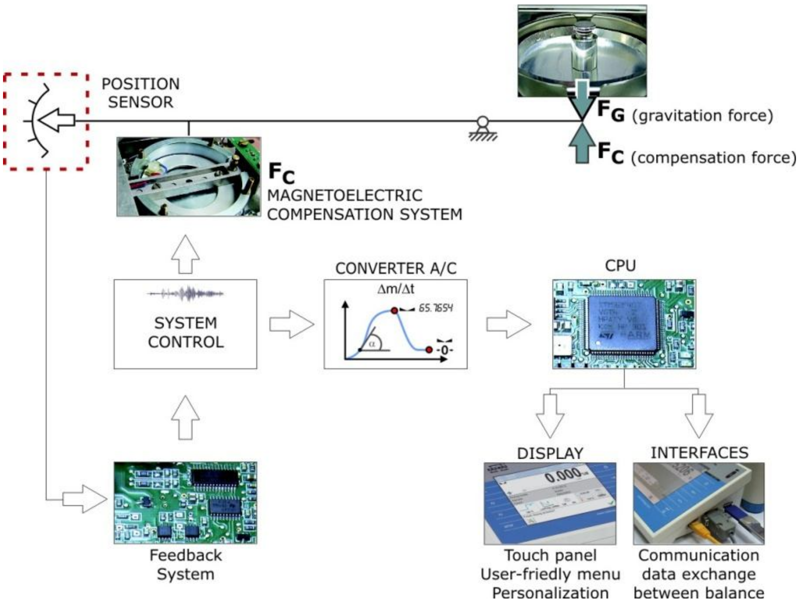


Fig. 11 Magneto-electric balance diagram

A seemingly simple operating principle requires not only precise balance construction elements. Electronic elements and software play a significant role too. It should be emphasized that this measuring system allows to achieve resolution of 20 million divisions., while the MPE is only several divisions. Only three manufacturers, including RADWAG, can produce this type of balances. Construction of a balance with such converter is shown on the example of an XA line balance.

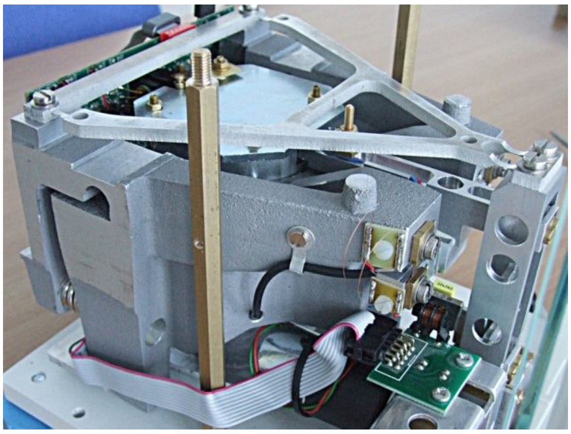


Fig. 11.1 Balance construction

4.2. Theory of errors

There are a lot of publications on the theory of errors, therefore there are no detailed discussions here. Below you can find only a list the most important terms most commonly used not only in the laboratory.

A difference between the measurement result and the real value of a measured quantity is commonly called the measurement error. There are following errors:

- Thick
- Systematic
- Random
- In control point
- In zero point

Thick error

Thick error happens when the operator is not careful enough or when the conditions are changeable (e.g. vibrations, drafts). The below data show an example of a thick error:

1. 45,5010
2. 45,5009
3. 45,5012
4. 45,5080 ← thick error /significant change +70 divisions/
5. 45,5012

Thick error should not be taken into consideration in a test cycle analysis. It is usually removed and the measurement is incorrect. You can and even should analyze what was the source of this error.

Systematic error

Systematic error is a measurement error component which is constant at a series of measurements or can be foreseen. It results from the instruments and measuring methods imprecision. Systematic errors should be considered by introducing a correction to the result. It can constitute a correction, a multiplier or a value listed on the table. The standard error included in the calibration certificate is a good example of systematic error.

Random error

Random error is a measurement error component which cannot be foreseen in a series of measurements. It results from different conditions (e.g. temperature changes, air movement). Lack of repeatability of a series of measurements of the same value is caused by random error (testing the repeatability of balance indications).

Control point error

It is a measuring instrument measuring error or measuring system error at certain tested value. A good example of this kind of error is balance calibration in selected testing points. In everyday use a balance is seasonally checked with a mass standard (usually after adjustment). It is also a determination of error in control point. It would be ideal when this control point coincide with the tested samples mass.

Zero indication error

It is control point error when the determined measured value equals zero. For electronic balances this error means stability of zero indication. This stability might be meaningful at long testing of the same sample. Obviously, the smaller sample size, the bigger contribution of so called 'zero indication error'. Indication of zero on the electronic balance display should not be taken for no tested value. In reality, the weighing range (0-Max) covers only a certain fragment of the balance measuring scope. It usually happens that a number of the balance reading units (Max/d) is much lower than a number of the converter reading units. Therefore, the indicated zero result 0,000 is a certain value of the balance converter reading units. This dependence is reflected in the diagram below:

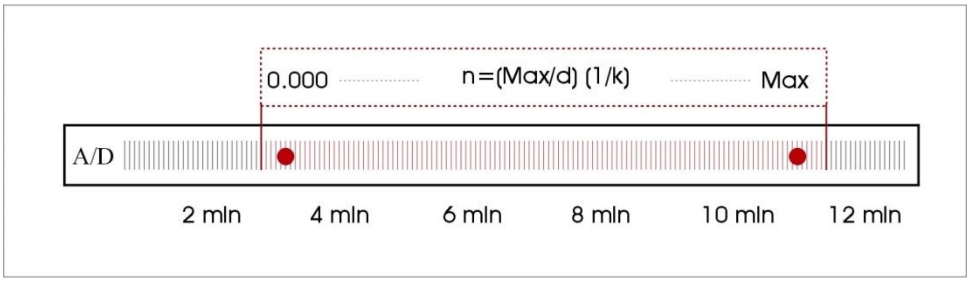


Fig. 12. Electronic balance measuring range

Errors of indication in electronic balances result from both their measuring possibilities and external conditions. The measurement methodology also matters. Therefore, all the efforts to decrease indication errors should be focused on the following fields:

- Improvement of metrological properties processes;
- Introducing new technologies, measuring methods, decreasing influence of external conditions,
- Designing and testing specific equipment connected with mass measurement processes;
- Improving the staff qualifications by trainings on measuring techniques.

Chapters concerning balances repeatability and linearity contain more information on the balances indication errors.

4.3. Mass measurement for electronic balances

Understanding of how balance works is the key in using it optimally. This information can also be essential in determination of errors which result from changeable conditions. Obviously, it is not important to focus on particular elements of the balance, but it is perceived as a measuring element working on certain conditions. We say that we weigh an object but what does it mean in practice? The key terms in metrology are [weight] and [mass].

Weight

it is the gravity force with which an object attracts another object, e.g. the Earth. Every two bodies attract each other with the force directly proportional to the product of their masses and inversely proportional to the squared distance between them (Newton's law of universal gravitation).

$$F = G \cdot \frac{m_1 \cdot m_2}{r^2} \qquad (3)$$

where: G – gravitation constant ($6{,}67428 \cdot 10^{-11}$ $m^3/kg\ s^2$)
m_1, m_2 – object masses
r – distances between the objects centres

This equation shows a simple dependence: if we assume that the mass of the Earth and the samples are constant, there will be differences in measurement results when we make the weighing in a place more distant from the Earth centre. It happens when we take the balance from the lowland to the mountains.

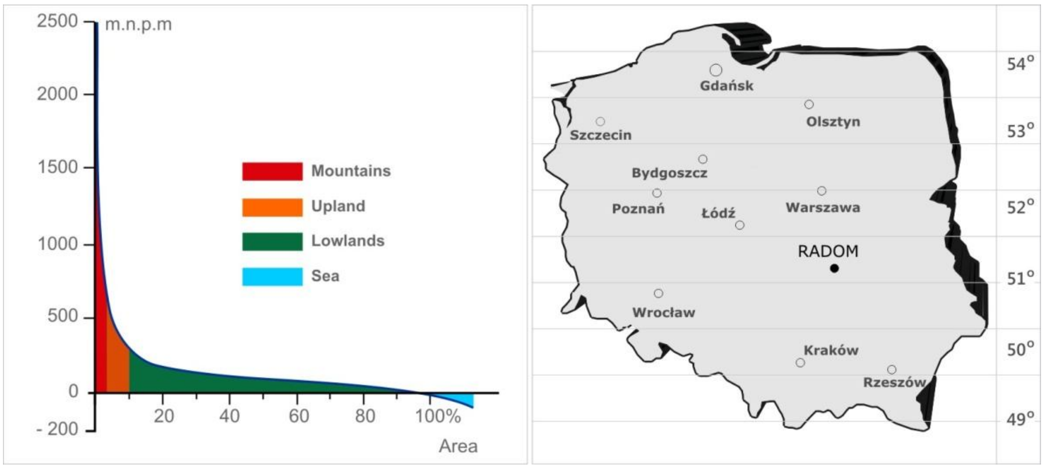


Fig. 13. Poland – the terrain shape

This is a global dependence. As a result of the Earth flattening on the poles, the same object weighs a little bit more on the poles than on the equator. The object is more distant from the Earth center on the equator, which has an influence on the object's weight. Therefore, **the weight is the force**. In order to determine the weight, you need to measure the force with which the object is attracted.

Mass

It is the measure of inertia, which is the tendency of the object to remain standstill or move with a given speed. It is colloquially understood as the amount of matter and energy concentrated in the object. The bigger mass, the more difficult it is to speed it up or change the speed. Therefore, **the object mass is constant** and it is independent on the object location; the weight is dependent on the location (the latitude and the absolute height). The mass constant is the basic characteristic of mass standards.

In the measuring systems of electronic balances the sample mass is not directly compared to the mass of the mass standard. In order to obtain the result, you need to measure indirect values like voltage, the filling level (for balances with magneto-electric conversion) or the bridge resistance change (in tensometric balances).

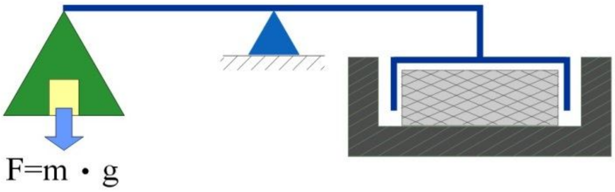


Fig. 14. A simplified diagram of magneto-electric balance

Those indirect values are then processed by electronic systems which generate the weighment result in grams or kilograms. The correctness of functioning of such systems requires the adequate scaling (adjustment). During this process a given measured quantity is 'linked' to the mass of an appropriate mass standard. During adjustment process the whole balance weighing scope is tested in order to achieve the accuracy of indications, no matter what balance scope will be used in practice. The key element of this process is to select the adequate mass standards: their maximum errors (deviation from the nominal value) should be much lower than the balance interval.

Obviously, there are a lot more weighment methods in electronic balances; but generally speaking, in order to obtain the result, you need to measure the force with which the object is attracted by the Earth first:

$$F = m \cdot g \tag{4}$$

For a mass standard 200 g we will achieve:

- According to the dependence → $F = 0{,}2\text{kg} \cdot 9{,}81\text{m/s}^2 = 1{,}962\ \text{N}$
- This is the force with which the standard is attracted by the Earth (in stable conditions we can assume that it is constant)

This force makes the measured quantity value constant in electronic balances (voltage, resistance, frequency etc.). This determined state of the measured value is defined as mass measurement and displayed as 200.0000 g. This dependency was set during factory adjustment. At this stage mass standards we use are very important.

A change of balances indication accuracy resulting from the latitude change concerns all electronic balances. This problem appears only when we move the balance from one place to another. It is eliminated by automatic adjustment, which is standard for most balances. The further part of this publication shows how it works.

Changes in gravitational acceleration depending on the latitude and the absolute height is depicted in the below diagram:

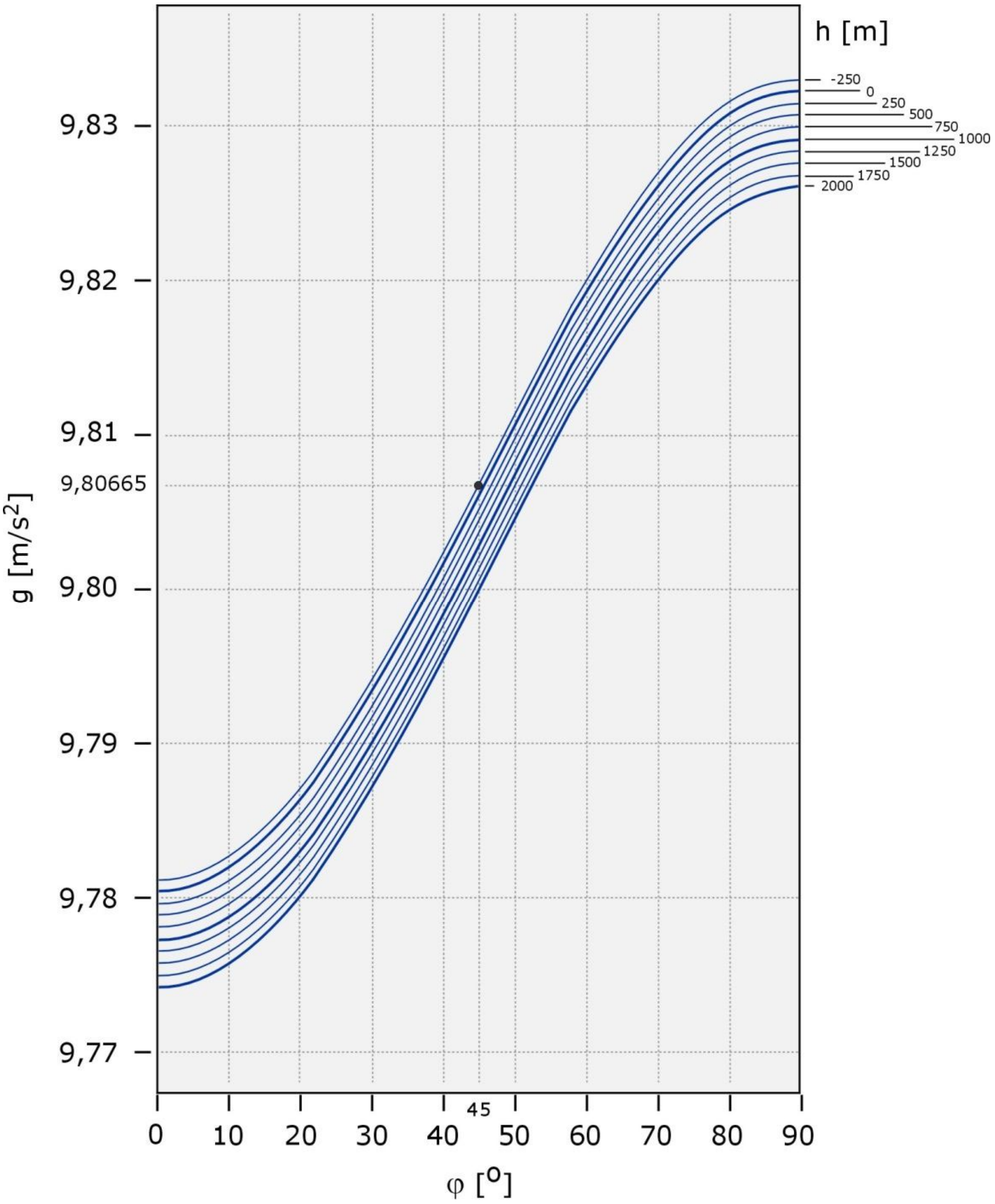


Fig. 15. Gravitational acceleration depending on the latitude and height

Conclusions:

1. Electronic balances scaling in mass units requires considering gravitational acceleration “g” in the adjustment place. It results from the balance working principle F = mg. if we assume that mass (m) is constant, gravitational acceleration is left. It is dependent on the latitude and height.
2. Changing the balance location requires another adjustment of the balance. It is connected with a change in gravitational acceleration. This dependency is true for balances with resolution at least ten thousand reading units, e.g. PS 6000/C/2 balance.

Balance parameters:

Max 6000 g
d=0,01 g
e = 0,1 g

For this reason this type and series balances have a built-up adjustment mass – the balance will carry out adjustment process itself. The balance will always be accurate, independently on the location.

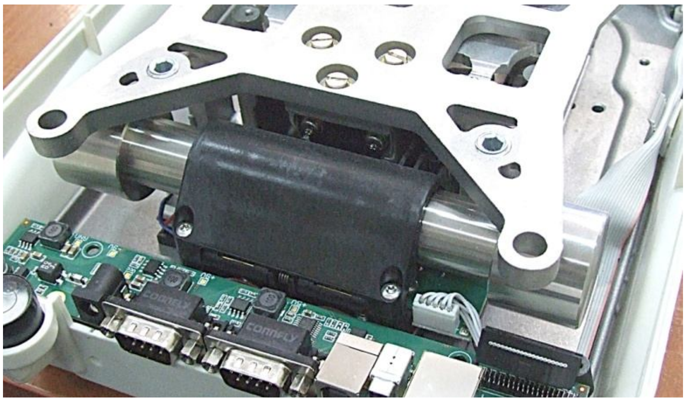


Fig. 16. PS 6000.R2 balance adjustment standard

Adjustment in different places is required even for class III accuracy balances (resolution of 3 000 e). The detailed requirements regarding balances errors depending on gravity acceleration are described in publication WELMEC 2, issue 3.3. *Gravity zones*.

3. Mass standard used during the balance scaling should be exact, namely its deviation from the nominal mass value should be the lowest possible. It is essential for balances whose accuracy is set with an external mass standard. Obviously, the mass standard characteristics might change with time (depending on exploitation). After subsequent calibration the standard error should be checked. It should not be higher than the balance reading unit.

4.4. Diagram of weighing process

During mass measuring two physical phenomena take place. One results from gravity force [F_g] – we measure the force the Earth attracts the sample mass. The other one is caused by buoyant force directed reversely to gravitation force. It can be said that the mass measurement concerns the resultant force. This force is processed into electric signal by the converter systems and displayed as the result. The converter has its own characteristics of stability in time, resistance to temperature changes etc. putting all the weighing elements together, we have a quite complicated equation presented in numerous publications:

$$R_D = \underbrace{F_{CAL}[f(1+CZT)(1+\Delta m_{cz}t)]}_{A}\ \underbrace{g}_{B}\ \underbrace{(1-\rho a/\rho)}_{C}\ \underbrace{m}_{D} + \underbrace{\delta_D+\delta_R+\delta_L+\delta_{ECC}}_{E} + \underbrace{F_{ZERO}T + CZ_{ZERO}t}_{F} \tag{5}$$

where:

R_D - indicated result

Section A*: F_{CAL} - balance calibration coefficient
f - coefficient of force converter for electric value
CZ - sensitivity temperature coefficient of force converter
T - temperature changes since the latest sensitivity adjustment
Δm_{cz} - indication of force converter sensitivity drift in time
t - time period since the latest sensitivity adjustment

** Section A is constant, results from the balance construction.*

Section B: g - gravity force in the testing place (constant)

Section C: **ρa** - air density in the testing place
ρ - the tested object density

Influence of air buoyancy on the result is insignificant. However, high resolution balances feature a function of mass correction depending on air density and the sample density. This issue is described later.

Section D: **m** - the tested load mass (the sample specific feature, usually constant)

Section E: **δ_D** - reading accuracy component (constant)
δ_R - balance repeatability component (dependent on the external conditions and the sample)
δ_L - balance non-linearity component (constant)
δ_{ECC} - non-centricity component (constant)

Section F: **F_{ZERO}** - coefficient of force converter zero point
CZ_{ZERO} - coefficient of force converter zero point drift in time function

Assuming that the balance indication is brought to zero point before the weighing, parameters connected with the balance zero point are irrelevant. The balance zero point behavior during significant temperature and humidity changes is another issue. It is described in further chapters.

It is common to simplify some issues, what makes them transparent. In case of the actual weighing model, it gets down to the below equation :

$$\mathbf{R_D = mg + \delta_{R,L}} \tag{6}$$

The weighment result is dependent on the sample mass, gravity force in the weighment place and the balance weighing capability (repeatability and linearity). Centricity error can be left out – the load is placed on the pan centre. Influence of zero drift is eliminated by indication clearing before weighing.

Another solution is turning off so called autozero function. Then you can see zero indication drifts, it is enough to correct the weighment result by zero drift. This solution is required when you slowly pour powder on the pan or for absorption and evaporation processes. When the function of keeping ‘zero’ might interfere in the result. Mass loss (or increase) should be big enough for the balance to register them. The changes dynamics of the tested object is also essential $\Delta m/\Delta t$.

The correctness of converter sensitivity is assured by automatic systems of sensitivity correction. They are commonly called the balance calibration (more adequately adjustment). Those systems register even the slightest temperature changes and time flow. However, it is also common in laboratories to carry out adjustment process manually. It is enough to press an appropriate key on the balance elevation.

4.5. When is the measurement accurate?

The answer to this basic question seems to be simple: when the result is situated within the scope of our acceptation. Practically speaking, when the maximum error is smaller than the requirements regarding the weighment. Those requirements can be included in some standardizing documents or the user’s quality system.

This simple answer implies a quite complicated issue which includes several fields: the balance characteristics, parameters stability in time, mass standards, ambient conditions, the sample specification, the weighment method, the operator’s skills and uncertainty of measurement. Pondering over this issue we need to remember that accuracy in a given measurement point can be determined only with a mass standard(a comparison of indication with a mass standard value). Several weighments of the same sample will define the measurement precision. We also need to determine uncertainty of sample mass determination. We need to achieve an accurate, precise result with uncertainty.

The measurement accuracy implies several elements. Some of them result from the balance measurement possibilities, others from e.g. ambient conditions or the sample condition. Some of the are discussed later in this publication.

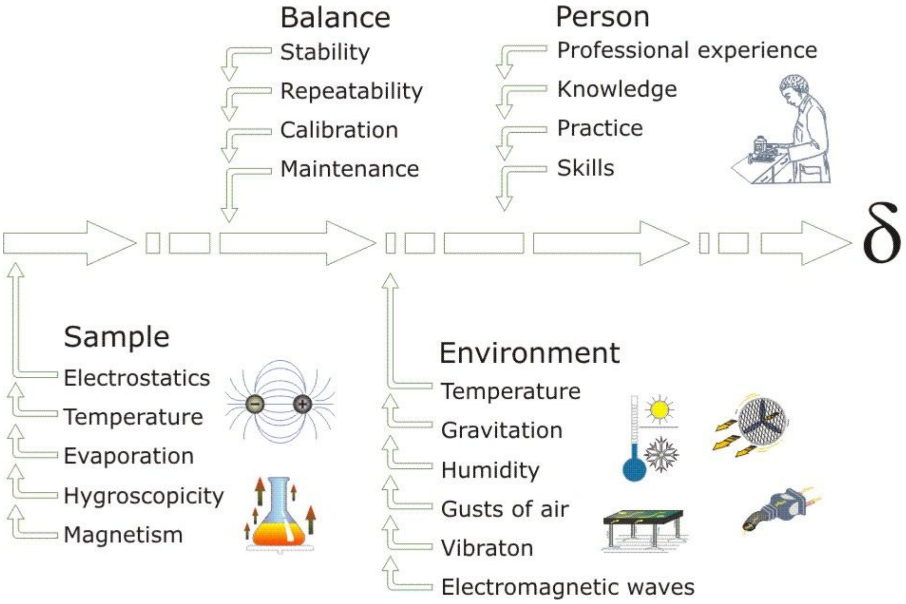


Fig. 17. Elements that have impact on the measurement error

It seems to be problematic for the operators to determine how accurate their results should be. The usual answer is: as exact as the balance indicates. Obviously, it is impossible to do, which is described later in this publication.

4.6. Selecting a balance for particular purpose

Selecting a balance for some measuring process we often follow the requirements listed in the norms. In many cases the balance description is limited to a short sentence:

analytical balance enabling weighing with 0,1 mg accuracy

This sentence is usually interpreted as: ‘balance with reading unit d=0,1 mg’. However, it is a wrong interpretation as reading unit does not define measuring accuracy of the balance. It results mainly from the measurement itself – it is never accurate. Every measuring process is afflicted with an error which comprise:

- Inaccuracy of the weighing instrument,
- The weighing method,
- Specific conditions connected with the sample

Meeting demands concerning accuracy requires a different perception of the balance as a weighing instrument. How accurate the mass can be determined depends on two parameters:

- indications repeatability
- linearity

These parameters are determined by the producer. XA 52.3Y balance parameters are listed below:

	XA 52.3Y
Max capacity	52 g
Min capacity	1 mg
Indication accuracy	0,01 mg
Tare range	-52 g
Repeatability	0,01 mg
Linearity	±0,03 mg
Non-centricity	0,03 mg
Min load (USP)	20 mg
Min load (U = 1%, k = 2)	4 mg
Pan size	ø 85 mm
Stabilization time	5 s
Sensitivity drift	1ppm/°C in temperature +15 ° - +35 °C
Working temperature	+10 ° - +40 °C
Relative air humidity	40% ÷ 80%
Calibration	Internal (automatic)

4.6.1. Repeatability of indications

Indications repeatability is defined as the measurement precision in conditions of the measurement repeatability. Practically speaking, we can talk about very high repeatability when a series of weighments of the same sample gives the same result or the differences between results are insignificant, e.g. a few reading units. The result is objective on condition that the sample mass is constant, namely there is no absorption or evaporation. Repeatability can be defined as:

- max spread between measurements or
- in terms of quantity as standard deviation in the series

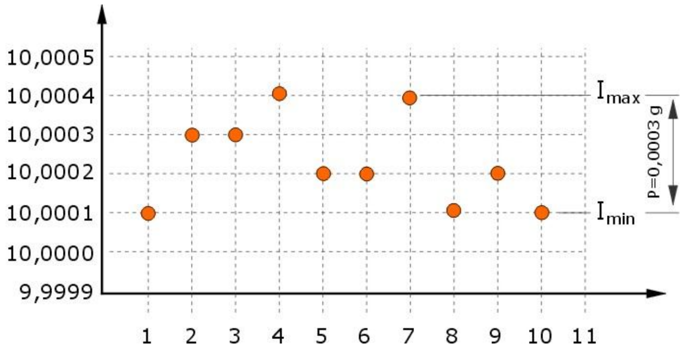


Fig. 18. Indication repeatability as a spread

Understanding this parameter as a max spread between the cycle of 10 measurements is conformable with PN-EN 45501 norm, therefore:

$$P=I_{MAX}-I_{MIN}\leq Mpe \tag{7}$$

where: I_{MAX} – max indication
I_{MIN} – min indication
Mpe – max error accepted for a given load

This way of defining repeatability is used while determining the balance errors at verification process. It can be adapted to our own procedures of balance parameters testing. Its main advantage is simplicity. Repeatability as STANDARD DEVIATION in a series of measurements is expressed in the below equation:

$$s=\sqrt{\frac{\sum_{i=1}^{n}\overline{(x_i-\overline{x})}^{2}}{n-1}} \tag{8}$$

where: s – standard deviation
xi – another measurement
$\overline{x}$ – arithmetic mean in a series of measurements
n – a number of repetitions in a series of measurements

Standard deviation provides information how wide the measurement values (in a series) are spreaded around the mean value. The smaller deviation value, the better concentration around the mean (the higher precision). It can be assumed that standard deviation shows the spread of measurements regarding one another. In a series of measurements depicted in the picture, repeatability as standard deviation equals 0,00012 g. Therefore, it is three times smaller than spread defined as I_{MAX} - I_{MIN}.

4.6.2. Repeatability – semi-automatic testing method

In case of technologically advanced balances, e.g. 3Y series RADWAG balance with a touchpad, standard deviation in a series is determined semi-automatically. We do not need to use external applications to determine this parameter.

Example:

determination of indications accuracy of XA 82/220.3Y balance at weighing a pill. The balance parameters: Max 82/220 g, d=0,01 /0, 1 mg. The balance repeatability defined as standard deviation equals 0,02 mg. This value has been determined by testing with a mass standard. Standard deviation for a sample like a pill has been determined in a series of repetitions using the SQS balance module.

XA 82/220.3Y balance features two pans. The first one is a 'regular' pan and it is recommended to use it for weighments with d=0,1 mg. For weighments with d=0,01 mg a grid pan is recommended.

It limits the influence of wind drafts on the indications, which can significantly worsen the balance repeatability. However, it is not a rule in every case. The drafts influence is meaningful in air-conditioned rooms. The situation is depicted in the below picture.

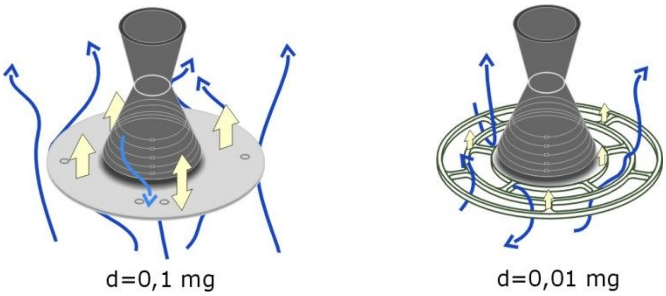


Fig. 19. The drafts influence on the pan surface

A grid pan was used in the test. An exchange of a regular pan for a grid pan one does not require any corrections in the balance accuracy scope.

N	10	a number of weighments
SUM	11,1113 g	masses sum
X	1,11113	mean value
MIN	1,11111 g	nominal value
MAX	1,11115 g	max value
D	0,00004 g	spread
SDV	0,0000118 g	standard deviation

The acquired data show that the balance repeatability of indications is following:

- 0,04 mg (spread)
- 0,012 (standard deviation)

The acquired value is smaller than declared by RADWAG. Therefore, we can say that:

- The balance works properly,
- The sample specification (shape, abrasion, absorption) does not influence the balance measurement accuracy
- Relative error of the sample mass determination is 0,0018% (see: 'Basic metrological terms in the laboratory – min capacity').

A series of measurements can be analyzed as a chart on the balance display:

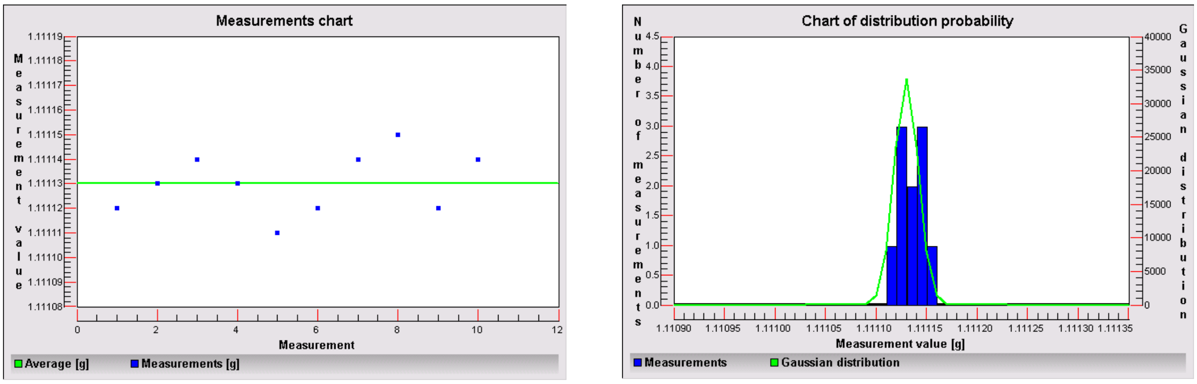


Fig. 20. Repeatability as standard deviation - a series of measurements

The value of determined standard deviation is at the same time the measurement error which can appear during weighing pills of the same mass. It is assumed that the test conditions are stable and do not influence the balance parameters. The influence of factors like linearity, centricity is missed disregarded. This assumption is justified because for such small loads linearity practically does not exist, the object has too small mass.

With the determined value of standard deviation we can define with certain probability the pill mass. The three-sigma rule is applied for the below relations:

$-3 \cdot sd \le \overline{x} \le +3 \cdot sd$ with 99,7 % probability

$-2 \cdot sd \le \overline{x} \le +2 \cdot sd$ with 95,5 % probability

$-1 \cdot sd \le \overline{x} \le +1 \cdot sd$ with 68 % probability

The below chart interprets these relations:

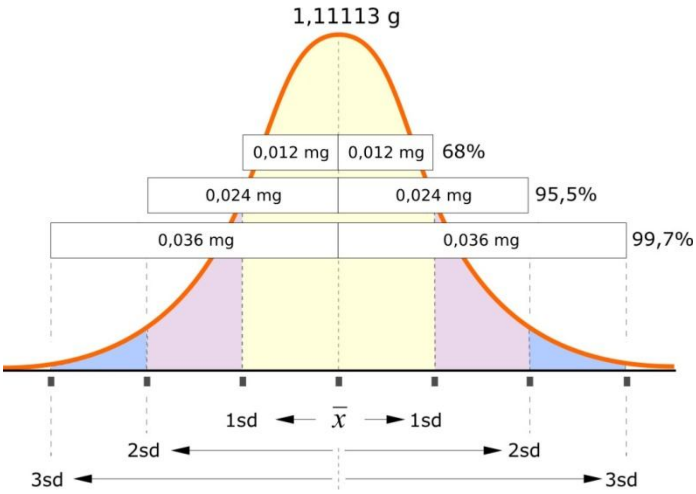


Fig. 21. Repeatability - The three-sigma rule

In this case we can safely assume with probability of 99,7% that the pill mass lies in the range 1,11113 g ±0,000036 g

4.6.3. Linearity

Linearity as a parameter describing the balance technical condition is not defined in the state system of control over a weighing instrument (VIM does not define it either).in this case we use term indication error without saying what it implies.

Balances producers define linearity as the balance real characteristics deviation from the line connecting two A-B points, which describes an ideal balance equation . In practice there are no ideal balances, therefore, no balance characteristics is a line. We rather aim at achieving this characteristics. It is hardly possible as the adjustment process itself is afflicted with errors from mass standards and the balance measuring possibilities, mainly repeatability. They are two basic parameters deciding about the balance linearity.

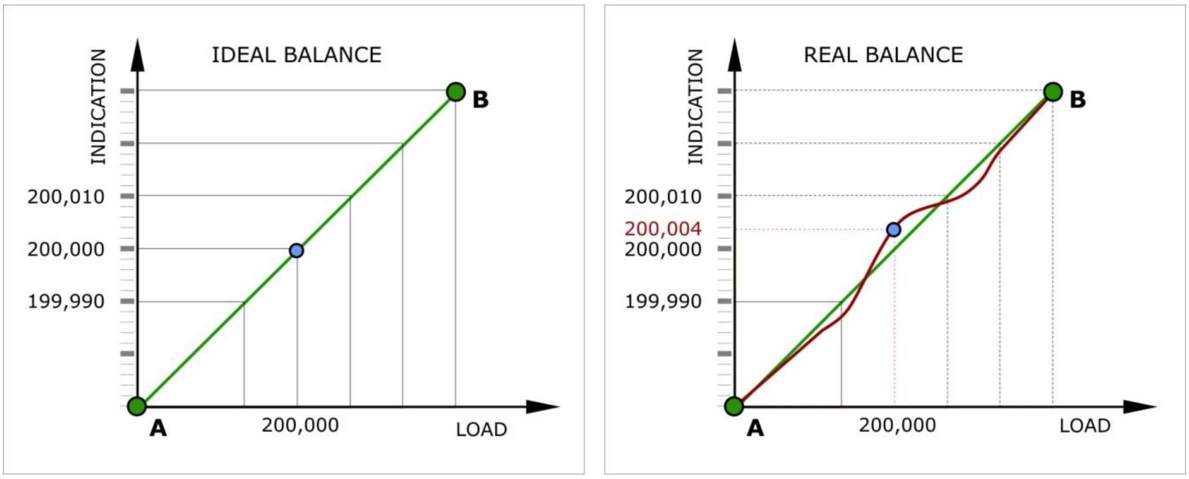


Fig. 22. Electronic balances linearity

Nonlinearity detection in the balance is a quite complicated problem, as it often coincides with repeatability. Mass standards used during the tests are meaningful here (their errors and uncertainties) as well as the used testing method.

Therefore, generally speaking, for balances with quite low resolutions and quite big reading unit value [d], it is enough to compare the result with the standard mass. This procedure can be applied for PS 1500.3Y precise balance (d=0,01 g) or AS 220/C/2 (d=0,1 mg). Another testing method should be applied for balances with reading units d < 0,1 mg. Regardless the testing method, the key condition is selecting appropriate precision class mass standards considering the reference mass standard error and uncertainty.

4.6.4. The reference mass standard parameters during linearity testing

In order to test any metrological parameter of the balance, you need to prepare the appropriate mass standards set. By their selection two aspects should be taken into consideration:

- The reference mass standard error (its nominal value deviation)
- The standard uncertainty

The nominal mass value should be corrected by the standard error.

Example:

- Nominal standard mass: 50g
- The determined mass: 50 g + 0,031 mg → 50,0000[31] g

On condition that the balance was properly adjusted, the mass standard error will be displayed when the balance reading unit is at least 0,01 mg (see the picture - AS series RADWAG balance).

For balances d > 0,01 mg, the result should be 50, 0000 g (not considering the indication repeatability error).

When different standard sets are used, their errors should be properly added. Obviously, mass standards whose error was not precisely determined should not be used. It all gets down to mathematical operations.

Regarding the standard mass determination uncertainty, it defines with 95,5% probability what its mass should be (k=2). Our mass standard 50 g was determined with 0,030 mg uncertainty. Uncertainty of determination according to the three-sigma rule is determined (±), so the standard mass can be placed within limits:

- 50,000031 – 0,030 mg = 50,000001 g
- 50,000031 + 0,030 mg = 50,000060 g

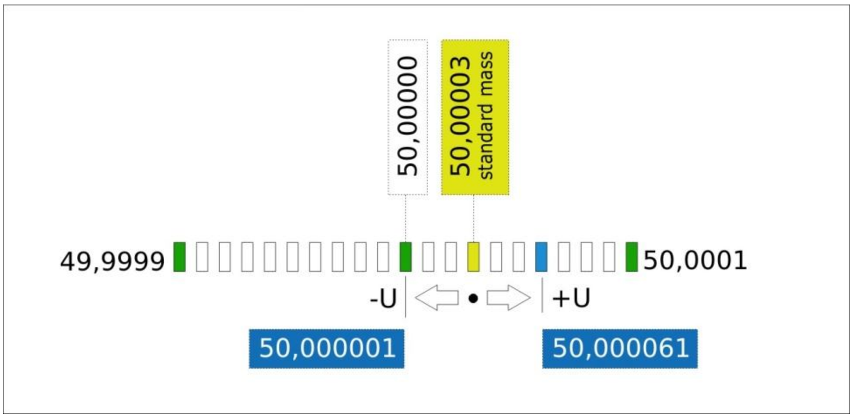


Fig. 23. Mass standard uncertainty

The best solution would be to have the mass standard with very low mass standard uncertainty (not bigger than 1/3 of balance reading unit). The acknowledged standard is relation u ≤ 1/3 MPE for a given class. For balances with reading unit d = 0,01 mg (precision class I) MPE is $_{200\ g}$ = 1,5 mg, so u_{200} ≤ 0,5 mg - 50 reading units, which is meaningful.

Low values of mass standards uncertainty depend on the Calibration Laboratory possibilities, and in details on:

- The reference used,
- The used comparators (repeatability, reading unit).

If we assume that the reference standard is of appropriate class, the key issue is to develop and improve mass comparators in order to achieve better repeatability and stability. As previously noted, uncertainty value cannot be used for the balance indication correction during testing.

Linearity testing using supplementary weights

The calibrating laboratory measuring possibilities practically determines the selection of method used at balances control. For balances with quite big reading unit we usually use the direct comparison of the result with the mass standard. A problem appears when the balance reading unit is too small (0,01 mg ÷ 0,0001 mg). In this case, the standard mass is the key to achieve the proper linearity. It gets even more complicated as we need to check the whole measuring process of the balance, which implies using the heavy mass standards. Mass determination uncertainty for them might be significant.

A method in which only one mass standard is used and the load is increased using additional supplementary weights, might be a solution. At the same time it is assumed that:

- The standard mass has been properly determined,
- Its uncertainty is low.

The described method is depicted in the below diagram:

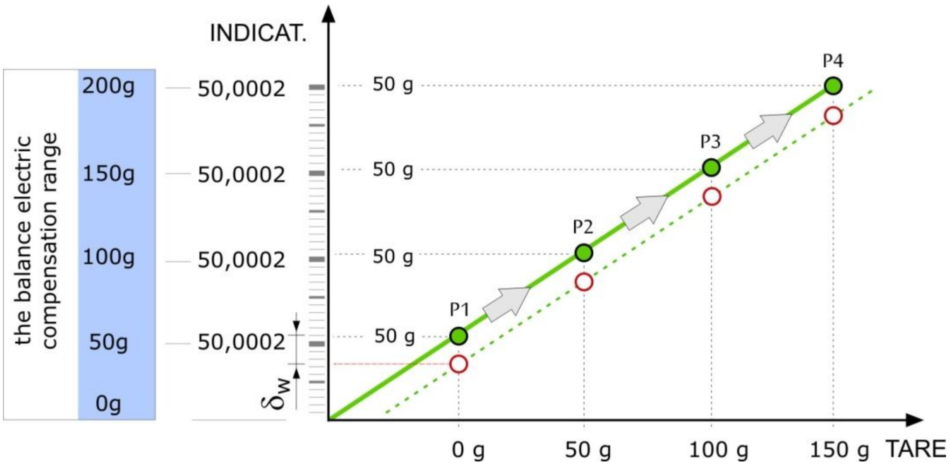


Fig. 24. Linearity testing using the supplementary

In P1 point the balance should be loaded with a mass standard 50 g, and we achieve indication e.g. 50,0002 g. Take off the standard and put the supplementary weight 50 g. When the indication is stable, clear it in order to achieve 0,000 g. Add the supplementary weight to the standard. Again we achieve 50,0002 g. Take off the standard and add another supplementary weight. Clear the achieved result. Then put the standard again etc. In this procedure we can clear the indications for supplementary weights or register them. In this case the standard weighing result should be corrected by the result we achieve for the supplementary weight.

In this way the whole weighing range can be tested (adjusted) by registering (entering)appropriate corrections. Using a lower mass standard, e.g. 20 g, allows to check linearity in a bigger number of points.

Note:

- In the whole procedure you need to consider the influence of indication repeatability in the tested range,
- The testing time should be as short as possible. Keeping quite a big load on the pan might cause its slight changes (drifts), which might be interpreted as indication error in a tested point,
- It is hardly possible to achieve linearity smaller repeatability error in a given point of weighing range.

Example:
XA 210.3Y, d = 0,01 mg balance linearity testing. The test was carried uou with the interval 20 g. The balance matrological specification:

- Max 210 g
- d=0,01 mg
- Tare range -210 g
- Linearity ± 0,1 mg
- Repeatability 0,02 mg

The balance during linearity testing in the whole measuring range.

Testing in point 20 g

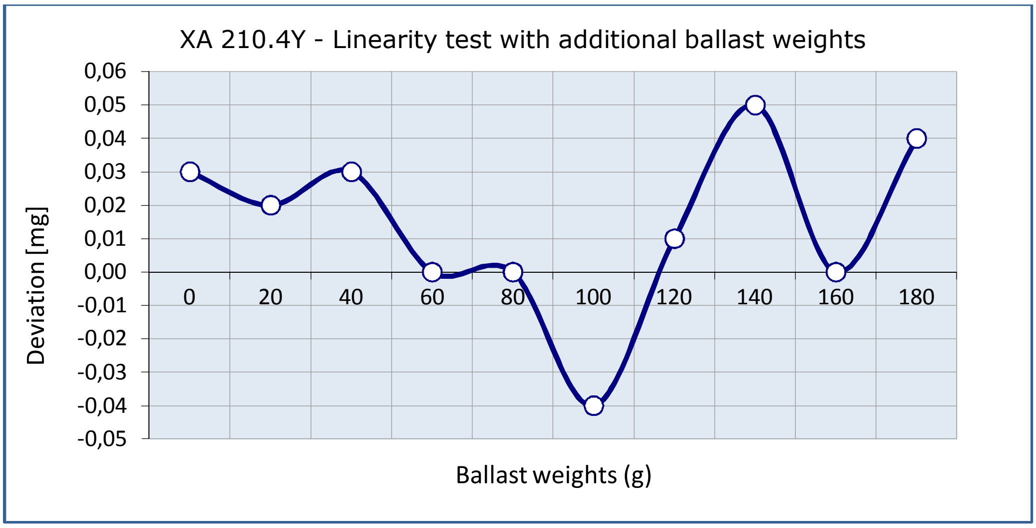
Testing in point 40g (T=20g)

Tests results:

No.	Supplementary weights	Standard mass	I_i	NL $I_{[i]} - m_{WZ}$		Producer's declaration
	[g]	[g]	[g]	[g]	[mg]	δ_{MAX}
1	0	20,00001	20,00004	0,00003	0,03	0,10 mg
2	20		20,00003	0,00002	0,02	
3	40		20,00004	0,00003	0,03	
4	60		20,00001	0,00000	0,00	
5	80		20,00001	0,00000	0,00	
6	100		19,99997	- 0,00004	- 0,04	
7	120		20,00002	0,00001	0,01	
8	140		20,00004	0,00003	0,03	
9	160		20,00001	0,00000	0,00	
10	180		20,00005	0,00004	0,04	

$E_{NL} = NL_{MAX} =$ 0,04 mg

During the test we achieved maximum nonlinearity deviation 0,01 mg. it is conformable with technical specification. Methodology for balance linearity test performed using supplementary (ballast) weights, allows to eliminate potential influence of errors of variable mass standards on indication. Only one precise 20g mass standard is used.



4.6.5. Centricity in mass measuring

Determination if a parameter is significant or not requires explanation. What is centricity error? It is deviation of indication when the load is not placed in the middle of the pan. We show differences in indication when the load is in the middle of the pan and in another place on the pan. The below charts depict the issue:

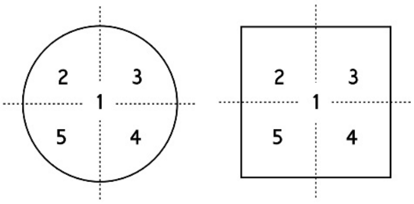


Fig. 25. The balance centricity testing points according to EURAMET

The standard position on the pan is defined by PN-EN 450501 norm in chapter 3.6.2. and A 4.7. 'Tests at noncentric load' and EURAMET/cg-18 item 5.3. „Eccentricity test".

Note: PN-EN 450501 norm defines only 4 measuring points (no measuring in the pan centre).

In practice, centricity influence on the testing might be disregarded. We owe it to the producer's efforts to monitor this parameter on the production stage as well as the laboratory practice (the load is placed on the pan centre). Majority of electronic balances do not require regulating centricity error. In RADWAG this correction takes place during the production stage and is insignificant (a few reading units. This results from the adopted rule 'quality is built in in the product' . Obviously, on the final control stage a centricity deviation is tested, and its value is listed in the final report.

Note:

It should be stressed that this parameter is tested with a mass standard of approximately 1/3 maximum capacity. Therefore, the smaller mass of a sample, the smaller centricity error. In practice, centricity testing is justified only when we weigh heavy samples. (more than ½ Max) which are placed away from the pan centre. For small mass samples this parameter is practically non-measurable (repeatability influence is dominant). Should this parameter be controlled then?

Certainly, this parameter should be checked after the balance installation. The check result will reveal if the balance transport did not distort the balance parameters. At everyday usage this parameter is constant, so the control should be regular (every several months).

Example of centricity error determination:

Equation : $E = R_{(i)} - R_{(1)}$

where: E - centricity differential error

$R_{(i)}$ - indication for another point

$R_{(1)}$ - indication for central position

$R_{(1)} = 70{,}0003$

$R_{(2)} = 70{,}0002$ $E_{(2)} = 70{,}0002 - 70{,}0003 = -0{,}0001$

$R_{(3)} = 70{,}0006$ $E_{(3)} = 70{,}0006 - 70{,}0003 = 0{,}0003$

$R_{(4)} = 70{,}0007$ $E_{(4)} = 70{,}0007 - 70{,}0003 = 0{,}0004$

$R_{(5)} = 70{,}0002$ $E_{(5)} = 70{,}0002 - 70{,}0003 = -0{,}0001$

In this case maximum centricity differential error is 0,0004 g.

Testing centricity error for XA 220/2X balance

During the test the standard mass was 100 g. It is better to use a solid sample; in case of producer’s tests, the requirements are more rigidly tested than the user would need.
The tested balance:

Measuring point no2

Measuring point no2

No	Load	Standard mass	Uncertainty	No of calibration certificate
1	100 g	100,000053	0,05mg	6536/1735/12

	Measuring point				
	1	2	3	4	5
Indication I $_{(i)}$ [g]	100,0001	100,0001	100,0001	100,0002	100,0001
$I_{CORR.}$ = I $_{(i)}$ – standard mass.	0,000047	0,000047	0,000047	0,000147	0,000047
Deviation= $I_{CORR\ (2\text{-}5)}$ - $I_{(CORR\text{-}1)}$		0,0000	0,0000	0,0001	0,0000
MPE acc. PN-EN 45501		0,0010 g			
Producer’s specification		0,0002 g			
Conformity to producer’s specification		YES			

4.6.6. Stability of sensitivity in time

It is obvious for every balance user that he will obtain the right result. Nobody wonders if a watch reading is right; the same concerns humidity or temperature reading. Why should we apply the same approach to electronic balances? Here we encounter a problem connected with resolution. It is clear in comparison with other values.

A typical balance used in the laboratory has max capacity 200 g and reading unit 0,1 mg. the sample mass determination error is usually not bigger than approximately three reading units. Referring this error to the length measuring would imply that measuring a 2 km distance we do not make a bigger error than 3 mm. How does an electronic balance ensure this level of accuracy?

The balance construction provides us with an answer. The balance has a highly stable electronic systems whose drifts in time are very low. Additionally, ambient conditions influence is checked and compensated at production stage. In this way we achieve stability and indication precision. The whole measuring range is tested with mass standards. Appropriate corrections are introduced in order to achieve a relation of indication and load.

There is also accuracy determination, which is determined by a comparison of the internal mass standard weighing result with its value. This process should be properly called adjustment (regulation); however, it is commonly called calibration. How it works is depicted below:

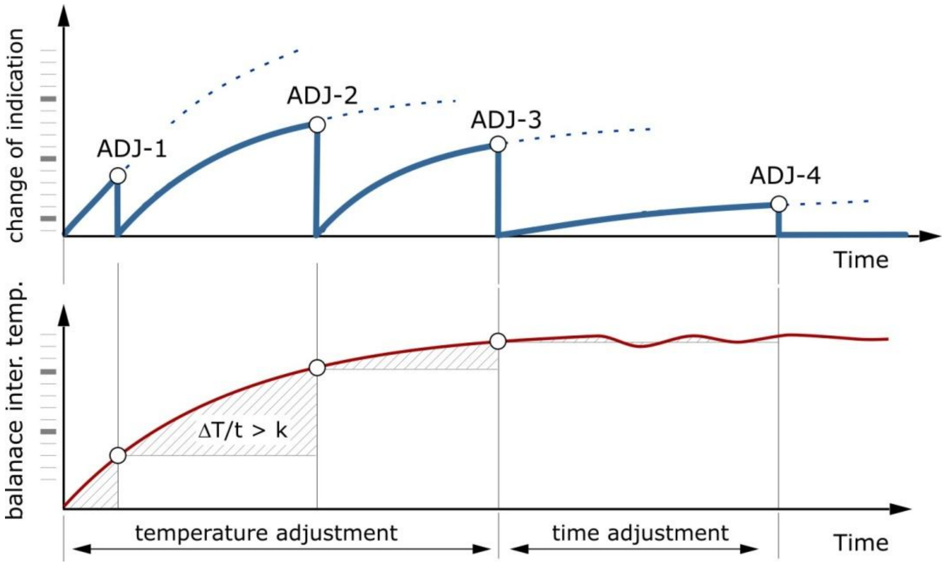


Fig. 26. Automatic adjustment (calibration)

The top diagram shows the balance indication error on turning it on. The bottom diagram shows the dynamics of internal temperature change of the balance. As electronic systems also require stability, it a slight indication error. For this reason, balances have so called start-up calibration, depicted by ADJ 1 point.

After calibration, the indication error is practically eliminated. The balance temperature is systematically monitored, so it is easy to diagnose its dynamics. This parameter is used for another calibration start-up, so called temperature calibration [ADJ 2]. It is essential in order to eliminate the dynamic indication error. The same mechanism is used during the further temperature changes.

Coefficient *k* is an experimentally selected value, characteristic of a given balance series.

When we achieve the balance thermal stability ΔT/t < k, a calibration mechanism in time period starts [ADJ 4]. It eliminates errors resulting from slight drifts of the balance measuring systems. The described solution is fully automatic ensuring indication accuracy in any moment.

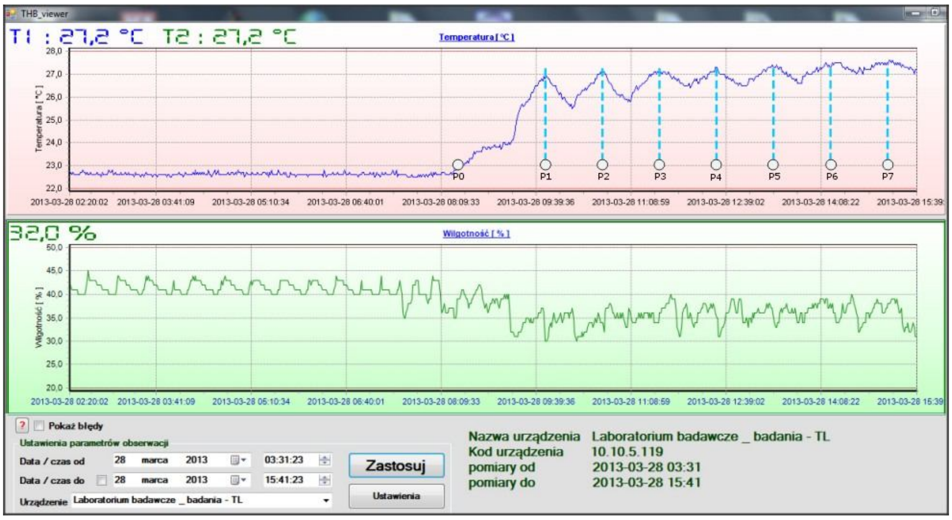
Preparing for the measurements it is a good idea to carry out a semi-automatic adjustment by pressing a button. Also, the dynamic temperature change is essential (ΔT/t). This condition will be a source of an error for some balances while for others it will be irrelevant. The below hint might be helpful:

The smaller value of reading unit, the bigger balance susceptibility to humidity and temperature changes

Note:

Using the balance in changeable ambient conditions does not have to cause significant indication errors. Whether they appear or not depends on the balance resistance. For the key products RADWAG carries out a series of tests of resistance to dynamic temperature changes. The achieved data help us to improve our products.

Balances are placed in the temperature chamber and their reference repeatability is tested. Later the temperature is changed systematically testing repeatability of indications of every balance [P1 - P7]. The ambient conditions changeability is depicted below:



☐ Pokaż błędy

Ustawienia parametrów obserwacji

Data / czas od 28 marca 2013 03:31:23

Data / czas do ☐ 28 marca 2013 15:41:23

Urządzenie Laboratorium badawcze _ badania - TL

Nazwa urządzenia Laboratorium badawcze _ badania - TL
Kod urządzenia 10.10.5.119
pomiary od 2013-03-28 03:31
pomiary do 2013-03-28 15:41

Fig. 27. The ambient conditions monitoring – THB module by RADWAG

5. Measuring system analysis (MSA)

Obtaining the optimal results while measuring requires the familiarity with the balance measuring possibilities. We do not aim at a deep analysis of every possible parameter, but only the most essential ones. Therefore, our activities should be initially analyzed (as suggested) and planned. At the beginning we might find it problematic what expectations exactly we have concerning the balance. It is easiest to say that as precise as the specification says. Meeting this requirement is not as easy as it seems. Every place has different conditions, changes dynamics, we have different skills, and differently interpret the balance behavior. Therefore, it is worth thinking what is the optimal measuring accuracy for our samples. To start with, we know that the mass measurement is afflicted with repeatability and linearity error.

5.1. MSA for mass measurement

Determination of mass for some object is one of the simplest activities. We place a sample on the pan and read the result which is intuitively accepted as true. How should we analyze this process? We should start from the beginning, namely with validation. And what is validation?

Validation is an action of a proved confirmation conformable with the Good Manufacturing Practice that the procedures, processes, instruments, materials activities and systems will produce the planned results. What do we achieve after the balance validation?

We achieve an objective evaluation that the measuring errors will be within the determined limits. We might also check requirements concerning functionality, ergonomics or speed. The following processes called qualifications are contained in the validation structure:

- Project qualification (DQ)
- Installation qualification (IQ)
- Operational qualification (OQ)
- Process qualification (PQ)

The validation process is quite precisely determined by the Validation Policy, Documentation and Qualification process. The basic requirements in this range are listed in the Minister of Health Regulation of 1st October 2008 ‘Regarding the requirements of the Good Manufacturing Practice’ Journal of Laws [Dz. U.] of 17th October 2008.

Our analysis of measuring system might fall into certain elements. Let us assume that we have covered the first two stages: the balance has been selected (DQ) and installed on the workplace (IQ). Now we have two paths to follow: the longer one is the analysis and control of all balance parameters, regardless of the range required on the workplace. This analysis usually includes accuracy testing for the net and gross masses, repeatability and linearity. These parameters have been already described.

Another approach is the analysis of only essential parameters. It implies weighing only small masses e.g. a filter mass measurement at pollination level testing. The key parameters in this case is the balance indication repeatability; other parameters are irrelevant.

Independently on the analyzed parameters we should determine the checking method and acceptation criteria. Most procedures use widely known legal requirements (PN-EN 45501, OIML R 76-1). Their advantage is their popularity and the fact that the balances are assessed according to them during verification (conformity assessment). It results mainly from those errors spread. In everyday use they can be twice as big as during verification (conformity assessment). These errors specification are listed in chapter ‘Acceptation Criteria’.

It is hard to imagine that for a 2 g sample weighed on the balance with reading unit d = 0,1 mg we accept the indication error 1 mg. Here the legal system (the state control) collides with requirements in laboratory processes. It is not only quality, but economic level (the sample assessment). The described discrepancy is clear for microbalances with reading unit d = 1 µg.

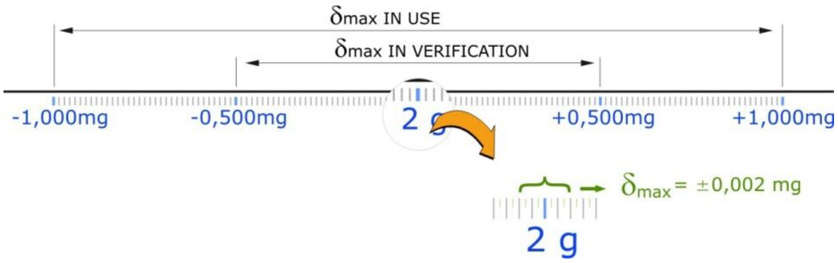


Fig. 28. Electronic balances errors according to the law

For those balances the law admits MPE 1 mg; in practice we can expect a 0,002 mg error. Therefore, it is important to use measuring methods, but the errors range needs to be defined taking into consideration our own requirements.

5.2. MSA for moisture determination

At least double mass weighment is the basis for moisture determination. The first stage is the initial mass of a sample, the other one is the final mass. What is happening between the stages is irrelevant. The sample can be heated in many ways. The moisture analyzer constantly measures the sample mass when it is being heated. We are not going to focus on the process itself, but on the methods of checking if the moisture analyzer works properly.

MSA in case of moisture analyzers should include two stages. The first one is mass measurement: it is a simple stage and implies determination of following parameters:

- Repeatability
- Linearity
- Centricity

We obviously use here the mass standards with determined errors. The results analysis will provide us with information about maximum errors during weighing samples. What we achieve is practically irrelevant for moisture determination. Why?

Moisture analyzers do not have high resolution, therefore, their linearity is ideal. The only error of sample mass measurement will result from ad of repeatability. We can expect the spread of several reading units (2- 3 d). It does not matter if we determine moisture with initial mass of 2,997 g or 2,995 g. So should we check these parameters?

The answer to this question depends on how the moisture analyzer is used. This device is used also for the mass determination, but the scope of its application is limited (the chamber size, coating density, etc.).

The moisture analyzer accuracy after the Mass measurement error in the first adjustment with an external mass standard stage. In case of stability in time you need to:

- Take into consideration the fact that the moisture analyzer is adjusted with an external mass standard;
- All measurements should be done after adjustment: in this way we eliminate the drifts.

The MSA issue is a little bit more complicated for moisture determination as there are a few fields where it is necessary:

- To determine stability of drying temperature
  The test requires using the external controlling thermometer with a valid calibration certificate. The test implies determination of a difference between the target temperature and control temperature after stabilization period. In case of moisture analyzers MA 3Y series or MAC/MAX (produced since June 2013), this test can be registered and printed out. An example below:

```
----------------- Drying chamber test -----------------
User                    service
Start-up time           2013.06.04 12:09:16
Balance type            MA 3Y.NP
Balance ID              392675
Calibration kit no      PT-105
Target temperature      120 °C
Final temperature       120 °C
Measured temperature         121 °C
MPE                     +/- 3 °C
Status                  OK
________________________________________________________
```

Here we can ask: how does the changing temperature influence the sample moisture determination result? There is no simple answer. It is generally accepted that the drying temperature drift of 2^oC does not influence this result.

- To determine the moisture determination accuracy of the moisture analyzer
  This stage implies testing moisture of a sample with repeatable parameters. The simplest method used in metrological institutes (Belarus, Ukraine, Russia) is to dry distilled water with high-silica sand of constant grammage. By mixing water and sand in appropriate proportions it is possible to achieve moisture of several up to several dozen percent. This procedure is time consuming so the producer's declaration should be enough.
  Another solution are so called zeolites, i.e. samples of known humidity. The test consists in drying of a particular sample in specified temperature, wherein the obtained result is corrected by particular value, dependent on humidity and ambient temperature. Humidity of the reference sample is not "accurately" specified, its value is comprised within 1-1.5 % tolerance range. This implies that the method does not guarantee precise determination of humidity value. This test mostly serves to prove that all moisture analyzer mechanisms are valid.

- To determine the moisture determination accuracy for our own needs
  Two stages. First of all, use reference method in order to determine the sample moisture. Next, optimize the moisture analyzer parameters, namely select the drying temperature, the sample size and the finishing mode so that to obtain a similar result. A difference between the reference result and the moisture analyzer result will provide us with the accuracy of moisture determination. Some samples tend to provide spread of humidity value, even for reference method tests.

- Determine indication changeability
  When the optimization process is finished, we carry out moisture determination of a series of samples taken from the same place. There is a spread of indications around the real (reference) value. This parameter might be linked to the previous stage.

And what about the sample stability in time? On condition that the air humidity is around 30% - 50% we can expect that the sample will absorb humidity. The issue of the sample preparation, storing and stabilization is the key. The obtained result might be afflicted with additional errors resulting from the whole process run.

Note:
The measuring system analysis of the moisture analyzer is the first and most important stage for validation of drying methods. Universality of moisture analyzers application should encourage this kind of activities, especially that they are supported by the producer, at least in case of RADWAG.

It is worth mentioning that the validation idea was thought up in order not to hinder the technical progress. The progress implies not only building and construction, but also the method. Why don't we use them especially when we can obtain the same results as in the reference method.

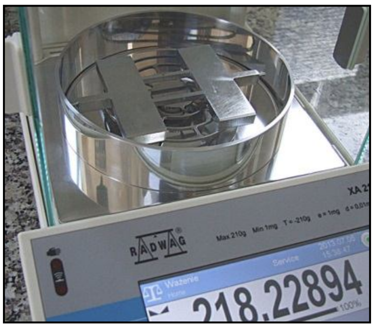
6. Mass standards vs. weights

There are two basic differences between mass standards and weights.

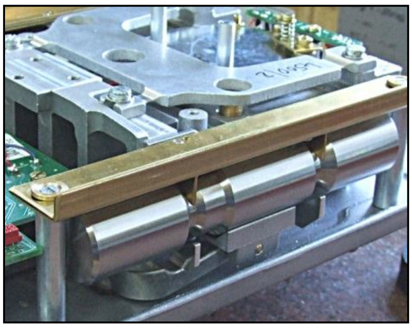
1. **The weights mass is determined with certain tolerance; mass standards might have any mass. Therefore, any element of constant mass parameter might be a mass standard.**

2. **The weights have a determined size, mass standards might adopt any size. It depends on their purpose. This applies to electronic balances. The internal adjustment mass is shaped in order to fit the balance construction, which is pictured below:**

weights as mass standards



determination of standard mass (AS balances, produced for 11.2014)



mass standard installed inside the balance PS (produced for 11.2014)

So every weight might be a mass standard, but not every mass standard might be a weight. A mass standard might have any mass, e.g. 95,7654 g. No particular error is determined for this mass, but uncertainty of this mass determination.

Adjustment or testing particular parameters requires proper weights (mass standards). They are afflicted with MPE marked as δm (e.g. 20 g ± 0,8 mg). requirements concerning the weights are also listed in some standardizing documents, e.g.

PN-EN 45501, issue 3.7.1. Weights:
Mass standard error (weight) used for verification should not be bigger than 1/3 of MPE for a given load.

OIML R 111-1, issue 5.2. Extended uncertainty
For every weight extended uncertainty U for k=2 of conventional mass should be smaller or equal 1/3 of MPE:

$$U \leq 1/3\ \delta m$$

Below you will find a set of requirements for several weights in accuracy classes acc. to OIML R111-1. It is important to add that not only MPE of a weight but also uncertainty of its mass determination decides which class it belongs to.

Nominal value	**E 1**	**E 2**	**F 1**	**F 2**
	MPE δm			
200 mg	± 0,006 mg	± 0,02 mg	± 0,06 mg	± 0,2 mg
2 g	± 0,012 mg	± 0,04 mg	± 0,12 mg	± 0,4 mg
20 g	± 0,025 mg	± 0,08 mg	± 0,25 mg	± 0,8 mg
200 g	± 0,1 mg	± 0,3 mg	± 1 mg	± 3 mg

[d] balance	Mass standards application range			
0,001 mg	o	☒	☒	☒
0,01 mg	o	o	☒	☒
0,1 mg	o	o	o	☒
1 mg	o	o	o	o

7. Air density in mass determination

When we think about the buoyancy force, we usually have in mind its effect in water. It is natural, everyone has seen this phenomenon. The density of air is much lower than water, so we do not feel the buoyancy force. It has some influence on weighing the samples of different density. Later in this publication we will focus on the possibilities of the buoyancy force influence compensation by using two methods. The first one uses mass standards, the other one – electronic sensors.

It is important to remember that mass measurement by electronic balances implies the determination of force with which an object is attracted by the Earth. This relation can be expressed as:

$$F_G = m \cdot g \qquad (9)$$

Where : F_G – gravity force [N]
m – an object mass [g]
g – gravitational acceleration [ok. 9,81 m/s^2]

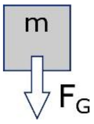


Fig. 29. Gravity force in weighing

The process of obtaining the result of weighment is briefly discussed while focusing on the measuring systems (issue 4.1.)

7.1. Buoyancy force

Buoyancy force is a force that act on any body immersed in a liquid or gas and acts against gravity. It is equal to the weight force of the displaced liquid.

$$F_w = \rho \cdot g \cdot V \qquad (10)$$

where: *ρ* – density of the liquid or gas
g – gravity force
V – volume of the liquid which equals the volume of a part of the body immersed in it

In case of electronic balances the force system in a weighing process is following:

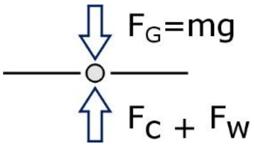


Fig. 30. The force system in a weighing process

where: F_G – gravity force
F_C – force balancing gravity force
F_W – buoyancy

Analyzing this force system we can say that the gravity force is constant in a given workplace. The balancing force is the balance reaction to the gravity force, so it is constant too. The only variable which should be taken into consideration for balances of high resolutions is the buoyancy force.

This requirement results from the fact that the buoyancy force depends on the air density. Density depends on temperature, pressure and humidity.

Correcting the obtained result by the buoyancy force, we achieve the real mass of a sample, like during weighing in vacuum. It is possible to analyze drifts of mass in time, e.g. differential weighing, eliminating an error resulting from the buoyancy force variable. It is essential as the measurement is done with high resolution e.g. 200 g x 10 µg ÷ 2g x 0,1 µg.

It is obviously assumed that the weighing process is carried out accurately, namely: the smaller sample mass, the bigger balance accuracy. In practice, this procedure is applied to calibration of the state mass standards and the highest accuracy class mass standards.

7.2. Estimation of errors resulting from the buoyancy force

A variable of the buoyancy force during measurements might influence the indication error. The value of this error depends not only on the buoyancy force, but also on the sample density and mass. The balances are factory adjusted by means of steel mass standards of density 8000 kg/m^3. Therefore:

- Measurement of samples mass of similar density will almost always be correct,
- For samples of lower density 500 – 4000 kg/m^3 error resulting from air density changes might be significant.

In order to correct to influence of the buoyancy force on the weighing process, it is necessary to determine two parameters. One is the air density, the other is the tested sample density.

Below you will find air density determination equation :

$$\rho_a = \frac{0,348444 \cdot p - h(0,00252 \cdot t - 0,020582)}{273,15 + t} \tag{11}$$

where:
ρ_a – air density [kg/m^3]
p – atmospheric pressure (600 hPa $\le$ p $\le$ 1100 hPa)
h – air density (20% $\le$ h $\le$ 80%)
t – air temperature (15°C $\le$ t $\le$ 27 $^{\circ}$C)

In order to determine the mass correctly (corrected by the buoyancy force), you need to multiply the weighing result by a coefficient following the below equation :

$$m_c = m \cdot \frac{1 - \frac{\rho_0}{\rho}}{1 - \frac{\rho_0}{\rho_c}} \qquad (12)$$

where: m_c – sample mass

ρ_0 – gęstość powietrza [kg/m^3]

ρ – density of mass sample used for the balance adjustment [8000kg/m^3]

ρ_c – density of the tested sample [kg/m^3]

m – the weighment result indicated by the balance

Example:
Atmospheric pressure 996 hPa, humidity 45 %, temperature 25 °C, sample: leather piece of density 860 kg/m^3 and mass m_1=80 g
Air density determination:

$$\rho_a = \frac{0{,}348444 \cdot 996 - 45 \cdot (0{,}00252 \cdot 25 - 0{,}020582)}{273{,}15 + 25} = 1{,}1576 kg/m^3$$

Determination of the real sample mass m_2:

$$m_2 = \frac{1 - \frac{1{,}1576\text{kg/m}^3}{8000\text{kg/m}^3}}{1 - \frac{1{,}1576\text{kg/m}^3}{860\text{kg/m}^3}} \cdot 80g = 80{,}096238g$$

The real mass of the sample, namely the mass in the vacuum equals 80,096238g. In practice it means that the buoyancy force contribution to this weighing process is following:

$$m_2 - m_1 = 80{,}096238 \text{ g} - 80 \text{ g} = 0{,}096238 \text{ g}$$

Measuring of sample mass in the vacuum is hardly ever carried out in laboratory practice because of lack of proper equipment. Therefore, it is justified to use a coefficient balancing the buoyancy force, which is a much simpler solution.

In RADWAG 3Y series balances all the calculations are done automatically. In fact, the only value to enter is the sample density.

7.3. Practical aspects of correction of the buoyancy force influence on the measurement result.

A coefficient correcting the influence of the buoyancy force on mass measurement is necessary when:

- The real mass of a sample is required. It might be significant when the same sample is weighed several times in large time intervals;
- The sample mass changes in a long time period.

The influence of air density variable on the result might be significant in this case. In order to eliminate it, we need to know how changing of air density influences the measurement. The value of error that might appear when the sample is weighed several times in some time intervals depends on:

- Changes of air density in time;
- A difference between the density (8000 kg/m^3) of mass sample which adjusts the balance and the sample density.

Assuming that a typical air pressure change is approximately 30 hPa, and the room temperature and humidity are constant, it is possible to determine the mass changes of practically any sample. This procedure is justified when we register the sample mass with high accuracy. Below you will find the diagrams showing the air pressure drift in a shorter and longer time period:

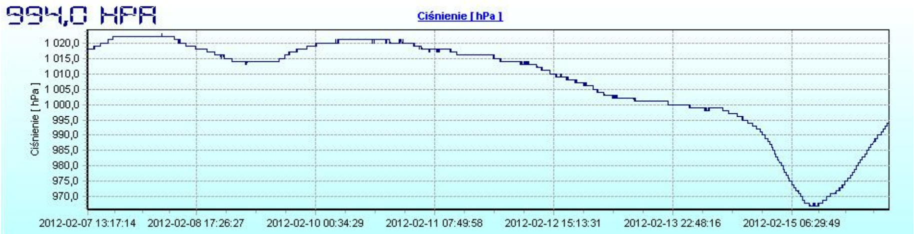


Fig. 31. Registering changes in air pressure between 7th and 15th February 2012

The total change of air pressure in this time period was 55 hPa, and between 13th and 15th February it changed by 35 hPa.

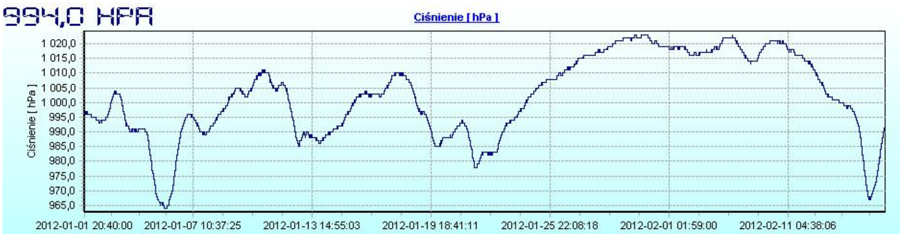


Fig. 31-1. Registering changes in air pressure between 1st January and 16th February 2012

Registering changes in air pressure in a longer time period (47 days) shows that this coefficient is highly changeable. It should be taken into consideration when we test the same sample mass in a long time period.

7.4. The buoyancy force value while weighing materials of different density

The error resulting from the buoyancy force influence on the weighing process can be determined if we assume that all parameters in relative conditions are constant. A difference between the mass indicated by the balance and the mass corrected by the buoyancy force will depend on the load volume (its mass). If we assume that air pressure is 1013 hPa, temperature = 20°C, humidity = 40%, we will obtain the following values for the tested materials:

Sample mass	**Wood** 800 kg/m^3	**Water** 1000 kg/m^3	**Rubber** 1600 kg/m^3	**Chalk** 2000 kg/m^3	**Tantalum** 16600 kg/m^3
	Deviation from the real value [mg]				
0,001 g	0,001	0,001	0,000	0,000	0,000
0,01 g	0,013	0,010	0,006	0,003	0,000
0,1 g	0,135	0,105	0,060	0,033	- 0,008
1 g	1,352	1,051	0,600	0,330	- 0,078
10 g	13,520	10,513	6,005	3,302	- 0,777
20 g	27,041	21,025	12,009	6,603	- 1,554
40 g	54,081	42,051	24,018	13,206	- 3,109
60 g	81,122	63,076	36,027	19,810	- 4,663
80 g	108,163	84,101	48,036	26,413	- 6,217
100 g	135,203	105,127	60,045	33,016	- 7,772

The data presented in the above table show the following relations:

- The smaller sample density, the bigger deviation from the real value;
- The smaller sample mass with a determined density, the smaller deviation from the real value.

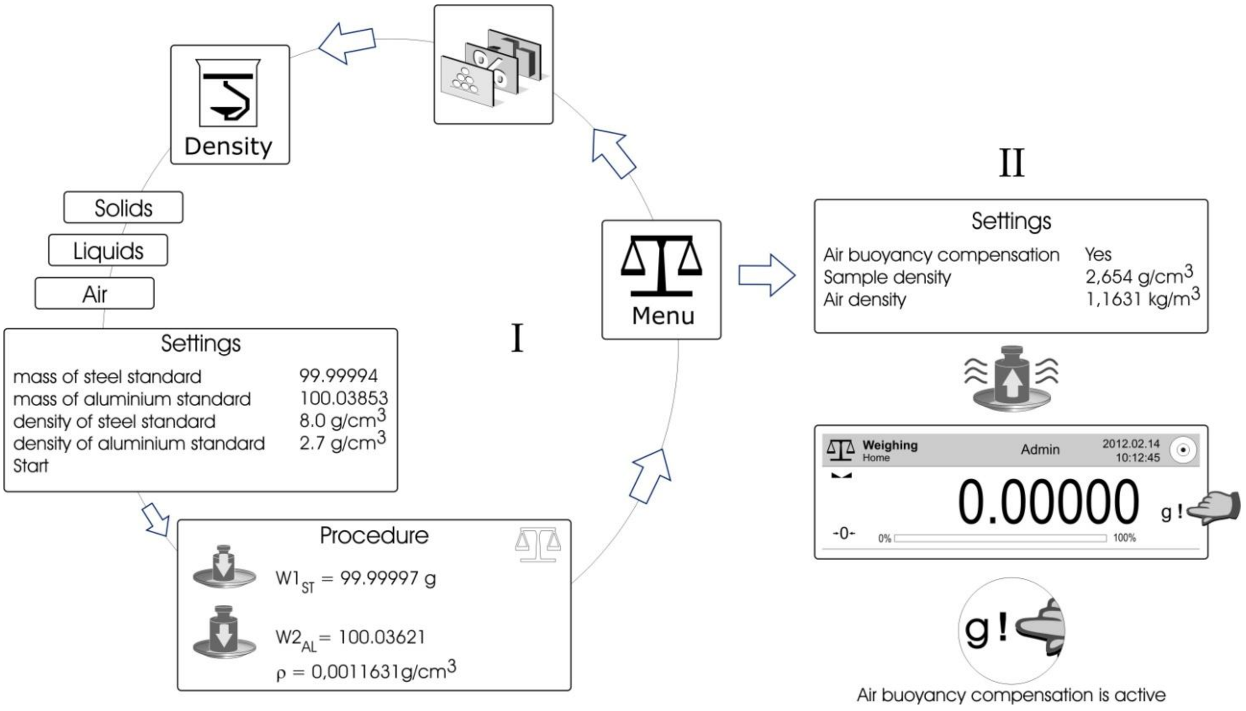
The real value in this case is obtained by weighing in the vacuum (without the buoyancy influence)

7.5. The methods of the buoyancy force correction used in RADWAG balances

The buoyancy force correction function requires information concerning the updated air density and the tested sample density. On the basis of this data we determine a corrective coefficient. During the measurement only the gravity force plays a meaningful role. In 3Y series balances RADWAG uses two methods of the buoyancy force correction. The next chapters focus on how it works.

7.5.1. Method 1: a semi-automatic method using mass standards

It is a two-stage method in which it is necessary to determine air density by weighing two standards (steel and aluminium) of the same mass but different density. The below diagram shows how it works:



Settings

mass of steel standard 99.99994
mass of aluminium standard 100.03853
density of steel standard 8.0 g/cm^3
density of aluminium standard 2.7 g/cm^3
Start

Procedure

$W1_{ST}$ = 99.99997 g
$W2_{AL}$ = 100.03621
ρ = 0,0011631g/cm^3

Settings

Air buoyancy compensation Yes
Sample density 2,654 g/cm^3
Air density 1,1631 kg/m^3

Fig. 33. Activities in method 1.

This method comprises of three basic elements which can influence the inaccuracy. The first one concerns the standards mass and density. Both parameters are listed in the calibration certificate. A more detailed analysis would imply testing how the uncertainties of these parameters determination influence the weighing result.

Mass standards kit for air density determination
(1)- aluminium standard, (2) - steel standard

The second element is weighing the two standards masses. Assuming that the balance sensitivity is constant, the only meaningful parameter is the balance indication repeatability. Air density is calculated according to the below equation :

$$\rho_a = \frac{m_{AL} \cdot W_{ST} - m_{ST} \cdot W_{AL}}{\frac{m_{AL} \cdot W_{ST}}{\rho_{AL}} - \frac{m_{ST} \cdot W_{AL}}{\rho_{ST}}} \tag{13}$$

where:

m_{AL} – corrected mass of *aluminium mass standard*
m_{ST} – corrected mass of *steel mass standard*
W_{ST} – *steel mass standard weighing result*
W_{AL} – *aluminium mass standard weighing result*
ρ_{AL} – *aluminium mass standard density* (2.7 g/cm^3)
ρ_{ST} – *steel mass standard density* (8.0 g/cm^3)

The corrected mass of aluminium and steel mass standards is determined using the below equation s:

$$m_{ST} = M_{ST} \cdot \frac{1 - \frac{1{,}2kg/m^3}{8000kg/m^3}}{1 - \frac{1{,}2kg/m^3}{\rho_{ST}}} \qquad m_{AL} = M_{AL} \cdot \frac{1 - \frac{1{,}2kg/m^3}{8000kg/m^3}}{1 - \frac{1{,}2kg/m^3}{\rho_{AL}}} \tag{14}$$

where: M_{ST} – steel mass reference weighing result
M_{AL} – aluminium mass reference weighing result

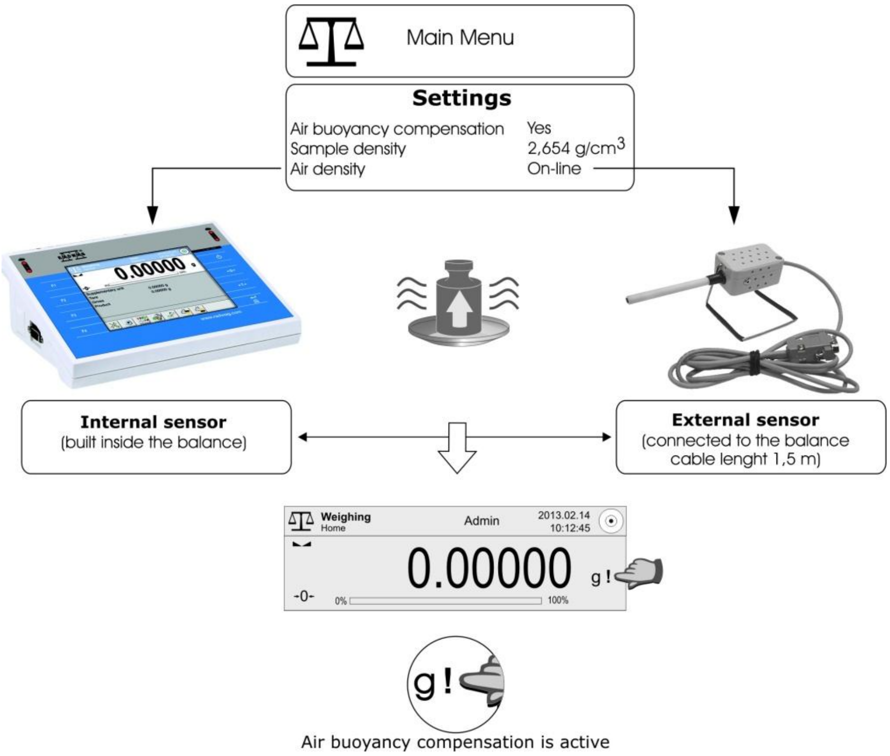
We can assume that in ideal conditions the reference mass weighing result equals the reference mass. The third element implies using the determined air density in the buoyancy correction function. On this stage the values are only calculated, so a potential error should be excluded. The density determination analysis might produce a conclusion that the weighing process which decides about the method accuracy is the key element.

7.5.2. Method 2: automatic method using the sensors

The technical solution used in this method is a novelty in laboratory balances construction. RADWAG as the first balance manufacturer used the electronic measurement of pressure by sensors integrated with the balance. The only required data is the sample density; all other data connected with the ambient conditions are monitored automatically in online mode. Temperature, humidity, air pressure and density data might be:

- Sent from the sensors installed inside the balance or,
- Collected from the external THB module. The module is a mobile measuring system connected to the balance port.

The below graph shows how it works:



Settings

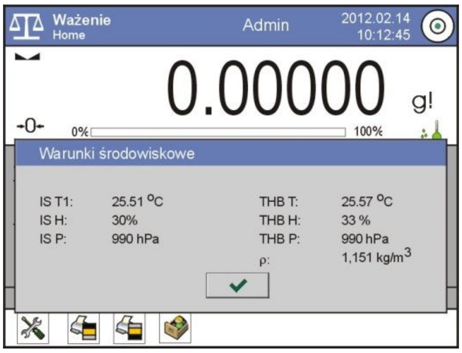
Air buoyancy compensation Yes

Sample density 2,654 g/cm^3

Air density On-line

Fig. 34. Method 2.

The environment module can support both internal and external sensors. Therefore, it might be used to measure temperature and humidity in another part of laboratory. The cable is 1,5 long. An additional advantage of the external THB module is the possibility of connecting it to the computer software. The balance display with active internal sensors and connected environment module is presented below:



Warunki środowiskowe

IS T1: 25.51 ^{o}C

IS H: 30%

IS P: 990 hPa

THB T: 25.57 ^{o}C

THB H: 33 %

THB P: 990 hPa

ρ: 1,151 kg/m^3

Fig. 35. The balance display with active environment *panel*

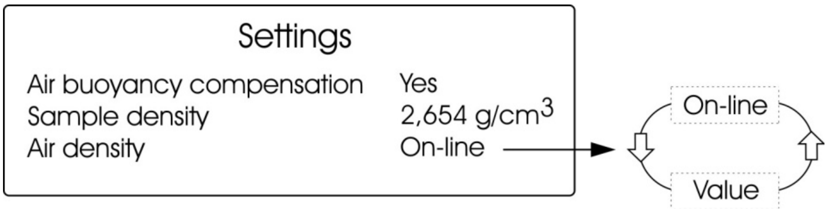
The internal sensors are marked IS, the external sensors – THB. Additional information they provide is the current air density marked as ρ.It is calculated using data from the external module. When it is not active, this information is calculated on the basis of external sensors indications.

The internal sensors are used when there are no cables, connections or additional elements. The fact that the measuring takes place inside the balance is a restriction. Taking into consideration its mobility, a possibility of usage with other 3Y series balances or the parameters measurement in the balance neighborhood, the external module seems to provide a better solution. The solution we select depends on our requirements.

The user can determine a coefficient correcting the buoyancy force after the function activation as following:

1. Enter the sample density; the balance software will calculate a correction for the air buoyancy (knowing the air density),

2. Enter the sample and air density, the software will calculate a correction for the air buoyancy. In this case the air density data might be collected from other sources (instruments, metrological stations, etc.)



Settings

Air buoyancy compensation Yes
Sample density 2,654 g/cm^3
Air density On-line

Fig. 36. The source of data for the ambient conditions collection

7.5.3. Balances with integrated environment sensors

3Y and 4Y series balances with the reading unit 0,1 mg or smaller feature internal integrated temperature, humidity and air pressure sensors. Reading pressure from the external sensors require activating the THB-2 environment sensor. It is external equipment of laboratory balances.

MYA.3Y (4Y) microbalance

Technical data

Max 2 g ÷ 21 g

d = 0,1 µg ÷ 1 µg

e = 1 mg

Interface:

2×USB, 2×RS 232, Ethernet, 2 inputs/2 outputs

XA.3Y (4Y) analytical balance

Technical data

Max 52 g ÷ 310 g

d = 0,01 mg ÷ 0,1 mg

e = 1 mg ÷ 10 mg

Interface:

2×USB, RS 232, 2 inputs/2 outputs

AS.3Y analytical balance

Technical data

Max 110 g ÷ 510 g

d = 0,1 mg

e = 10 mg

Interface:

2×USB, RS 232, Ethernet, 2 inputs/2 outputs

possibility of connecting only external sensor

7.5.4. The methods comparison

The basic difference between the methods is the way of the air density determination. Method 1 uses two mass standards to weigh. In this case the balance indication repeatability has some influence on the final result of air density reading – a double mass weighment takes place.

Method 2 uses the air pressure sensors installed inside the balance or in external modules. The air pressure data is measured electronically and processed later: we obtain the air density data. This measurement accuracy depends on the pressure sensor accuracy class. Obviously, method 2 is quicker and troublesome. You will find a more detailed comparison below:

Method 1	Method 2
Uses mass standards to determine air density	Uses internal or external sensors to determine air density
Two-staged procedure: weighing mass standards and next activation	One-stage procedure: air buoyancy compensation activation
The necessity to determine air density twice	Online work (the density verification is done every minute
The necessity to have mass standards (steel and aluminium)	Does not apply
The influence of the indication repeatability on the weighment	Does not apply
The speed (the necessity to use indirect functions - air density)	The speed (immediate use of functions)

It appears that method 2 is a better solution. It applies innovative solutions. it is less prone to the operator's errors connected with the weighment process. It eliminates a potential error of mass standards which can appear in method 2.

8. Gravimetric method of the samples density determination

Density compares different materials weight. It is a well-known fact that the bigger density, the bigger weight of a given material. Weighing samples of the same dimensions, e.g. a 1 m cube, we will obtain 8000 kg for steel, 1,3 kg for air, 1000 kg for water. Therefore, density definition is following:

Density is the ratio of the body mass to its volume in a given temperature. Density characterizes cramming the matter in a body. Density unit is kg/m^3 or g/cm^3

$$\rho = \frac{m}{V} \tag{15}$$

where: ρ – density
m – mass (commonly understood as the measure of cramming the matter in a body)
V – volume (space enclosed by a body)

For a macro scale it has a practical aspect used during transport or storing: the bigger density, the bigger mass; the bigger density, the bigger volume. In a micro scale density is one of the parameters characterizing the sample. In fact, every liquid or semi-liquid is a mixture of several ingredients of different density which are appropriately mixed. Therefore, it is necessary to test and control density of many materials regardless of their state.

8.1. Physical phenomena in density determination

Measuring density we use relations from Archimedes' Principle: the upward buoyant force that is exerted on a body immersed in a liquid, whether fully or partially submerged, is equal to the weight of the liquid that the body displaces". The sample density determination by gravimetric method comes down to weighing the sample in the air and then in liquid of determined density (usually distilled water). The body mass determination in the air is expressed in the below equation :

$$F_G = m_1 \cdot g \tag{16}$$

where: F – force that is exerted on a body
m_1 – a body mass
g – gravitational acceleration

During a body mass measurement in water, apart from gravity force there is also buoyancy force:

$$F = F_G - F_W \tag{17}$$

where: F_G – gravity force
F_W – Buoyancy force

$$F_G = m_1 \cdot g \rightarrow \rho_c \cdot V \cdot g \tag{18}$$

where: ρ_c – the body density
V – the body volume
g – gravitational acceleration

$$F_W = \rho_W \cdot V \cdot g \tag{19}$$

where: ρ_w – liquid density
V – volume of the displaced liquid equal to the volume of a part of the body emerged in the liquid
g – gravitational acceleration

This system can be graphically depicted in the following way:

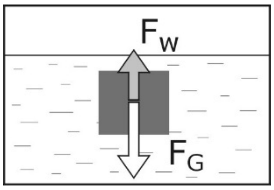


Fig. 37. Determination of a body mass in liquid

A solid body density is determined in the following equation :

$$\rho_c = \frac{m_1 \cdot \rho_w}{(m_1 - m_2)} \tag{20}$$

where: ρ_C – the body density
m_1 – the body mass weighed in the air
m_2 – the body mass weighed in the liquid
ρ_w – liquid density

A liquid density is determined in the following equation :

$$\rho_W = \frac{(m_1 - m_2)}{V} \tag{21}$$

where: V – the body volume

8.2. Weighing methods used for the body density determination

Depending on the expected accuracy and the sample size and kind, for determination of solid bodies and liquids density we use different measuring methods. The most common methods are following:

- Pycnometer method,
- Aerometric method,
- Oscillating method,
- Hydrostatic method,

Below you will find information on how they work, their advantages and restrictions.

8.2.1. Pycnometer method

It allows to determine the liquid density on the basis of comparison of the tested liquid mass with the mass of the same volume of water in the same temperature. This method also determines the solid bodies density and volume. The most commonly used pycnometers are made of glass and metal.

Glass pycnometers

It is a glass flask of determined volume [1] closed with a close-fitting glass polished stopper [2]. The cork features a capillary hole [3].

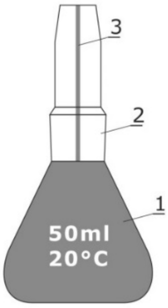


Fig. 38. Glass pycnometer

The pycnometer is slightly filled with the tested liquid, next it is tightly closed with a stopper and its temperature is controlled. Remove the redundant liquid which escapes the pycnometer through the capillary hole. Then determine the weight of the pycnometer. During the test the liquid volume contracts (its level in the capillary hole goes down). If the temperature conditions are stable and the pycnometer fully filled with liquid, this phenomenon does not matter. The liquid evaporation is minimalized with a small capillary hole diameter.

Density determination of liquids

In order to determine density of a solid body, you need to weigh a dry pycnometer. Next, fill the pycnometer with the tested liquid and after the thermal balance between the tested liquid and the surroundings is set, weigh the pycnometer with the liquid. Next, empty the pycnometer, dry up and fill with distilled water. Knowing the standard liquid density in a given temperature and its mass, you can determine its volume, and the pycnometer volume at the same time.

$$V_P = \frac{m_W}{\rho_W} \tag{22}$$

where: V_P – pycnometer volume
m_W – distilled water mass
ρ_W – distilled water volume

The liquid density is determined according to the following equation :

$$\rho_C = \rho_W \cdot \frac{m_{PC} - m_P}{m_{PW} - m_P} \tag{23}$$

where: m_P –empty and dry pycnometer mass
m_C –tested liquid mass
m_{PW} – standard liquid mass which fills the pycnometer
m_{PC} – tested liquid mass which fills the pycnometer

$$\rho_C = \frac{m_C}{V_P} = \rho_W \cdot \frac{m_C}{m_W} \tag{24}$$

$$m_C = m_{PC} - m_P$$
$$m_W = m_{PW} - m_P$$

The solid body density and volume determination

In order to determine the solid body density and volume, you need to determine the solid body mass and the mass of pycnometer with water and the solid body immersed in it. The solid body volume V^3 can be expressed by an equation :

$$V_S = \frac{m_S - m_{PWS} + m_{PW}}{\rho_W} \tag{25}$$

where: m_S – tested substance mass
m_{PWS} – mass of pycnometer with the tested substance
m_{PW} – standard liquid mass which fills the pycnometer
ρ_W – distilled water density

The tested substance density is calculated in the following equation :

$$\rho_S = \frac{m_S}{V_S} = \rho_W \cdot \frac{m_S}{m_S - m_{PWS} + m_{PW}} \tag{26}$$

The undeniable advantage of pycnometer method is a possibility to test density of powders. A little complicated formula, possibility of testing small samples, determination of apparent density are the method disadvantages.

Metal pycnometers

This type of pycnometers is widely used by production of paints, varnish, cosmetics and food in order to determine density of materials, especially liquids of low and average viscosity. Pycnometer consists of two elements: the vessel [1] of determined volume and a lid [2] with a hole for the redundant substance removal .

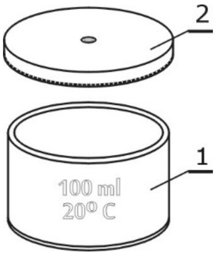


Fig. 39. Metal pycnometer

Experimental procedure:

- Determine the weight of empty, dry pycnometer and register it [m_1]
- Control temperature of the instrument and the tested substance in 20ºC ±0.5 ºC
- Fill the pycnometer with the tested substance
- Put the lid on, fitting it in the instrument corpus
- Remove the redundant substance
- Weigh the filled instrument [m_2]
- Determine density from the below equation

$$\rho = \frac{m_2 - m_1}{V} \quad (27)$$

where: ρ – body density
m_1 – empty pycnometer mass
m_2 – mass of pycnometer with the tested substance

8.2.2. Aerometric method

This method uses aerometer to determine a liquid density. It is an empty glass tube which upper part features a scale [3]. The bottom part [2] is a bulb filled with material of high density [1]. This type of construction allows the aerometer to keep vertical position during the test when it is emerged in the liquid. Depending on the tested material, there are the following kinds of aerometers:

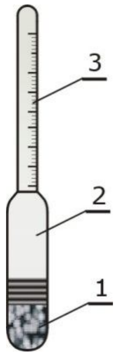


Fig. 40. Aerometer

1. Densimeters for density determination of:

- Any liquid – universal;
- Liquid of determined parameters or within the limits of surface tension;
- Particular liquids or solutions, especially densimeters for alcohol whose purpose is to determine density of ethyl alcohol and water mixture.

2. Aerometers used for measuring the following physical quantities connected with density:

   - Mass fraction, especially: alcoholometers used for measuring the contents of alcohol expressed as the mass fraction, saccharometers used for measuring the saccharose mass fraction in water solutions;
   - Volume fraction, especially alcoholometers used for alcohol contents measure expressed as the volume fraction,
   - Mass concentration.

Aerometers are usually calibrated in temperature 20°C, therefore the tested liquid should have the same temperature. How deep the bottom part of aerometer is immersed depends on the difference between the aerometer weight and the weight of liquid displaced by the aerometer.

In order to determine the density of liquid with aerometer, you need to pour the tested liquid to the slim tube so that it can freely immerse. Next we put the aerometer and read the result on the scale. This method is quick and simple, you can read the density directly on the scale, there is a big variety of instruments. Its disadvantage is the need of temperature correction (testing in temperature different than 20°C and the required large volume of the tested sample).

8.2.3. Oscillating method

During tests we use so called U-tube measuring its vibration frequency which depends on the tested liquid density. The measuring system features the vessel of mass [m] and volume [V] which is filled with the tested liquid. The system is hang on a spring so the pendulum vibration period is expressed by the equation:

$$T = 2\pi\sqrt{\frac{m}{c}} = 2\pi\sqrt{\frac{M+\rho V}{c}} \tag{28}$$

where: T – pendulum vibration period
m – nominal mass
c – elasticity coefficient
ρ – liquid density
M – empty U-tube mass
V – U-tube volume

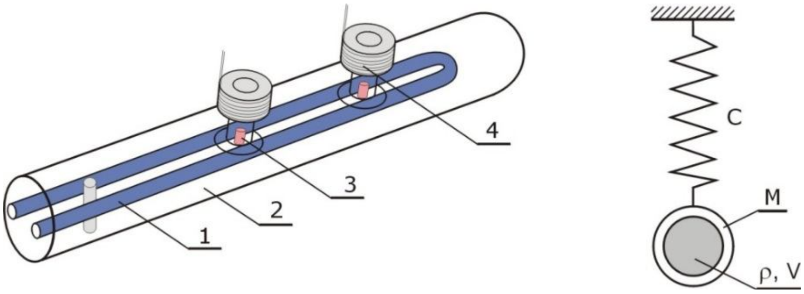


Fig. 41. Oscillating principle – measuring principle

1 – U-tube
2 – glass cylinder
3 – magnet
4 – coil

The tested liquid density is determined from the following equation:

$$\rho = A \cdot T^2 - B \tag{29}$$

where: A, B – the instrument constant values

The instrument constant values result from the calibration we carry out for the two standards of the same density. The method advantages: a small sample volume (approx. 1 ml), quick measurement, a very high accuracy and repeatability, true density testing. This method is used to determine the homogeneous liquids density determination.

8.2.4. Hydrostatic method

Hydrostatic method implies weighing the sample in the air and later in liquid of determined density, usually distilled water. This procedure has been adopted to the modern electronic balances and now constitutes one of the basic elements of their software. Obviously, this method requires using a different pan system. For laboratory purposes it is usually a construction that takes place of a regular pan; in industry the products are weighed under hook. Both solution are depicted below:

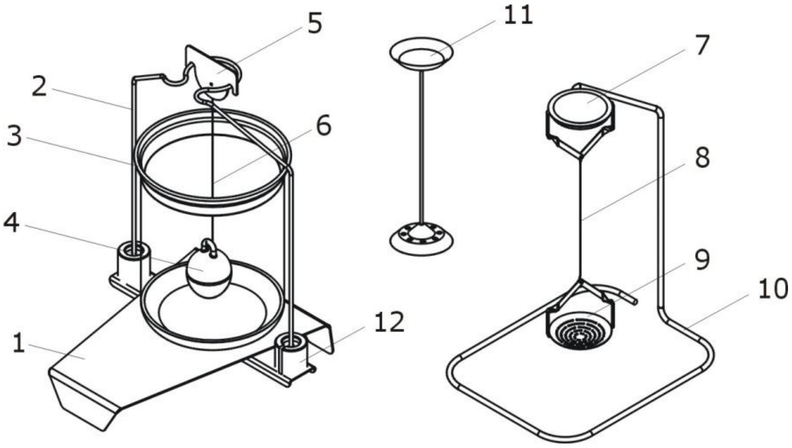


Fig. 42. Density determination kit. Laboratory solutions by RADWAG

1. Beaker basis	7. Top weighing pan
2. Weighing pan stand	8. Sinker flexible connector
3. Beaker	9. Bottom weighing pan
4. Sinker	10. Hook
5. Hook	11. Additional set of pans
6. Sinker flexible connector	12. Additional weight

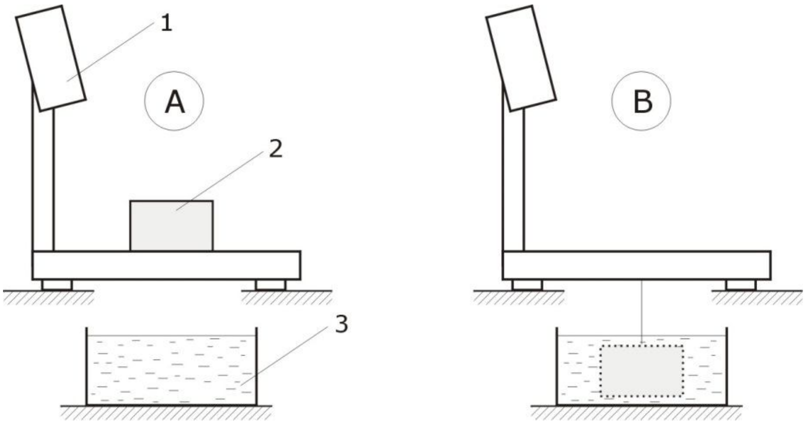


Fig. 43. Density determination stand, solution for large samples

1. *Balance*
2. *Sample*
3. *A vessel with liquid*

Solid bodies density determination

During laboratory tests you determine the solid body density in the air on the top pan [A] of the kit and then in the liquid on the bottom pan [B]. It is essential to know the density of this liquid. You read the liquid temperature on the thermometer and enter the result to the balance software. Knowing the relation of liquid density in the temperature function, the balance software refers to the proper liquid density quantity from the table. This solution is used for distilled water and ethyl alcohol. Appendix B contains the tables of distilled water density in temperature function.

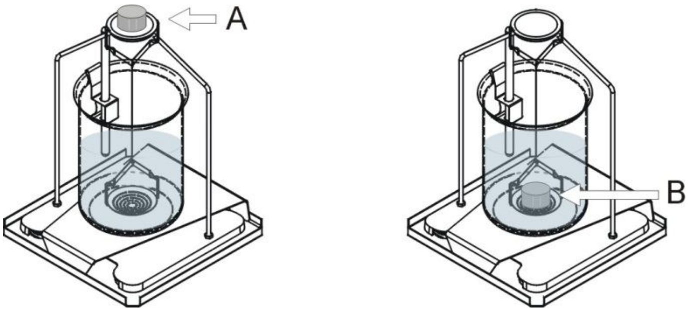


Fig. 43-1. Solids density determination

Regardless of the applied solution, the solid bodies density is determined according to the following equation:

$$\rho = \frac{A}{A-B} \cdot \rho_C \tag{30}$$

where: ρ – sample density
A – sample mass in the air
B – sample mass in liquid
ρ_C – liquid density

If the analysis requires to consider the air buoyancy, the sample density is calculated according to the below equation:

$$\rho = \frac{A}{A-B}\left(\rho_c - \rho_p\right) + \rho_p \tag{31}$$

where:
ρ – solid body density
A – sinker mass in the air
B – sinker mass in water
ρ_C – liquid density
ρ_p – air density

Liquids density determination

For density determination you use sinker [4] of determined volume. You need its mass in the air [A] and in the tested liquid [B].

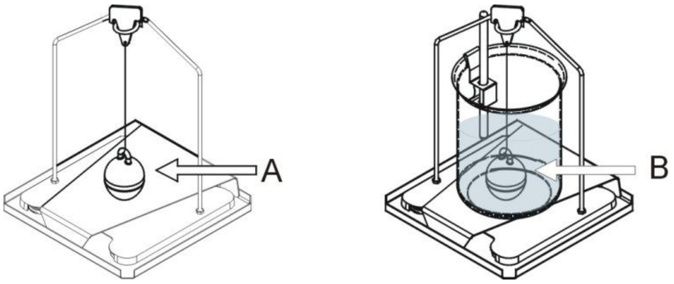


Fig. 44. Liquid density determination

Liquids density is determined according to the below equation:

$$\rho = \frac{A-B}{V} \tag{32}$$

where:
ρ – liquid density
A – sinker mass in the air
B – sinker mass in water
V – sinker volume

Considering air buoyancy we use the below equation:

$$\rho = \frac{A-B}{V} + \rho_P \tag{33}$$

where:
ρ – liquid density
A – sinker mass in the air
B – sinker mass in water
V – sinker volume
ρ_p – air density

While determining density with hydrostatic method, several elements which influence the result accuracy are meaningful:

- Mass measurement accuracy resulting from repeatability of indications
- Liquid temperature stability
- Porosity of the tested body
- Air bubbles on the tested sample surface
- The tested sample size

The influence of those elements on the density determination process is discussed later in this publication.

8.3. Methodology in hydrostatic measurements of density determination

During density determination two main processes take place: the sample preparation and weighing. The sample construction, size and condition are quite essential for the process. Below you will find a few remarks connected with sample preparation:

- The sample surface should be degreased as the air bubbles adhere to the greasy surfaces more easily, which contributes to the measurement error;
- The sample size should be suitable to the kit dimensions (easiness of measuring);
- If the same sample is weighed several times, it should be carefully dried before every weighment;
- In case of porous bodies the kit can only roughly determine density, because of the sample structure;
- In case of bodies of density lower than 1 g/cm3, another set of pans should be used;
- If ethanol is used as the standard liquid, it is necessary to check if it does not dissolve the tested sample.

Specification of mass measurement during density determination process

Accuracy of sample mass determination depends on the balance indications repeatability. For samples of lower mass other parameters like centricity or linearity do not matter. Repeatability parameter listed in the technical parameters cards was determined while weighing a steel standard. This weighing is usually quick when it is carried out in stable conditions.

Weighing in liquids is slightly different because of additional influence of buoyancy force. For this reason, during weighing in liquid other criteria concerning indications stability should be used. Therefore, the balance indications repeatability during the standard weighing will be slightly different than while weighing the tested sample in liquid. Similar relations take place during the sinker mass determination.

8.3.1. Application of XA 220.4Y balance for density determination

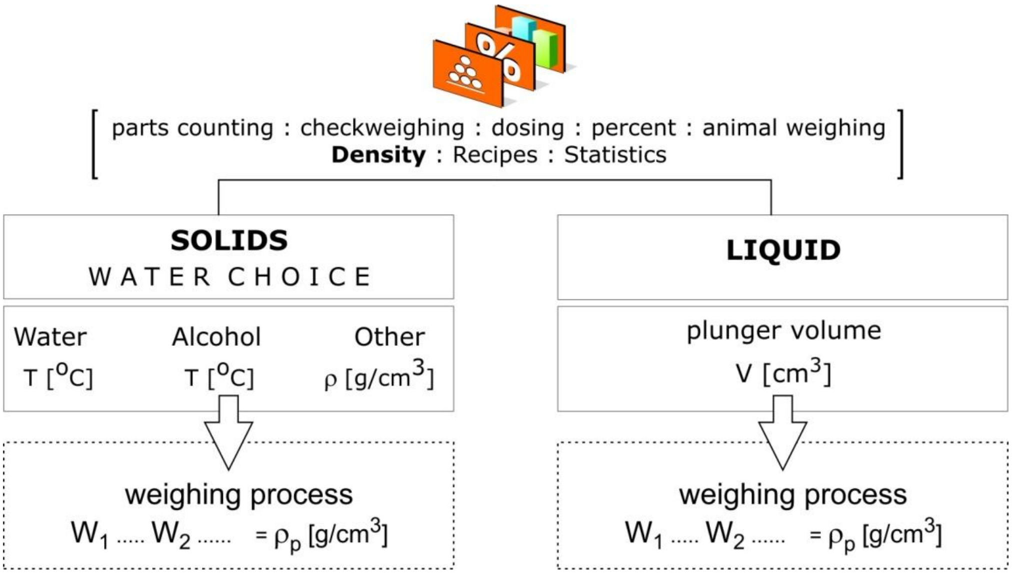
Now it is common to use automatic or semi-automatic solutions during tests. All RADWAG laboratory balances, also XA 220.4Y offer this functionality. The below table features the balance a short characteristics:

XA 220.4Y

Max capacity:	220 g
Min load:	10 mg
Indication accuracy:	0,1 mg
Tare range:	-220 g
Pan size:	ø 85 mm
Interface:	RS 232, USB, ETHERNET

We can determine density of solid bodies, liquids and gases. In order to determine density of solid bodies, liquids, you need an additional kit, namely KIT 85.

It was described while focusing on hydrostatic method. A simplified measuring procedure is depicted below



In order to determine a solid body density you need to:

- Select the liquid kind,
- Read the liquid temperature and enter it to the balance,
- When the selected liquid is other than water or alcohol, you need to enter its density,
- Weigh the body in the air [W1] and liquid [W2],
- The display will show the tested sample density.

In order to determine a liquid density you need to:

- Enter the sinker volume to the balance menu (data on the hook).
- Weigh the body in the air [W1] and in the tested liquid [W2],
- The display will show the sample density

Solid body density determination (weighing in the air)

Liquid density determination (weighing the plunger in the air)

8.4. Gravimetric density determination of porous solids

Porosity is a measure of the void spaces in a material. It is expressed as a fraction of the volume of voids V_p (pores) over the total volume V.

$$p = \frac{V_P}{V} \tag{34}$$

Because of its specific construction, porous solids have open pores which can be filled with liquid and closed pores, usually filled with gas. In case of porous solids we can talk about apparent and true density.

The total volume of a porous solid together with the pores constitutes so called apparent volume. It is easy to determine the apparent volume when a body has a regular shape. Apparent density is a ratio of dry material mass to its apparent volume. For irregularly shaped samples, apparent density is determined by hydrostatic method.

Relative density is a ratio of apparent density to true (absolute) density expressed in percentage. True density of a material is defined as a ratio of the sample mass to its volume without pores.

Density determination of porous solids requires the following measuring procedure:

- Determine the sample mass in the air [m1];
  Because of the pores, the sample should be carefully dried before the test. After that it is stabilized to the room temperature and weigh.
- Saturate the sample with a liquid (usually distilled water);
  The process might imply the sample heating in a vessel, which fills all the pores with the liquid.

- The sample stabilization;
  The sample is put to a vessel filled with deaerated distilled water, it is stabilized to the room temperature here.

- Weighing the sample in liquid [m2];
  After stabilization you take the sample out of the vessel and weigh it in the liquid (on the bottom pan of the kit).

- The saturated sample weighing [m3];
  You take the sample out of the liquid, remove water from the sample surface and weigh it, you obtain the mass of the saturated sample (water fills the pores).

The sample true (volume) density is calculated according to the below equation:

$$\rho_o = \frac{m_1}{m_3 - m_2} \cdot \rho_{fl} \tag{35}$$

where: m_1 – dry sample mass (weighing in the air)
m_2 – saturated sample mass (weighing in a liquid)
m_3 – saturated sample mass
ρ_{fl} – liquid density

With information of sample masses, you can determine open porosity expressed in volume percentage π_a and apparent density π_t.

$$\pi_a = \frac{m_3 - m_1}{m_3 - m_2} \cdot 100 \tag{36}$$

$$\pi_t = \frac{\rho_t - \rho_o}{\rho_t} \cdot 100 \tag{37}$$

8.5. Pycnometric density determination of porous solids

Solid bodies density determination with the use of liquid pycnometer was described in unit 8.2.1. You need to select the appropriate pycnometer size to the tested body size – it cannot be too big. In case of porous structure, water will not displace the air out of all pores, so the determined density might be afflicted with an error.

Therefore, using this method seems to be problematic. Gas pycnometers are used for determination of the samples true volume. Knowing the sample mass, you can determine its density (weighing it on the balance). Before the analysis you need to enter the tested sample quantity to the pycnometer. Therefore, the sample density determination is a two-staged process.

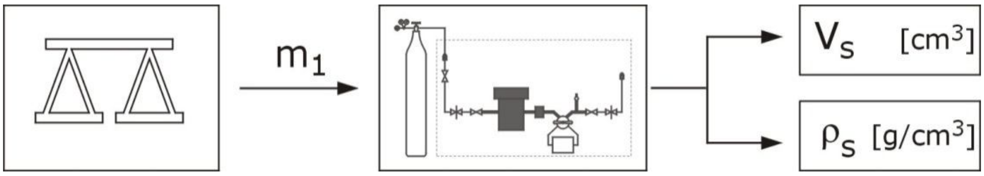


Fig. 45. Gas pycnometer – weighing procedure

During the sample volume determination with a gas pycnometer you use Archimedes principle and the perfect gas equation. In practice, the process involves determination of gas pressure in the test chamber when it is empty and with the tested sample. An empty chamber filled with gas is described by the following equation:

$$p_a \cdot V_c = n \cdot R \cdot T_a \tag{38}$$

where: p_a – pressure in test chamber that equals atmospheric pressure
V_C – test chamber volume
n – number of gas moles in test chamber at volume V_C
T_a – gas temperature

The test chamber condition with the tested sample inside is described by the following equation:

$$p_a \cdot (V_C - V_P) = n_1 \cdot R \cdot T_a \tag{39}$$

where: V_P – sample volume

n_1 – number of gas moles in test chamber at volume V_C with the sample

Next, the gas compression process takes place in the chamber to the state p_2, and after connecting the test chamber and the reference chamber to the state p_3.

The tested sample volume is determined in the following way:

$$V_P = V_C + \frac{V_a}{1-(\frac{p_2}{p_3})} \tag{40}$$

where: V_a – reference chamber volume

The below diagram shows a gas pycnometer view:

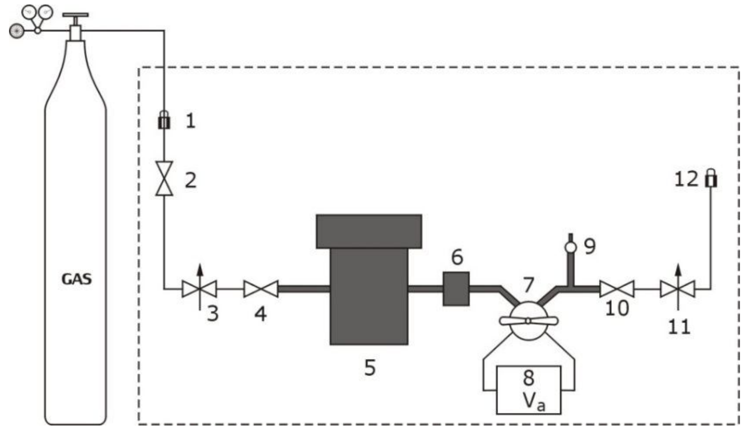


Fig. 46. Gas pycnometer construction

1 – gas supply
2 – excess flow valve
3 – needle valve
4 – flow on-off valve
5 – sample cell holder
6 – filter
7 – selector valve
8 – reference chamber of defined volume
9 – pressure transducer
10 – vent on-off valve
11 – needle valve
12 – gas offtake

Conclusions:

The biggest advantage of gas pycnometer in comparison with fluid pycnometer is the measurement speed a possibility of ambient conditions on the measurement accuracy. Despite the fact that those instruments reach the volume measurement accuracy even 0,0001 cm^3, the real accuracy of the sample density depends on the accuracy of the sample determination.

8.6. ‘Floating’ bodies density determination

It is usually simple to determine any body density. It is enough to measure mass in the air and in a fluid, we achieve:

$$m_{air} > m_{fluid}$$

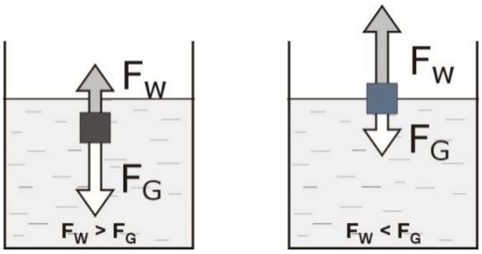
However, it might be problematic to determine density of objects whose density is lower than the tested fluid density:

$$\rho_{fluid} > \rho_{sample}$$

In this case the sample will float, therefore, a different pan set should be used and the whole kit should be additionally loaded if necessary. This results from the relations between the body gravity force and the buoyancy force: the body will float when the buoyancy force is larger than the gravity force.

$$F_W > F_C$$

The below pictures depict this relation:



where: F_G - gravity force
F_W - buoyancy force

Fig. 47. Relations between the forces during measurement in liquid

In laboratory conditions an additional pan set should be used (set KIT 85, KIT 128). During weighment in a fluid you put a tested sample under the bottom pan of the kit [8].

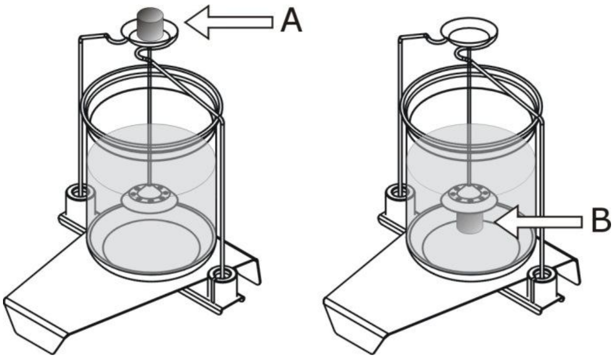


Fig. 48. ‘Floating’ bodies density determination

8.7. Density determination of high viscosity fluids

Viscosity is the effect of different layers of the fluid exerting shearing force on each other, or on other surfaces, as they move against each other. Because of friction between the liquid or gas particles, the moving particle drags the neighbouring particles with velocity which is closer to its own velocity when the fluid or gas is more viscous.

During the weighment of a glass sinker in a fluid, the gravity force is partly leveled by the buoyancy force. The result of a weighment in a fluid is smaller than weighment in the air. It is therefore possible to determine a fluid density applying the Archimedes principle:

$$\text{sinker mass}_{\text{air}} > \text{sinker mass}_{\text{liquid}}$$

When the test concerns a highly viscous liquid, the forces interacting between the fluid and sinker are significant to the extent that it is difficult to put immerse it in the tested fluid. It happens as the sinker hangs on a thin connector and its density is relatively low (2,4 -2,8 kg/m^3). In this case you can use a sinker with a much higher density. Usually, it is a steel ball called 'gamma sphere' used for the tests:

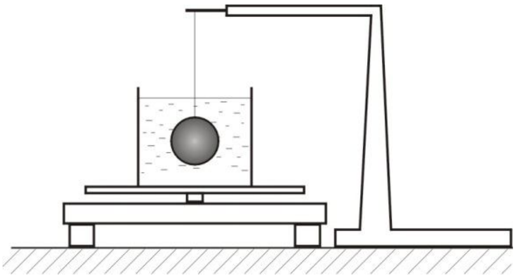


Fig. 48-1. Gamma sphere at fluids density determination

Put a beaker with the tested fluid on the balance and tare the indication. Next, immerse the steel sinker. The balance will indicate the displaced fluid mass. Knowing the sinker volume, you can determine the fluid density from the equation:

$$\rho_C = \frac{m_C}{V_S} \tag{41}$$

where: ρ_C – fluid density

m_c – fluid mass

V_s – sinker density

Testing density of highly viscous fluids (suspended solids), you need to be careful not to separate the phases: the sinker should be immersed in the tested fluid quickly.

8.8. Measuring accuracy at solid bodies density determination using hydrostatic method.

Every method is afflicted with some errors which result partly from the conditions and partly from the used instruments. Assuming that the conditions are stable, the potential errors result from the balance construction.

In hydrostatic method it applies to the following elements:

- The balance indication repeatability at the sample weighment,
- The buoyancy force connected with the air bubbles occurrence,
- The influence of the connector diameter on the liquid buoyancy,
- The fluid temperature indication accuracy,
- The sinker volume determination accuracy,
- The liquid surface tension.

8.8.1. Indications repeatability

In order to determine liquid or solid body density, you need to carry out a test in the air and then in water. Therefore, the balance repeatability should be tested during the sinker weighment in the air and ten in a liquid. It would be best measured with an object mass close to the tested sample mass. The top pan for solid bodies construction requires to put the sample centrally, which contributes to the repeatability accuracy. If there are no other elements, we can assume that repeatability will be the same as determined by the mass standard an a regular pan. During the sample (sinker) mass testing in water there are similar relations.

The data analysis leads to the following conclusions:

- Density determination error resulting from the indications spread can be max 0,04 g/cm3 when the indication repeatability is following:

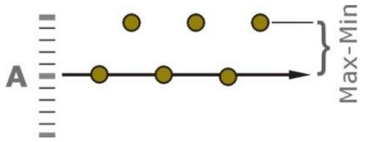


Fig. 49. Indication repeatability – extreme solution

- In reality this error might be much smaller, usually for the measuring data the following case takes place:

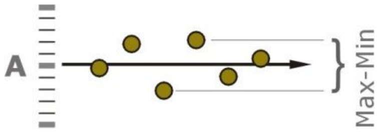


Fig. 50. Typical balance indications spread

8.8.2. Buoyancy force of air bubbles

During density determination process the buoyancy force of the air bubbles contributes to the measurement error. Air bubbles most often adhere to the greasy surfaces.

The tested material hydrophobicity also matters.

The force that affects a single bubble of 1 mm diameter is 0,5 mg

8.8.3. The connector resistance

During solid bodies density determination some fluid is displaced by the immersed body on height h. The displaced liquid meets the resistance of the connector linking the pans. The connector linking the top and bottom pans consists of a thin stainless wire. For a very detailed analysis the influence of this effect might be disregarded by introducing a corrective coefficient. It is assumed that the measurement deviation caused by this coefficient is usually disregarded.

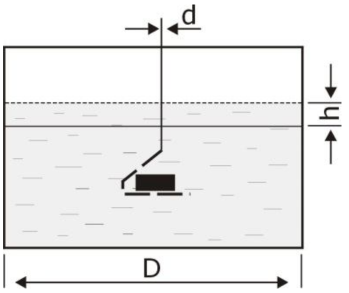


Fig. 51. Force affecting the connector during weighment in a fluid

Weighing a 30 g sample, the contribution of wire to the sample density determination is following:

Weighing in the air: A = 27,79062 [g]

Weighing in liquid: B = 17,47962 [g]

Liquid density: ρ_C = 0,999823 [g/cm^3]

The tested sample density Determined without a correcting coefficient	The tested sample density Determined with a correcting coefficient
2,694763 [g/cm^3]	2,694782 [g/cm^3]

Difference: **0,000019** [g/cm^3]

Conclusions:

1. The influence of the connector linking the kit pans on density determination is insignificant, it causes indication error 0,000019 g/cm^3.
2. The error is insignificant and therefore it can be disregarded for regular weighments in the laboratories.

8.8.4. Liquid temperature

Temperature stability is a required parameter for both solid bodies and liquids density determination. In first case, lack of liquid temperature stability or an incorrect reading will contribute to an error of the sample density determination. In the latter case, there will be density indication spread changing together with the tested liquid temperature.

As density determination process is usually carried out in stable laboratory conditions, an element of liquid instability (distilled water) practically does not exist. There is a correct temperature reading issue: we assume that the error is 1^oC so this error might occur in practice as the thermometer reading unit is 1^oC. it might also result from giving the result in round figures. It will slightly affect the sample density: an error equals 0,000056 [g/cm^3].

8.8.5. The sinker volume

The sinker is a glass element whose volume was determined by weighing. It is afflicted with an error 0.001 g/cm^3. Taking it into consideration, we will obtain the max deviation in the tested liquid density equaling 0,00009 g/cm^3.

8.8.6. The liquid surface tension

The liquid surface tension takes place when a solid body, gas or other liquid touches the liquid surface. It causes the liquid surface behave like an elastic membrane. This property is caused by cohesion of similar molecules. The surface tension on the border of two phases might be decreased by adding surface-active substances, so called surfactants.

On the contact of two phases there are also other forces affecting the liquid molecules. As a result, the liquid surface adopts a concave meniscus. These properties influence on the density determination is insignificant.

8.8.7. Uncertainty of measurement

The determined solid body or liquid density is incomplete without indicating determination uncertainty: its range is not clear.

The uncertainty budget connected with the solid body density determination contains all errors, whether they occur or not:

$$u = \sqrt{(Sp_1)^2 + (Sp_2)^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{pp}{\sqrt{3}})^2 + (\frac{c_{sz}}{\sqrt{3}})^2 + (\frac{t_c}{\sqrt{3}})^2} \tag{42}$$

where: sp_1 – indications repeatability during tests in the air
sp_2 – indications repeatability during tests in a liquid
d – balance reading unit
pp –air bubble error
c_{szt} – connector buoyancy force error
t_c – temperature indication error

The uncertainty budget connected with a liquid density determination additionally contains a coefficient connected with the sinker volume:

$$u = \sqrt{(Sp_1)^2 + (Sp_2)^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{pp}{\sqrt{3}})^2 + (\frac{c_{sz}}{\sqrt{3}})^2 + (\frac{t_c}{\sqrt{3}})^2 + (\frac{V}{\sqrt{3}})^2} \qquad (43)$$

where: sp_1 – indications repeatability during tests in the air
sp_2 – indications repeatability during tests in a liquid
d – balance reading unit
pp – air bubble error
c_{szt} – connector buoyancy force error
t_c – temperature indication error
V – sinker volume error

8.9. Density determination in practice – 3Y series balances

3Y series balances were designed in a modern and functional way using the latest technologies. They feature several systems which facilitate the operator's work, register a lot of data and enable a smooth communication flow which facilitates the data exchange with external devices.

Solid bodies density is usually determined in distilled water, rarely in alcohol or other liquid of defined density. The procedure goes as is following:

1. Preparation of a sample for analysis: See unit 'Methodology in hydrostatic tests of solid bodies and liquids density determination'.
2. Balance preparation to the tests: The balance should be have stable temperature (the self-warm-up time); carry out the adjustment, replace the pan with a density determination kit, clear the balance indication after the installation.
3. Solid bodies density determination:
   - The testing liquid temperature should be stable,
   - Select density function, and then solid bodies density,
   - Select the liquid kind (distilled water, alcohol, other),
   - Read the liquid temperature and enter it to the dialog in the balance software,
   - Press START button,
   - Put the sample on the top pan and approve the stable weighment,
   - Put the sample on the bottom pan (in a liquid) and approve the stable weighment,
   - The sample density will be displayed.
4. Liquid density determination:
   - select function liquid density
   - read the sinker volume from the hook and enter this quantity to the balance menu,
   - press START button,
   - hang the sinker on the hook and approve the stable weighment,
   - hang the sinker in the tested liquid and approve the stable weighment,
   - The liquid density will be displayed.

The weighments documentation is registered automatically in the database. Every finished density determination procedure contains:

- The sample identification,
- Date and the procedure start time,
- Date and the procedure finish time,
- The sample density,
- The sample volume,
- The procedure name (solid bodies, liquids).
- The user's name,

- The sample name (if it is registered in the products database),
- The used standard liquid (solid bodies density determination),
- The used standard liquid density,
- The liquid temperature,
- Weighment 1 – in the air,
- Weighment 2 – in liquid,

Every entry might be printed out or exported to USB.

8.10. Summary

Gravimetric density determination using the electronic balance facilitates the procedure of liquids and solids density determination. Simplicity and reliability of this solution makes it widely used especially when speed and accuracy matter. Density determination by means of pycnometer allows to test liquids, solids and loose substances. Because this method implies weighing, the accuracy of mass determination is a decisive element. The method's disadvantage in case of liquid pycnometers is a slow and complicated procedure.

Density determination by oscillating method requires the proper instruments and rigid conditions. The required weighing chamber temperature is $\pm$ 0,02^{o}C; in order to calibrate the instrument you need two standard liquid types. After the test, the U-tube should be cleaned. All these elements make up quite a complicated procedure.

Porous bodies density might be determined in different ways, depending if we want to determine true or apparent density. For the accurate and quick test of a sample with small pores which cannot be properly filled with water, you need to use a gas pycnometer (all types of sponge). Hydrostatic method is longer because it implies soaking the sample with water. Another, much shorter solution, is an oil bath.

Bodies of density **ρ<1g/cm^3** feature a property of buoyancy. Density determination of those bodies by hydrostatic method requires a different pan system and usually loading the whole kit. Density of semi-fluids of high viscosity can be determined using a stainless steel sinker – so called 'gamma sphere'. The procedure is slightly different. The process itself is quite simple and does not require specialist equipment.

9. Methods of sample moisture determination

It is widely known that moisture has impact on different properties of the substances. Therefore, it is necessary to determine the moisture contents on different production stages or quality control. This parameter decides of the following properties:

- **Possibility of caking,**
- **Microbiological stability,**
- **Dry mass contents,**
- **Constant of other substances contents in the material, material purity,**
- **Product quality,**
- **Nutrition value.**

In relation to the legal regulations, it is also possible to acquire confirmation of compatibility with requirements. The process of determination of dry mass or humidity should be quick and quite reliable. Therefore, both instruments and methods should fulfill those requirements. When we have more time, we use so called normative methods. When a quick reaction is required, moisture analyzers are used. It is a two-functional instrument: it weighs and dries (analyzes the moisture). The construction features the weighing module and the drying chamber.

MA 60.3Y Moisture analyzer

The moisture analyzer weighs the sample before the drying and during the process without taking it out. It determines the sample moisture [%M], the dry mass contents [%D] and the ratio of moisture to the dry mass [%R].

$$[\%M] = \frac{(M_1 - M_2)}{M_1} \cdot 100\% \qquad (44)$$

where: M_1 – initial mass;
M_2 – final mass

$$[\%D] = \frac{M_2}{M_1} \cdot 100\% \tag{45}$$

$$[\%R] = \frac{(M_1 - M_2)}{M_2} \cdot 100\% \tag{46}$$

The drying process is finished automatically and the result is registered, stored or exported to other devices (USB, RS 232, Ethernet).

9.1. What is the materials moisture?

In thermogravimetrics methods (also moisture analyzer) all elements evaporate during the sample heating. These elements include water, fats, aromatic substances, organic solvents, chemical additives and other ingredients that are formed in thermal decomposition (namely combustion products). Therefore, materials moisture is a **set of all elements** in the sample which evaporate during the heating.

In practice, it is impossible to separate the evaporated clean water from other elements. Drying temperature plays a big role in this case. Too high temperature will burn the sample and make other elements evaporate.

A commonly used term in drying processes is ‘free water’, namely the water that evaporates from the sample in 105^{o}C. Therefore, it is justified to use term ‘dry matter’.

9.2. Legal requirements

The state supervision over the weighing instrument is limited to the mass indicator. It does not matter what it displays (a number of details, humidity, sample moisture), it is the weighing result (in grams or kilos) that is controlled. Other units are only used to achieve the result. It is reasonable for balances, but not for moisture analyzers. The weighing result depends not only on the mass quantity, but also on the sample size, drying temperature etc. As there are no official moisture standards, this parameter assessment is impossible. It is an awkward situation, as moisture analyzers are widely used in areas supervised by the state, e.g. in environment protection.

Therefore, moisture analyzers should be used with type approval certificates. However, certification and later verification procedure concerns measurement in grams. This result does not determine humidity. It does not make any sense. The drying procedures verification might be a solution. It is a series of activities that proving that the instrument meets the requirements.

The requirements should concern mass measurement, drying temperature stabilization, moisture determination accuracy etc. Therefore, technological solutions are ahead of the law. Perhaps the calibration of mass indicator and the drying chamber temperature. Official documents regarding weighing instruments do not mention moisture determination instruments like moisture analyzer. (Ordinance of the minister of Economy [Journal of Laws – Dz. U. - 2008, no 3 issue 13 and Journal of Laws 2010, no 110, issue 727]).

9.3. Physical effects in drying processes

During the sample heating radiation and convection processes occur simultaneously. Radiation implies a transfer of heat from one body to another, while the heat amount depends on:

- The temperature difference between the emitter (sender) and receiver (sample),
- The environment,
- The emitted wave length.

Radiation is mainly absorbed by water vapour particles. It is connected with the fact that intermolecular vibration energy is the same as infrared radiation quantum energy. This phenomenon occurrence depends on radiation of determined wave length.

Convection phenomenon uses the heat transmission based on the air particles movement which circulate in the moisture analyzer chamber. Warm thinner air is lifted up, while colder air goes down. This circulation allows to transfer energy using the medium.

The sample absorbing energy increases its own temperature, which might lead to several unintentional effects. The first one is surface burning of the sample which is recognizable by the sample changed colour. The solution is simple: lower the drying temperature. Another effect is forming an impermeable coating on the sample surface: the measurement results will be too low. The solution: cover the sample with a filter , place the sample between the filter s. For liquids of high surface tension it is necessary to increase the active evaporation surface. High-silica sand, filter s and absorbent paper are useful in this case.

Another issue is the heat emission from the drying chamber to the construction elements (housing, screens, holders). It is the constructor's task to construct a safe product; hence the informative stickers and manuals.

9.4. Preparation of samples for drying

The sample preparation includes two activities: the sample collection and storing. The sample source is very important in reliability and results repeatability: the sample should adequately represent the whole analyzed product.

- **Collecting and preparation of different samples**

  It is necessary to think how to obtain a homogenous sample that represents the whole. The product can be prepared by mixing or stirring before the sampling. It is also common to take several samples from different parts of the product and calculate the mean from the obtained value. Another solution is to mix several samples from different parts of the product. Some products should be broken up, which increases repeatability.

  This activity might generate heat, therefore, you need to pay attention to moisture loss. In practice, this problem does not apply typical samples of several percent moisture. Obviously, the samples should be protected from the ambient conditions on every stage by storing them in hermetic packages or vessels.

Semi-liquids like yoghurts or cream cheese should be stirred as they are a mixture of several ingredients of different density. The thicker ingredients settle on the package bottom, therefore, the dry matter contents in the bottom and upper layers will differ considerably. Liquid samples should also be stirred, especially liquids of high density. It is assumed that the medium density is the same, but stirring will only support it.

- **The sample storing**

  It is crucial for the stored sample not to lose moisture because of ambient conditions influence. In some cases moisture might condense on the package walls. Before the sample analysis, the condensed moisture must return to the sample. The package size must match the sample.

9.5. Drying parameters

Obtaining correct results during the drying process depends mainly on the drying temperature. The sample mass and the process finish criterion are also meaningful. If we use some additional elements, e.g. filter s, this makes up a system of elements which constitute drying parameters. A detailed analysis of every element is not necessary, as they have been described in publications on www.radwag.pl.

9.5.1. Drying temperature

It is generally believed that the sample drying temperature should be the same as the temperature specified in the normative documents. Therefore, 105°C is always declared as proper, independently on the results, which is not a correct approach. It is important to remember that using the moisture analyzer requires the method validation. This means setting the instrument in the way it shows the results similar to the reference results. A possible incompatibility of drying temperatures results mainly from a different drying method (radiation, convection), drying chamber construction, a short analysis time etc.

Controlling drying temperature is the key, so apart from value declaration we also need to select the temperature increase dynamics, as depicted below:

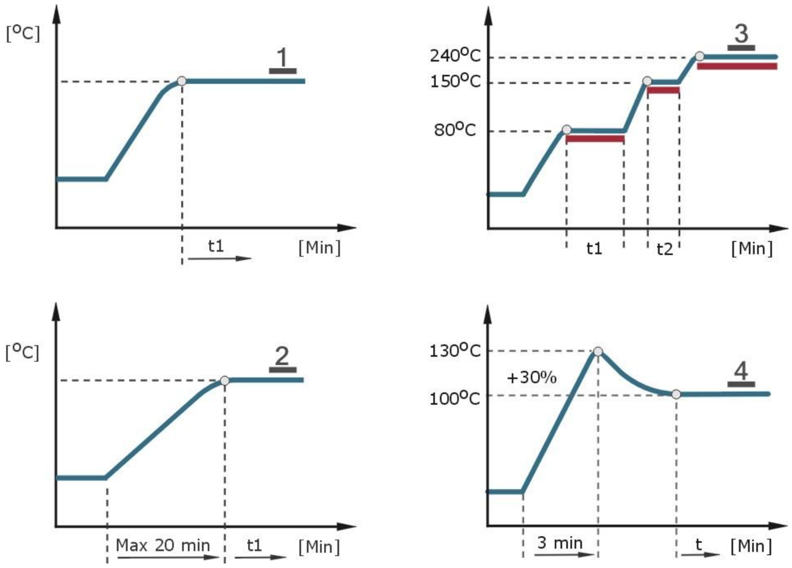


Fig. 52. Drying profiles

1. Standard profile
   Temperature grows quite rapidly, reaching the target temperature after 2 minutes of drying. It is the most commonly used drying profiles.
2. Mild profile
   Used for samples sensitive to the temperature increase. Applied when a too rapid temperature increase makes other elements than water evaporate from the sample.
3. Threshold profile
   Applying this profile allows to determine the surface moisture and chemically bound moisture.
4. Fast profile
   Used for samples of high moisture in order to eliminate the temperature drop caused by evaporation heat

9.5.2. Finishing drying process

This parameter defines moisture result to some extent. While in reference methods drying time is determined, in case of moisture analyzer it must be set, adjusted. The below picture depicts the issue:

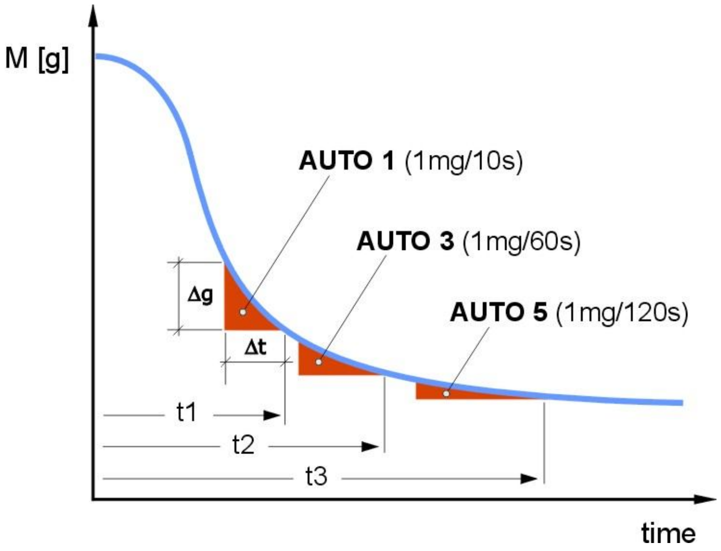


Fig. 53. Drying process finish in AUTO mode

Drying process finish mechanism in AUTO mode implies observation of 1 mg mass in determined time. There is a possibility of selecting the process finishing moment. When the temperature is optimal for removing the moisture from the sample, it is only necessary to accept the process finishing moment. While the reference mass is constant (1 mg), the time changeability allows to set this parameter so that it matches the reference result.

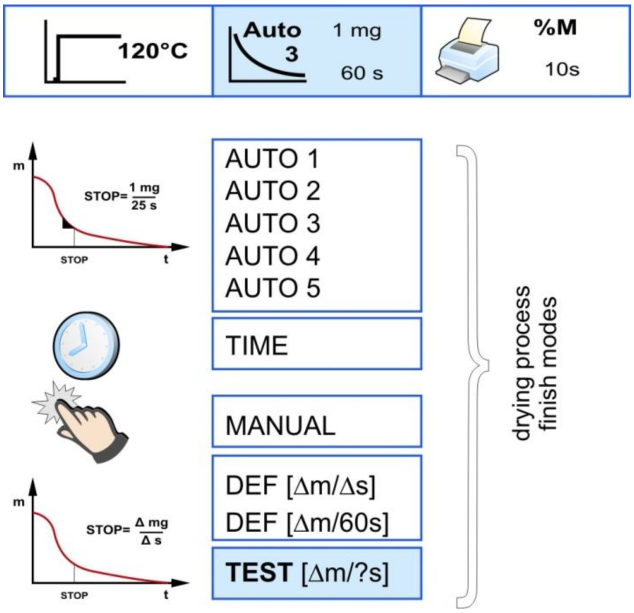
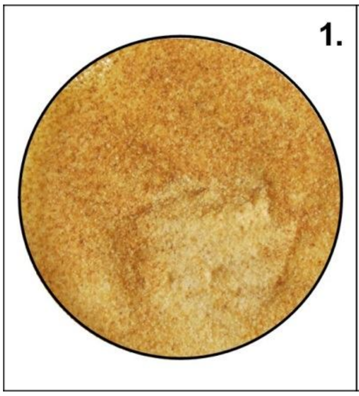


Fig. 54. Drying process finish – software possibilities

There are a lot more possibilities. The selected mode will depend on the obtained results and required accuracy.

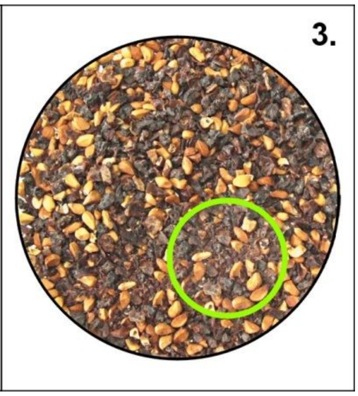
9.5.3. Errors in moisture determination

Drying process as any other process is afflicted with an error which has two sources. The first source of errors is the sample: its inhomogeneity, absorption and evaporation ability when it is prepared, the possibility to close up during the analysis.



1.

2.



3.

Sample no 1 - too high temperature, visible surface burning. The changed colour. Drying time is too long.

Sample no 2 - shows the close-up effect. There is a 'coating' on the surface. Inside there is too much moisture, which is incorrect: you need to increase the active evaporation surface. Glass fibre filter are the solution.

Sample no 3 - it is inhomogeneous. It has larger fractions and very small elements. When the temperature grows, the fine fraction is partly burnt, so there will be a big spread of results.

The second source is the moisture analyzer and its indication repeatability, sensitivity and zero drift as a result of temperature changes, correctness of indications of drying chamber temperature. Combination of all those elements allows to assess the moisture analyzer in a given analysis. This approach is necessary for materials of low moisture e.g. ABS (Acrylonitrile-Butadiene-Styrene) or PA (Polyamide) and other materials which have very low contents of dry matter (liquids).

9.5.4. The method validation

The procedure is familiar: determine the sample moisture by standardized method, select the appropriate drying parameters of the moisture analyzer. Optimization should concern temperature, the sample size, finishing mode, sample preparation. You need to determine the tolerance of moisture determination. It is important to remember that moisture analyzers supplement standardized methods, not the other way round.

10. Piston pipettes, the volume control (gravimetric method)

Apart from the material aspect (sample), there is also another aspect connected with the instruments. It is essential to control, test, calibrate, namely check if the instrument works properly. For balances we use mass standards. In case of instruments measuring volume like piston pipette, we use balances. In short, the liquid is ejected by the pipette to the weighing vessel. Knowing the liquid density and the ejected water mass, we can calculate the sample volume. It is assigned to the pipette volume. The volume is a quotient of the sample mass and its density.

$$V = {}^{m}\!/_{\rho} \tag{47}$$

Because of influence of temperature and pressure, it is logical to use coefficient Z [μl/mg] which corrects density.

$$V = m \cdot Z \tag{48}$$

Z coefficient is calculated in the below equation:

$$Z = \frac{1}{\rho_b} \cdot \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \tag{49}$$

where: ρ_w – water density

ρ_a – air density

ρ_b – density of mass standard used for balance calibration (8000 kg/m3)

The weighing procedure requires 10 series of weighments for every tested volume. The mean is calculated according to the below equation:

$$\overline{V} = \frac{1}{10} \cdot \sum_{i=1}^{10} V_i \tag{50}$$

The standard temperature of pipette testing is 20°C. When it is different, it is necessary to use a coefficient correcting the pipette thermal extension [Y]:

$$V = m \cdot Z \cdot Y \tag{51}$$

$$Y = 1 - \alpha_c (t_d - t_{d20}) \tag{52}$$

where: αc – volume extension coefficient expressed in °C-1

t_d – temperature expressed in °C

t_{d20} – constant temperature 20 °C

Piston pipettes have their own normative documents. The international standard is PN-EN ISO 8655-2:2003 norm '*Piston*-operated Volumetric Apparatus - Part 2: *Piston* Pipettes'. The norm contains construction requirements and MPE which can be used for setting our own requirements concerning accuracy.

Piston pipettes are afflicted with two kinds of errors: systematic error **es** and random error **CV**. In order to determine these errors weigh method is used; it is described in PN-EN ISO 8655- 6:2003 'Piston-operated volumetric apparatus -- Part 6: Gravimetric methods for the determination of measurement error' (later in ISO 8655-6).

10.1. Systematic error

As an absolute error, it can be expressed in microliters [µl] or as a relative error in [%]. It is calculated according to the below equation:

$$e_S = \overline{V} - V_S \tag{53}$$

$$e_S = \frac{\overline{V} - V_S}{V_S} \cdot 100\ [\%] \tag{54}$$

where: V_s – the tested volume value, for pipettes of constant volume it should be exchanged with nominal value V_0.

10.2. Random error

PN-EN ISO 8655-1:2003 norm defines this error as the volume measurement results spread around the mean volume value. Random error is expressed in microliters [µl] or in [%]. It is marked as CV. This error measurement is standard deviation:

$$s_r = \sqrt{\frac{\sum_{i=1}^{n}(V_i - \overline{V})^2}{n-1}} \tag{55}$$

$$CV = \frac{s_r}{\overline{V}} \cdot 100\% \tag{56}$$

10.3. Requirements for balances

Weighing the same sample several times shows that the most important parameter of the balance used for pipette testing is indication repeatability. Norm ISO 8655-6 states requirements listed below:

Pipette volume testing V	Reading units [mg]	Repeatability and linearity [mg]	Standard uncertainty of measurement [mg]
1 μl < V ≤ 10 μl	0,001	0,002	0,002
10 μl < V ≤ 100 μl	0,01	0,02	0,02
100 μl < V ≤ 1000 μl	0,1	0,2	0,2
1 ml < V ≤ 10 ml	0,1	0,2	0,2
10 ml < V ≤ 200 ml	1	2	2

The norm requirements can be checked carrying your own tests. It might be meaningful when our conditions are far from the standards. We can also rely on the producer's declarations. The norm indicates two parameters. The first one is repeatability, quite easy to determine. You can use data in unit 4.5. This test does not require any special standards, we test the balance capability to indicate the same results.

The other parameter is not as easy to determine as it require standards with determined errors. The smaller balance reading unit [d], the more accurate standards required, which is a source of economic and procedural problems. Therefore, we need to rely on the producer's declarations. When we know standard uncertainty (from the balance calibration certificate), it can be used as the approval criterion instead repeatability and linearity.

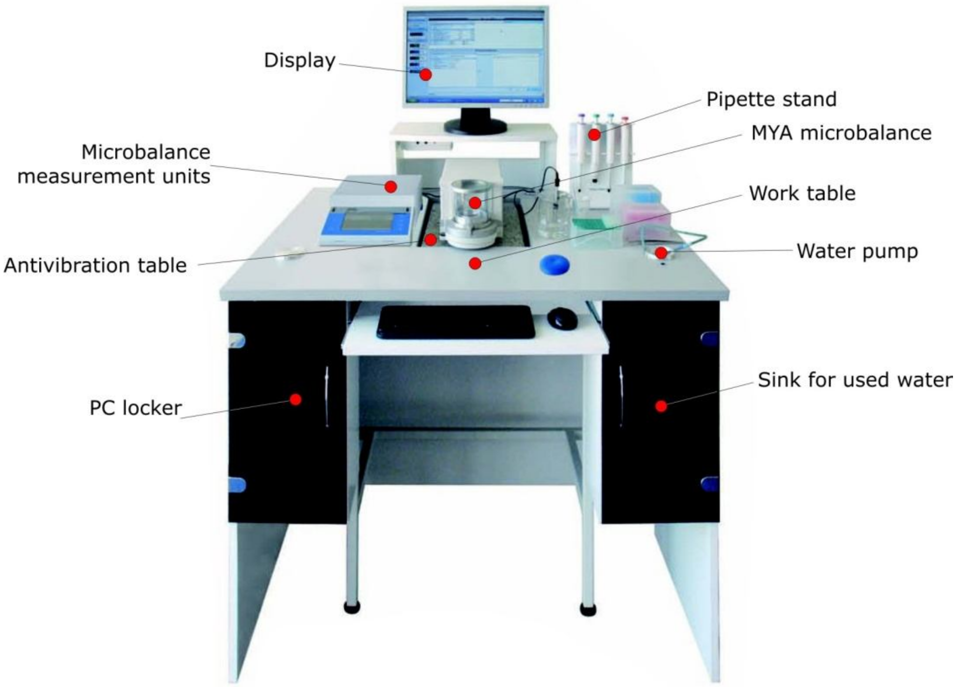
10.4. Evaporation trap

The process specificity implies non-standard solutions in mass measurement: the key element is to eliminate evaporation process of the tested liquid. The possible solution is 'evaporation trap' – a special vessel filled with liquid which ensures high humidity level in the weighing chamber. The MYA series microbalance evaporation trap' is shown below:

Before the test, the evaporation trap is filled with liquid, humidity in the trap is stabilized (approximately 90%). As the dozing aperture is inside the trap, the increased humidity prevents evaporation effect. Before dozing the liquid the aperture is uncovered and immediately covered after the dozing. The ejected liquid is carefully weighed.

10.5. Semi-automatic method in volume determination

Stating that a pipette measures properly requires a lot of data, especially measuring results. Assuming that we need to test several pipettes (adjustable volume), an integrated weighing workstation would be useful. It would be perfect if it could analyze the results, generate the final report and register the data. RADWAG workstation features all these properties:

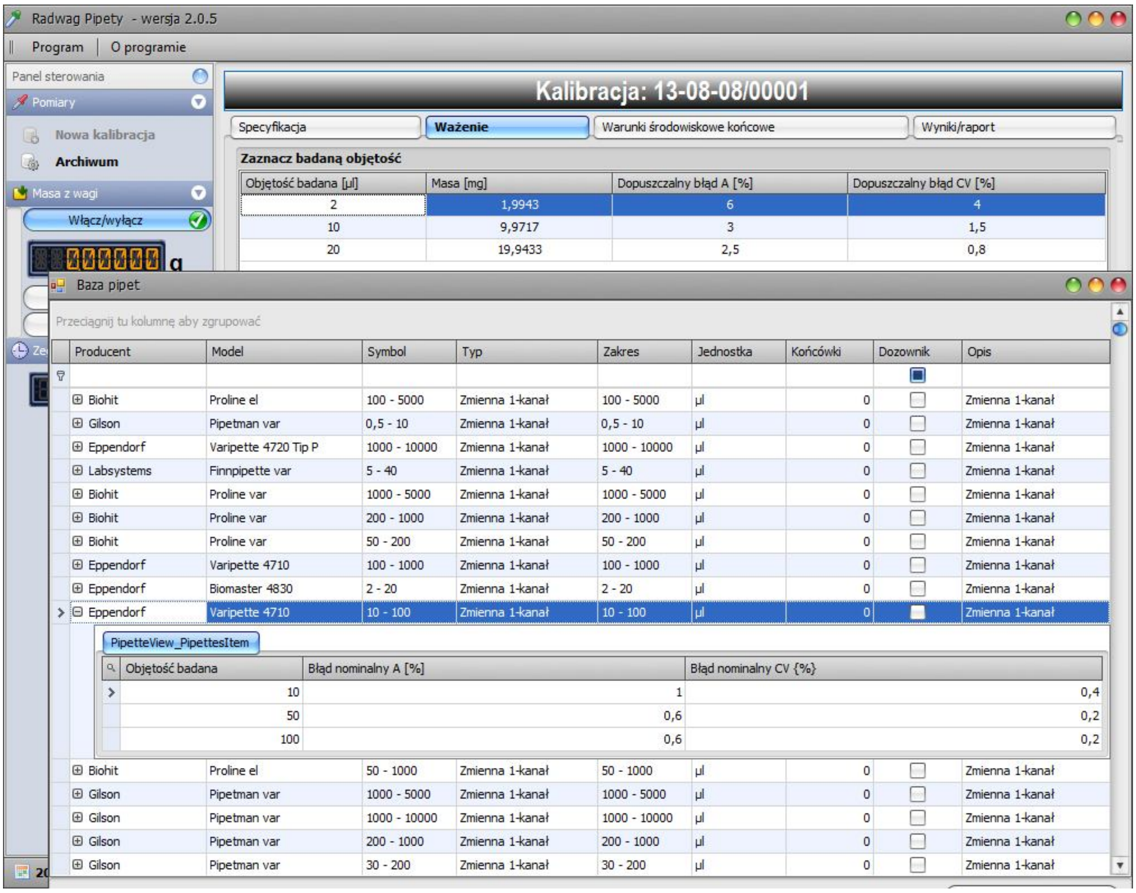


The most important element is the MYA microbalance. It features a magnetoelectric measuring system which allows to achieve very good metrological parameters.
A unique solution is a weighing pan kit which can be used interchangeably. After removing evaporation trap and installing the regular weighing pan we obtain the balance with reading unit d= 1µg and weighing range 21 g.

Functional possibilities of the software supporting pipette testing process:

- Calculating the result on the basis of
  - The mean pipette volume (channel);
  - Systematic error (accuracy error A);
  - Random error CV (repeatability error P);
- Calibration of pipettes of fixed (1 channel) and adjustable volume (1,8 and 12 channel pipettes);
- Automatized measuring procedures depending on the tested pipette type;
- Data concerning the pipettes stored in the databases (possibility of defining your own databases);

- Registering calibration results in databases (MS access);
- Creating safety copies of databases with calibration results;
- Pipette calibration protocol printouts;
- Test reports export to formats e.g. PDF, MS Word, Excel and others;
- Another calibration date planning;
- Filtering the planned pipette calibrations: in the current week or month;
- Cooperation with the balance connected with RS-232 computer port, all RADWAG models, a possibility of connecting different producers' balances;
- Possibility of manual entering the weighment results.



Kalibracja: 13-08-08/00001

Zaznacz badaną objętość

Objętość badana [µl]	Masa [mg]	Dopuszczalny błąd A [%]	Dopuszczalny błąd CV [%]
2	1,9943	6	4
10	9,9717	3	1,5
20	19,9433	2,5	0,8

Producent	Model	Symbol	Typ	Zakres	Jednostka	Końcówki	Dozownik	Opis
							■	
⊞ Biohit	Proline el	100 - 5000	Zmienna 1-kanał	100 - 5000	µl	0	☐	Zmienna 1-kanał
⊞ Gilson	Pipetman var	0,5 - 10	Zmienna 1-kanał	0,5 - 10	µl	0	☐	Zmienna 1-kanał
⊞ Eppendorf	Varipette 4720 Tip P	1000 - 10000	Zmienna 1-kanał	1000 - 10000	µl	0	☐	Zmienna 1-kanał
⊞ Labsystems	Finnpipette var	5 - 40	Zmienna 1-kanał	5 - 40	µl	0	☐	Zmienna 1-kanał
⊞ Biohit	Proline var	1000 - 5000	Zmienna 1-kanał	1000 - 5000	µl	0	☐	Zmienna 1-kanał
⊞ Biohit	Proline var	200 - 1000	Zmienna 1-kanał	200 - 1000	µl	0	☐	Zmienna 1-kanał
⊞ Biohit	Proline var	50 - 200	Zmienna 1-kanał	50 - 200	µl	0	☐	Zmienna 1-kanał
⊞ Eppendorf	Varipette 4710	100 - 1000	Zmienna 1-kanał	100 - 1000	µl	0	☐	Zmienna 1-kanał
⊞ Eppendorf	Biomaster 4830	2 - 20	Zmienna 1-kanał	2 - 20	µl	0	☐	Zmienna 1-kanał
⊟ Eppendorf	Varipette 4710	10 - 100	Zmienna 1-kanał	10 - 100	µl	0	☐	Zmienna 1-kanał

Objętość badana	Błąd nominalny A [%]	Błąd nominalny CV {%}
10	1	0,4
50	0,6	0,2
100	0,6	0,2

Producent	Model	Symbol	Typ	Zakres	Jednostka	Końcówki	Dozownik	Opis
⊞ Biohit	Proline el	50 - 1000	Zmienna 1-kanał	50 - 1000	µl	0	☐	Zmienna 1-kanał
⊞ Gilson	Pipetman var	1000 - 5000	Zmienna 1-kanał	1000 - 5000	µl	0	☐	Zmienna 1-kanał
⊞ Gilson	Pipetman var	1000 - 10000	Zmienna 1-kanał	1000 - 10000	µl	0	☐	Zmienna 1-kanał
⊞ Gilson	Pipetman var	200 - 1000	Zmienna 1-kanał	200 - 1000	µl	0	☐	Zmienna 1-kanał
⊞ Gilson	Pipetman var	30 - 200	Zmienna 1-kanał	30 - 200	µl	0	☐	Zmienna 1-kanał

View of window of Pipettes with Pipette Database software

10.6. Uncertainty of measurement

Specificity of testing piston pipettes causes two main sources of uncertainty:

- Uncertainty connected with the pipette,
- Uncertainty connected with the balance (gravimetric method).

Obviously, those two elements should be subject to further analysis in order to obtain complex uncertainty. Norm ISO 8655-6 states that contribution of uncertainty resulting from a series of measurements carried out by gravimetric method using measuring equipment is small in comparison to the measuring process results (on condition that the weighing equipment like balance, THB etc. are used in accordance with the norm).

Therefore, we can disregard this contribution in uncertainty budget, which allows to take into consideration only systematic and random errors in a series of measurements.

It should be emphasized that systematic error of measurement does not influence the uncertainty of gravimetric method assessment. It is the measurement result considering random error characteristic of volume determination. Taking the above statements into consideration, norm ISO 8655-6 offers a simplified uncertainty equation which can be used to determine uncertainty of piston pipettes calibration measurement obtaining 95% confidence level:

$$u = | e_S | + 2 \cdot s_r \qquad (57)$$

Uncertainty of measurement should be calculated adequately to the expected accuracy. Not all elements might influence the weighment result. Therefore, the simplified uncertainty equation should not be applied to very small volume or a more detailed analysis.

The detailed procedure of gravimetric method uncertainty assessment is described in ISO/TR 20461 document.

11. Uncertainty of mass determination

It is widely known that there are no accurate measurements: it is only possible to determine the range in which the result value might be positioned (with certain probability). Giving measurement results it is also necessary to assess accuracy of the test. It is essential for everyone using those measurement results at work to assess their reliability. Without this information the results can neither be compared with one another, nor reference values stated in specifications or norms.

What is uncertainty of measurement?
According to *Dictionary of Weighing Terms* uncertainty of measurement is 'a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used' while measurand is a physical quantity intended to be measured.

Since 1993 the widely accepted method of uncertainty of measurement determination was described in *Guide to the Expression of Uncertainty in Measurement* (first edition in 1999). The guide divides uncertainty into two types: type A and type B.

11.1. Uncertainty type A

Method A describes the calculation of standard uncertainty by analyzing the statistic series of observations. In such case the standard uncertainty is actually the standard deviation. This method requires large amount of measurements and their repetitions, and it is successfully implemented in case of random errors. Method A is applied if it is possible to perform a series of equal measurements in equal measuring conditions. Such is the case for checking the repeatability of an electronic balance. When the measurements are completed, it is possible to calculate standard deviation from the below equation:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}} \tag{58}$$

where:

n – quantity of repetitions (measurements)

x -i result of the measurement,

x – average value of all measurements for n repetitions, calculated according to below ` relation:

$$\overline{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{59}$$

Both relations are well known in mathematics, and they are commonly used for measurement analysis. The best measure of the arithmetic mean value is a positive square root called the experimental mean deviation:

$$s^2(\bar{x}) = \frac{s^2(x)}{n} \tag{60}$$

Standard uncertainty is expressed by the below equation:

$$u(\bar{x}) = \frac{s(\bar{x})}{\sqrt{n}} \tag{61}$$

For the uncertainty type A the standard distribution is employed, which is graphically expressed as Gaussian curve.

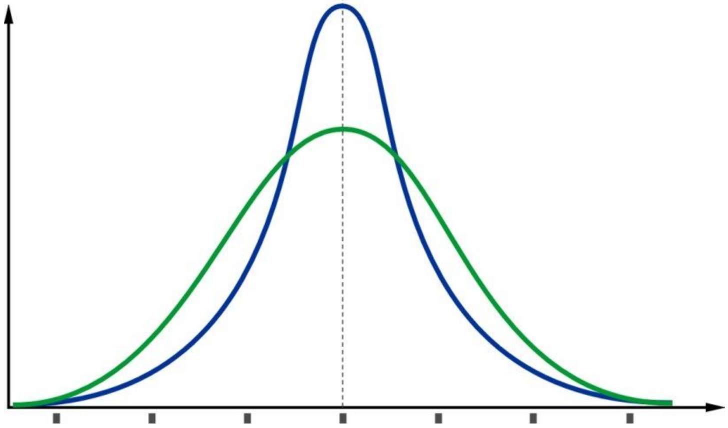


Fig. 55. Graphic interpretation of standard distribution.

11.2. Uncertainty type B

Uncertainty type B is determined by a scientific analysis based on all accessible information on changeability of initial value. Those data are: based on previously performed measurements, operator's experience, characteristic features of measured materials and measuring devices. Additionally, method B utilizes data from manufacturer's product specification, uncertainty reference data, handbook and manual content, all accessible publications and other. Data obtained from calibration certificate of a measuring device, standard masses and other certificates are also very important.

With application of an electronic balance, it is possible to determine the constituents of uncertainty type B, which are:

– reading unit d;

– repeatability, which is determined by standard deviation set earlier by an operator or during calibration process;

– balance indication error, specified in calibration certificate;

– uncertainty while determining an indication error with the defined coverage factor*k* (data enclosed in the calibration certificate).

In case of uncertainty type B analysis, rectangular distribution is employed:

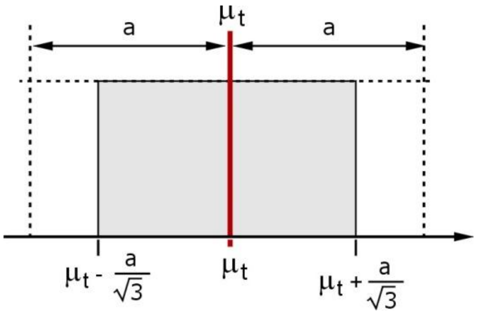


Fig. 56. Graphic interpretation of rectangular distribution.

Therefore, in order to calculate uncertainty value, initial data values should be divided by $\sqrt{3}$:

$$u_{typB} = \frac{a}{\sqrt{3}} \tag{62}$$

In case of resolution of a measuring device, where it is only possible to set the upper and lower limit of initial value, the uncertainty is determined by dividing the reading unit by 2√3:

$$u_{typB} = \frac{d}{2\sqrt{3}} \tag{63}$$

The uncertainty of determining the indication error is specified in the calibration certificate and is expanded uncertainty, standard uncertainty is calculated by dividing the expanded uncertainty (specified in the calibration certificate) by coverage factor k which is also specified in the calibration certificate:

$$u = \frac{U}{k} \tag{64}$$

11.3. Complex uncertainty

Complex uncertainty – in simple words – is a connection of uncertainty type A and type B. Most common is complex uncertainty. There are, however, some cases where complete uncertainty analysis is based on the type B.

$$u = \sqrt{u_A^2 + u_B^2} \tag{65}$$

One of the parameters is so called sensitivity ratio, which is related to the initial rate. It is a partial derivative which describes how the estimator of initial quantity changes in relation to changes in values of initial estimators. This parameter is characterized by a relation:

$$c_i = \frac{\partial f}{\partial x_i} = \frac{\partial f}{\partial X_i}\bigg|_{X_1=x_1 \ldots X_N=x_N} \tag{66}$$

where: c_i – sensitivity ratio
x_i – initial rate estimator
X_i – initial rate estimator

Participation in the complex uncertainty is expressed by a ratio:

$$u_i(y) = c_i \cdot u(x_i) \tag{67}$$

where: $u_i(y)$– participation in standard complex uncertainty
c_i – sensitivity ratio
$u(x_i)$ – standard uncertainty

11.4. Expanded uncertainty

Expanded uncertainty is a value describing the range of values surrounding the measuring result which, as expected, can cover a large part of values distribution, which are commonly assigned to measured.

According to Guide to Expression of Uncertainty in Measurements, letter **u** has been assigned to match uncertainty, and expression of expanded uncertainty is realized by capital letter **U**. Graphic presentation of measurement uncertainty is shown on below chart:

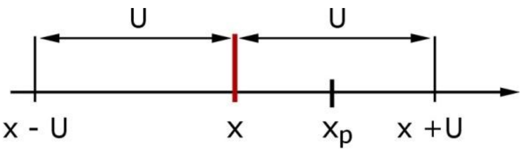


Fig. 57. Uncertainty of measurement

where: *x* – measurement result
x_P – measurand

As result of value measurement x_P value x has been obtained x. As seen above, the result of measurement is not equal to measurand - there are no accurate measurements: it is only possible to determine the range in which the result value might be positioned. Depending on the accuracy of a measuring process and the uncertainty related to it, the range can have bigger or smaller scope. Scope size depends for instance on the applied measuring device, environmental conditions, operator, as well as the proper analysis of measuring uncertainty.

An expansion ratio k is a numerically expressed ratio used as a multiplier of standard complex uncertainty, determined to set expanded uncertainty. The expanded uncertainty is expressed by a below relationship:

$$U = k \cdot u(x) \tag{68}$$

where: U – extended uncertainty
k – extension ratio
u(x) – complex uncertainty

The most commonly used expansion ration is $k=2$.The extended measurement uncertainty, correctly refers to confidence level, which equals approximately 95 %. Above case is correct in vast majority of calibration processes. For this reason international organizations decided that laboratories which perform calibration should specify the extended uncertainty U obtained by a multiplication of standard uncertainty by expansion ratio k = 2.

11.5. Uncertainty – mass measurement equation

The first stage of the measuring process analysis is introducing all the elements related to the measuring process. The mass measurement equation is presented below:

$$m = m_0 + \delta m_1 + \delta m_2 + \delta m_3 + \delta m_4 \tag{69}$$

where: m – measured mass
m_0 – weighed mass (the displayed weighment result)
δm_1 – correction connected with the balance repeatability parameter
δm_2 – correction connected with the balance reading unit d
δm_3 – correction connected with the balance indication error
δm_4 – correction connected with uncertainty of error indication determination

When measurement equation is correct, the next step is to make the measurement uncertainty equation which implies determination of all components uncertainty:

$$u^2(m) = u^2(\delta m_1) + u^2(\delta m_2) + u^2(\delta m_3) + u^2(\delta m_4) \tag{70}$$

The sensitivity ratio in this case equals 1 for all components of uncertainty.

$$c_i = 1$$

Below you will find the easiest way of uncertainty of measurement determination for 5 gram load, using the electronic balance with reading unit d=0,1 mg. According to the procedures of uncertainty of measurement determination, the first step is to specify the measurement equation which will include all the contributors and the equation of uncertainty of measurement.

Another step is to calculate uncertainty of particular elements of initial values:

Weighed mass – m0

As the sample is placed on the weighing pan of a balance, its mass is displayed as 5000 mg (for the purpose of simplification all below masses will be presented in mg).

Spread of balance indications – δm1

Based on several series of measurements, standard deviation of five repetitions s = 0,2 mg.

$$u(m_1)=u(s)=\frac{0{,}2\mathrm{mg}}{\sqrt{5}}=\frac{0{,}2\mathrm{mg}}{2{,}24}=0{,}09\mathrm{mg}\approx 0{,}1\mathrm{mg} \tag{71}$$

Balance reading unit – δm2

The applied analytical balance reading unit equals 0,1 mg, and thus the uncertainty referring to the resolution of the measuring instrument should equal:

$$u(m_2)=\frac{0{,}1mg}{2\sqrt{3}}=0{,}029mg \tag{72}$$

Balance indication error – δm3

The calibration certificate of the balance gives indication error of + 0,1 mg for 5 g, with uncertainty of measurement U = 0,02 mg and expansion ratio k = 2. The uncertainty is calculated from the equation:

$$u(m_3)=\frac{0{,}1\mathrm{mg}}{\sqrt{3}}=0{,}058\mathrm{mg} \tag{73}$$

Uncertainty of error of indication determination is 0,2 mg, but it is expanded uncertainty. It is necessary to obtain complex uncertainty, so 0,2 mg should be divided by factor k) usually k=2).

$$u(m_4=\frac{0{,}2\mathrm{mg}}{2}=0{,}1\mathrm{mg} \tag{74}$$

The next step is collecting all above results and formulating uncertainty budget, so that it is possible to observe which element influences the uncertainty the most. Uncertainty value is determined as a square root of all uncertainty squared elements sum (contribution to complex uncertainty). The uncertainty budget is presented below

Szmbol value	Value estimator	Standard uncertainty	Probability distribution	Sensitivity ratio	Contribution to complex uncertainty
m_0	5000 mg	-	-	-	-
δm_1	0 mg	0,1 mg	standard	1	0,1 mg
δm_2	0 mg	0,029 mg	rectangular	1	0,029 mg
δm_3	0 mg	0,058 mg	rectangular	1	0,058 mg
δm_4	0 mg	0,1 mg	standard	1	0,1 mg
m	5000 mg			uncertainty	0,16 mg

Standard uncertainty is calculated as below:

$$u(m) = \sqrt{(0{,}1)^2 + (0{,}029)^2 + (0{,}058)^2 + (0{,}1)^2} = 0{,}16 \qquad (75)$$

According to the procedure, the next step is calculating extended uncertainty U. It has been assumed in the above case that the expansion ratio k = 2. Expanded uncertainty is calculated as below:

$$U = k \cdot u(m) = 2 \cdot 0{,}16mg = 0{,}32mg \qquad (76)$$

The final measurement result, namely the balance indication at weighing 5 g equals

$$m = (5000{,}00 \pm 0{,}32)\ \text{mg} \qquad (77)$$

Uncertainty of measurement might be rounded off to the value of balance reading unit d, assuming that uncertainty of measurement should be always rounded up:

$$m = (5000{,}0 \pm 0{,}4)\ \text{mg} \qquad (78)$$

The test result with approximately 95% probability is placed in the range between 4,9996 g and 5,0004 g. The below picture shows how the balance reading unit influence uncertainty of measurement. Using the balance with reading unit smaller than 0,1 mg, e.g. d=0,001 mg will decrease uncertainty of measurement

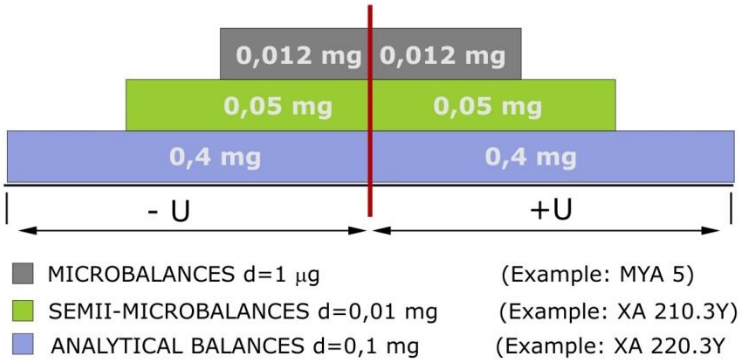


Fig. 58. Uncertainty of measurement depending on the balance reading unit

In practice, we can identify the following possible sources of uncertainty:

- imprecise sampling, i.e., the measured sample is not representative for defined measured quantity,
- Incomplete knowledge of the impact of environmental conditions on the measurement procedure, or imperfect measurement of the parameter,
- Subjective errors in reading the indications of analog instruments,
- Inaccurate values assigned to standard masses and reference materials,
- Simplifying approximations and assumptions used in methods and measuring procedures,
- Dispersion of values obtained in the process of observations repeated in seemingly equal conditions.

The success in estimating uncertainty of measurement depends on a thorough and correct analysis of the whole measuring process. It is very important that the estimation of measurement uncertainty should be adequate to its accuracy, since not always the components of the uncertainty influence the result.

11.6. Uncertainty for mass determination - comparison

For the electronic balance the uncertainty budget usually consists of the following elements:

▪ Balance repeatability	[Sd]	*Standard deviation in a series*
▪ Balance indications resolution	$[\ d = \frac{d}{2\sqrt{3}}]$	*d – balance reading unit*
▪ Balance indication error	$[\ \frac{E}{\sqrt{3}}\ ]$	*E – indication error from the calibration certificate*
▪ Uncertainty of indication error determination	$[\ \frac{U}{k}]$	*usually k=2* *U – expanded uncertainty from the calibration certificate*

Expanded uncertainty equals:

$$u = \sqrt{(Sd)^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{E}{\sqrt{3}})^2 + (\frac{U}{2})^2} \tag{79}$$

Expanded uncertainty equals:

$$U = u \cdot k \tag{80}$$

where: u – uncertainty
k – *coverage factor(2)*

11.7. Uncertainty of mass measurement at moisture determination

Uncertainty of the sample moisture determination should take it into consideration that this is a differential measurement. In order to obtain the final result it is necessary to weigh the sample before and after the drying. The uncertainty budget comprises of the following elements:

▪ Balance repeatability (standard deviation)	[Sd]	*Standard deviation in a series*
▪ Balance indications resolution	$[\ d = \frac{d}{2\sqrt{3}}\ ]$	*d – balance reading unit*
▪ Sensitivitz error (indication drift)	$[\ \frac{s}{\sqrt{3}}\ ]$	*s – indication drift*
▪ Uncertainty of indication error determination	$[\ \frac{U}{k}\ ]$	*usually k=2* *U – expanded uncertainty from the calibration certificate*

Uncertainty equals:

$$u = \sqrt{(Sd_1)^2 + (Sd_2)^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{d}{2\sqrt{3}})^2 + (\frac{s}{\sqrt{3}})^2} \qquad (81)$$

where: *Sd1 – repeatability for initial mass* *Sd1 = 0,3 mg*
Sd2 – repeatability for final mass *Sd2 = 0,3 mg*
d – reading unit for mass indicator *d=0,1 mg*
s – drift (the instrument basic error) *s= 0,5 mg*

$$u = \sqrt{(0{,}3)^2 + (0{,}3)^2 + (\frac{0{,}1}{2\sqrt{3}})^2 + (\frac{0{,}1}{2\sqrt{3}})^2 \ + (\frac{0{,}5}{\sqrt{3}})^2} \qquad (82)$$

Expanded uncertainty equals:

$$U = u \cdot k$$

where: *u* – uncertainty; *k – coverage factor (2)*

The achieved uncertainty result concerns the mass measurement. It should be applied to the initial and final mass of the sample. The inaccuracy of these mass value determination decides about moisture final result. This approach does not take into consideration uncertainty connected with the sample, taking the sample, its storing, inaccuracy of temperature measure, etc. The issue is complex. The practical tests reveal that the biggest mistakes result from the sample heterogeneity and its reaction to temperature (the coating forming, burning, careless drying). It should be emphasized that measuring using the moisture analyzer is not used instead of, but as a supplement of reference methods.

12. Measurement of small mass: minimal sample weight

Measurement of small mass is always problematic, not only for mass measurement. It results mainly from the accuracy of the used instrument. There are several elements influencing the electronic balance accuracy (previously described). Not all of them are essential for small mass measurement analysis. In the beginning it would be a good idea to pose a question what is small mass? Any explanation would do, especially that there is no formal answer. For further analysis it can be assumed that it is the sample mass smaller than 10% of max capacity. However, in some cases we measure a sample weighing several milligrams, in other situations several grams.

Analyzing the accuracy of this mass measurement, it is important to define what the balance accuracy in the beginning range depends on. The only necessary parameter is the balance repeatability of indications. It is defined as a standard deviation or so called spread (see unit 4.6.1.). For balances with a bigger reading unit d, we might achieve the same results. The difference between Max and Min equals zero in this case. What about standard deviation: does it also equal zero? In mathematical respect yes, but because of rounding the measurement results off, we should adopt the reading unit sd= 0,41d.

A series of measurements for AS 220.3Y balance, (Max 220 g d=0,1 mg):

1. 99,9998
2. 99,9998
3. 99,9998
4. 99,9998
5. 99,9998
6. 99,9998
7. 99,9998
8. 99,9998
9. 99,9998
10. 99,9998

Repeatability as spread (Max-Min), R=0,0000 g. Standard deviation sd = 0,41 x 0,1 mg = 0,041 mg.

Problems connected with small mass measurement are particularly important in the fields connected with health and safety. A good example would be pharmacy, especially American requirements. These are specified by Pharmacopeia document, section USP 41 (Balances) and USP 1251 (Weighing on an analytical balance). Section 41 contains guidelines referring to compulsory obligations, it determines requirements for balances intended for weighing substances that need to be accurately weighed. Weighing procedure has to be carried out using balance that can be adjusted within its full operating range and which meets requirements specified for repeatability and accuracy. For balances used for other applications, repeatability and accuracy shall depend on the balance use.

Requirements for repeatability take the following form:

Repeatability is satisfactory if two times the standard deviation of the weighed value, divided by the nominal value of the weight used, does not exceed 0.10%. If the standard deviation obtained is less than 0.41d, where d is the scale interval, replace this standard deviation with 0.41d. Here repeatability is satisfactory if two times 0.41d, divided by nominal value of the used weight does not exceed 0.10%. The test shall apply at least 10 cycles within one series.

$$\frac{2 \cdot sd}{m} \leq 0{,}10\% \qquad (83)$$

Requirements for accuracy take the following form:

The accuracy of a balance is satisfactory if its weighing value, when tested with a suitable weight(s), is within 0.10% of the test weight value. A test weight is suitable if it has a mass between 5% and 100% of the balance's capacity. MPE of test load, or alternatively its calibration uncertainty , shall not be greater than one-third of the applied test limit of the accuracy test.

MINIMUM WEIGHT notion is not comprised within section 41, nevertheless it can be found in section 1251, which contains information on weighing , operating conditions, possible disturbances of the process etc. The section refers to MINIMUM SAMPLE WEIGHT as follows:

a. Minimum weight is expressed by means of the below equation:

   M_{min} = k x s / required weighing tolerance

   Where:
   k – coverage factor (usually 2 or larger)
   s – standard deviation (of not fewer than 10 replicate measurements of a test weight).

The minimum weight describes the lower limit of the balance below which the required weighing tolerance is not adhered to.

b. For materials that must be accurately weighed section 41 stipulates that repeatability is satisfactory if two times the standard deviation of the weighed value, divided by the nominal value of the weight used, does not exceed 0.10%. for this criterion the equation above simplifies to:

   $M_{min} = 2000 \times s$

As it can be observed, determination of Minimum Weight consists in performance of repeatability test. Compulsory condition stipulated by section 41 is also tested. An indispensable help for this kind of tests is balance parameters optimization, carried out by a balance manufacturer (like Radwag).

12.1. Balance selection

Selecting a proper balance you can determine the max repeatability of this balance. If the sample weighs 80 g, the selected balance repeatability can be determined from the following equation:

$$s = \frac{A_{REQ}}{k} \cdot m_{\min} \qquad (85)$$

where: AREQ – the required weighing accuracy

Calculation:

$$s = \frac{0{,}10\%}{2} \cdot 80mg = \frac{80mg}{2000} = 0{,}04mg$$

The balance with repeatability 0,04 mg will probably meet the requirements, but it must be confirmed in the place of operation. You can choose e.g. XA 52.3Y balance; when you are planning to test different samples, XA 82/220.3Y balance will be suitable.

It is the balance manufacturer’s task to determine the minimal mass value; it is one of the most important metrological parameter. The user perceives the issue from a different perspective: which balance is suitable for the tested samples? The problem has just been explained.

Minimal sample weight values for particular balances are listed in the below table. The values are calculated for factor k=2.

Microbalances	UYA 2.4Y	MYA 2.4Y	MYA 5.4Y
Maximum capacity	2 g	2 g	5 g
Indication accuracy	0,0001 mg	0,001 mg	0,001 mg
MSW (USP)	0,8 mg	2 mg	2 mg

Microbalances	MYA 11.4Y	MYA 21.4Y
Maximum capacity	11 g	21 g
Indication accuracy	0,001 mg	0,001 mg
MSW (USP)	3 mg	3 mg

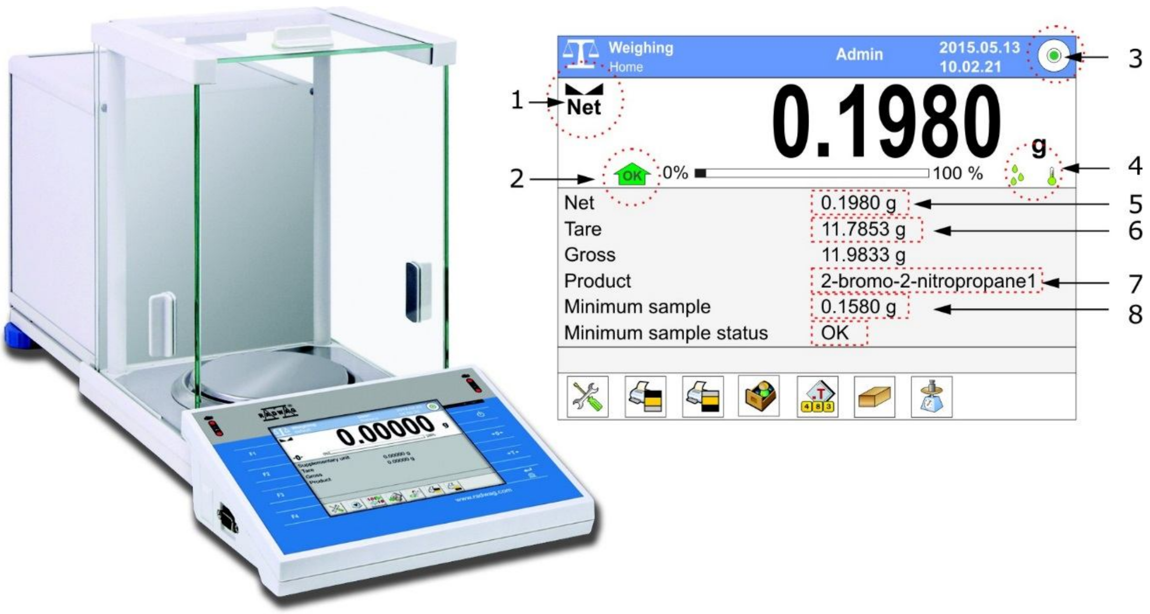
Anatytical balances	XA 52.4Y	XA 110.4Y	XA 210.4Y
	XA 52/2X	XA 110/2X	-
Maximum capacity	52 g	110 g	210 g
Indication accuracy	0,01 mg	0,01 mg	0,01 mg
MSW (USP)	20 mg	25 mg	30 mg

Anatytical balances	XA 82/220.4Y	XA 110 – 310.4Y
Maximum capacity	220 g	110 - 310 g
Indication accuracy	0,01/0,1 mg	0,1 mg
Min. naważka (USP)	20 mg	160 mg

Anatytical balances	AS 82/220.3Y AS 82/220.X2 AS 82/220.R2	AS 110 – 310.3Y AS 110 – 310.X2 AS 110 – 310.R2
Maximum capacity	82/220 g	110 - 310 g
Indication accuracy	0,01/0,1 mg	0,1 mg
Min. naważka (USP)	30 mg	200 mg

SUMMARY

We usually weigh the sample mass in packages, boxes or flasks, etc. the conditions are different for weighing small mass and big mass (mechanical stress, electronic systems working range, etc.). The tare range matters while determining threshold value for minimal sample weight. It can be assumed that for the tare value close to the balance Max capacity, the threshold for weighing min sample weight should be increased by 50%. It is a hint at the same time: the container size should be adjusted to the tested sample size. A valuable support when taking actions aiming to comply to the said requirements is MSW software of each 3Y/4Y series balance. See the figure below.



Net 0.1980 g
Tare 11.7853 g
Gross 11.9833 g
Product 2-bromo-2-nitropropane1
Minimum sample 0.1580 g
Minimum sample status OK

1 – stable measurement

2 – pictogram for Minimum Weight threshold, the weighed value is greater than the threshold value (OK.)

3 – balance level pictogram (OK.)

4 – ambient conditions pictogram, humidity / temperature (OK.)

5 – net weight

6 – used tare weight

7 – weighed sample name

8 – minimum weight threshold value (determined in course of the test)

13. External conditions in weighing processes

The specification of every weighing instrument features the usage conditions. The specification of electronic balances determine the temperature range, humidity, some determine the dynamics of changes, etc. However, fulfilling those conditions is a different story, which is sometimes noticed in a more detailed audit. For the user it is important if the balance still measures accurately in different conditions, regardless of the usage conditions stated in the manual. The detailed analysis would require a separate publication.

The balance operating conditions stability is a theoretical issue. We should discuss the dynamics of changes in time unit e.g. 0,5°C per hour. Whether those changes matter or not depends on their value, dynamics and the balance (reading unit).

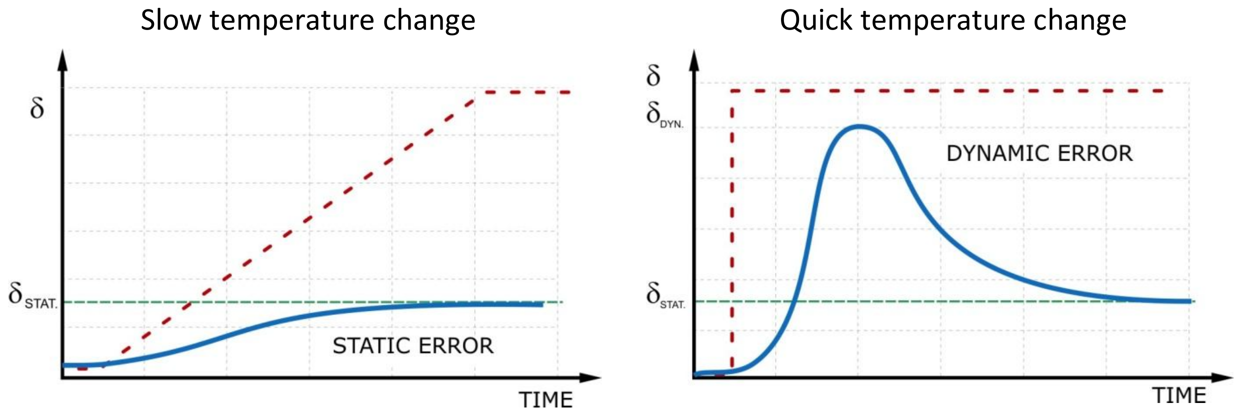
13.1. Temperature

Temperature is the measure of the object heat condition. When the two objects have the same temperature, in the direct contact they will not transfer the heat; when their temperature is different, the object of higher temperature will transfer heat to the object of lower temperature until the temperature of both objects is the same. Does it concern electronic balances?

A quick and dynamic temperature growth negatively influences metrological parameters. It is connected with the balance construction elements expansion and the temperature factors of the magnetoelectric converter. Balances with different reading units d will react differently. The widely known rule is following:

The smaller reading unit d, the higher requirements for the temperature stability

The below graph shows a hypothetical balance behavior:



Slow temperature change

Quick temperature change

Fig. 59. Balance accuracy at temperature changes

Graph on the left shows a slow temperature growth in the environment (dotted line). The balance does not react, as the balance system error is compensated. Graph on the right shows a quick temperature growth, which usually causes a dynamic error. The dynamics of changes is too big for the balance system to compensate it.

For balances with quite high resolutions (10-20 mln), dynamic temperature changes are responsible for repeatability deterioration. This parameter test might differ from the value declared by the manufacturer and achievable in stable conditions.

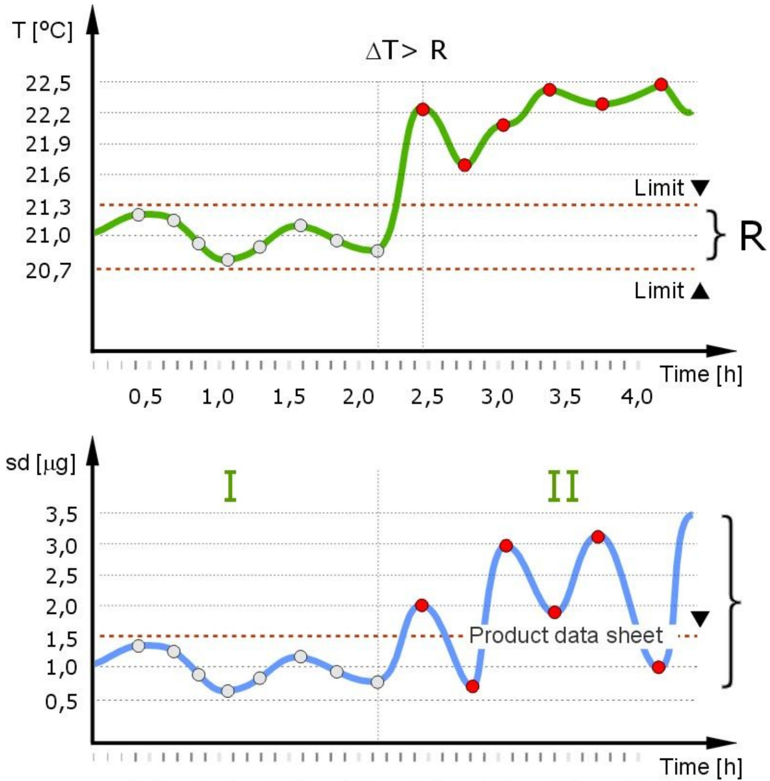


Fig. 60. Balance repeatability in dynamic conditions

When the temperature is stable in a given range, repeatability will be accurate, in accordance with the value declared by the manufacturer.

How to deal with the problem?
Quite easy solution – a frequent balance adjustment. It should be carried out before the tests. The weighing time is too short to deteriorate the balance measurement. Our actions effectiveness depends on the accuracy we would like to achieve. The issue of temperature change should always be discussed in the context of the balance resolution and the balance resistance. Operating temperature of laboratory balances remains stable in most of the cases therefore the problem is not that much significant. It may occur wherever there is lack of automatic temperature adjustment option and wherever day temperature and night temperature considerably differ.

What can the manufacturer do?
RADWAG monitors all balances with electromagnetic converter in the range of application temperature, which contributed to creation of mechanisms compensating the influence of temperature on the balance indication accuracy. Another aspect are electronic elements of very high parameters: it is necessary to use them for high resolution balances RADWAG offers, e.g. MYA 21 balance (21 000 000 reading units).

13.2. Humidity

Maintaining stable level of humidity, e.g. 50% ± 5%, requires use of humidifying and dehumidifying system. These two should be coupled but even though the problem of nominal value readjustment would not be solved. The described system is a highly complicated one and it must be adopted to the room size, intensity of its use, ventilation system etc. In practice, for humidifying purposes humidifiers are used, without the need of applying dehumidifiers. This means that as a result of change of atmospheric air parameters one may observe humidity increase in the laboratory. Does it affect weight measurement?

The answer depends on :

- Used balance type
- Weighed samples
- How accurate the sample weight must be

The balance, as every object, absorbs humidity settling on the construction elements, which affects the instrument proper work. The humidity absorption process will not influence every balance. This effect will be noticeable in case of balances with reading unit 10 μg, 1 μg and 0,1 μg. We notice the zero indication drift (when the pan is not loaded) and the change of the balance sensitivity (accuracy error). The below picture shows the balance behavior at humidity change:

The air is the quick medium, therefore, a 20% humidity change takes place quickly; the balance adopts to this change much longer.
It is reflected in zero indication drift, which will lead to the balance repeatability deterioration.

In the first period the balance reaction is slower [I], as humidity change must break the balance construction barriers.

Period marked as [II] is the stage when the air in the room is already stable, the balance still shows the indication drift, absorption process still continues. It is best to maintain humidity on the same level.

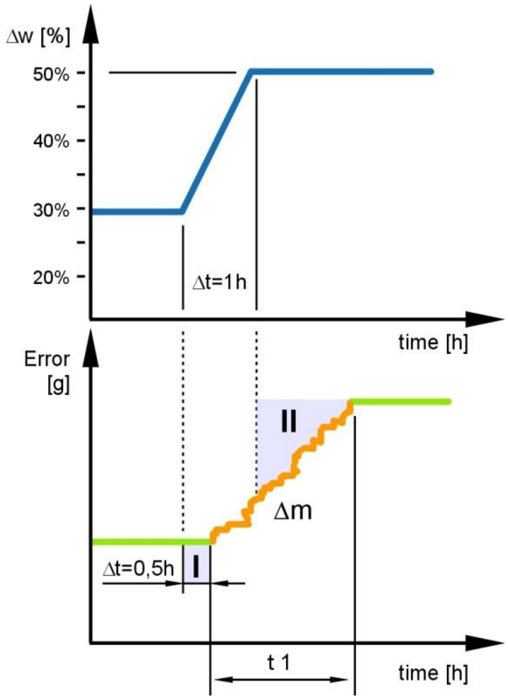


Fig. 61. Influence of humidity change on mass measurement

If the reading unit of your balance is not smaller than 0,01 mg, then the laboratory humidity level may vary dynamically. Variable humidity, 20% increase/decrease over a specified time period, shall not influence metrologically important parameters of the balance. When sample weight does not have to be precise, i.e. when it is enough to determine its value with less than 99 percent accuracy, then any parameters changes become insignificant.

It is commonly considered that low humidity results in occurrence of electrostatics, but practice proves that it is not necessarily true. Electrostatics occurrence actually depends on weighed samples type. Applied measurement methodology shall refer to problem of electrostatics creation, actions against its occurrence should be taken. As for the actions, in order to remove unwanted charges form the sample it is usually recommended to perform ionization.

13.2.1. Humidity influence on sample weight measurement

There are two aspects of humidity influence on a sample. The sample weight may vary due to absorption or desorption processes. Each of these adds to user dissatisfaction. It is clear that the user expects to get a stable result rather than observe drift of indication making him/her realize that sample weight determination is not possible. In order to conclude on source of such instability it is necessary to deposit a load characterized by constant weight on a weighing pan, e.g. mass standard. If the obtained result is stable, then it is certain that measurement instability is an effect of processes occurring within the sample.

Guidelines:

1. prior weighing the samples should be acclimatized to the ambient temperature, desiccator shall be applied for acclimatization purposes
2. for gross measurement, the packaging size shall be selected respectively to sample size
3. prior weighing the sample shall be mixed in order to provide homogeneity, it may happen that surface layers of the sample contain more moisture

Example processes where there are problems with sample weight instability:

a. **differential weighing of cellulose filters, measurement of dustiness**

   GUIDELINES:

   Use glass fibre, quartz or Teflon (PTFE) filters, these do not absorb humidity therefore it is the absorbed medium that is being measured, not moisture. Electrostatics process may occur in case of PTFE filters. If this is so then +/- charges ionization is recommended.

b. **not acclimatized sample weight determination after prior thermal processing (heating, burning)**

   GUIDELINES:

   Stabilize sample weight, using desiccator provide stable temperature and humidity. If the sample is to be weighted when it is still warm then the measurement must be performed quickly (optimization), the indication is certain to decrease. Such is the result of hot air convection currents formation occurring in a weighing chamber.

c. **dry powders weighing when the humidity level is high**

   GUIDELINES:

   The sample shall be kept in a closed container, it must be mixed prior weighing, weighing time shall be optimized (as short time as possible), the first stable indication shall be taken for analysis (successive measurements will be increased – process of absorption)

d. determining weight of cardboard sample, absorption of humidity

Samples comprising cellulose are hygroscopic samples which means that their weight changes over time. Sample weight increase depends on humidity level of a particular room and on the sample surface size. Balance reading unit is important too (possibility of variation detection).

GUIDELINES:

Isolation of a sample from the environment (weighing packaged samples), acclimatizing a sample to ambient conditions of a room.

The issue of humidity change concerns not only electronic balances, but also weights. OIML R 111-1 requirements ‘Weights of classes E_1, E_2, F_1, F_2, M_1, $M_{1\text{-}2}$, M_2, $M_{2\text{-}3}$ and M_3’ state the climate conditions that must be fulfilled for the weights storing and calibration. Therefore, the laboratory conditions must be the same. You will find the norm requirements below:

Standard class	Temperature change at calibration process
E_1	± 0,3°C within 1 hour (max. change ± 0,5°C/12 h)
E_2	± 0,7°C within 1 hour (max. change ± 1°C/12 h)
F_1	± 1,5°C within 1 hour (max. change ± 2°C/12 h)
F_2	± 2°C within 1 hour (max. change ± 3,5°C/12 h)
M_1	± 3°C within 1 hour (max. change ± 5°C/12 h)

Standard class	Air relative humidity range
E_1	40% do 60% (max. change ± 5% / h)
E_2	40% do 60% (max. change ± 10% / h)
F	40% do 60% (max. change ± 15% / h)

SUMMARY

Processes relating to humidity interactions are physical processes and they concern every single balance. Possibility to observe their effect depends on the given process scope, balance resolution and sample susceptibility. For low humidity level required, electrostatics processes may occur. Electrostatics process may be eliminated by particular balance design, e.g. antistatic shield, such one that is used for MYA or XA 4Y series microbalances.

13.3. Electrostatics

Electrostatics is a branch of physics that deals with the phenomena and properties of stationary or slow-moving electric charges with no acceleration. This property is described by Coulomb’s law:

$$F = k \cdot \frac{q_1 \cdot q_2}{r^2} \tag{83}$$

‘The force between two charges is proportional to the amount of charge on both charges and inversely proportional to the square of the distance between them’.

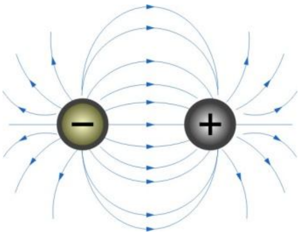


Fig. 62. Distribution of electrostatic field forces

The above situation (the field source is the charge focused in one point) is impossible in practice. The description is purely theoretical. In case of balances, electrostatic property is the force of the charge on the weighed instruments and the charges of the weighing chamber elements like e.g. glasses. In this case we can talk about the electrostatic field intensity between two fields. As those fields might be totally different, the effect between two plates is a certain approximation.

This intensity value is described below:

$$E = \frac{U}{d} \tag{86}$$

where: U – *potential difference between the plates*

d – *distance between the plates*

Depending on the charges kind and the fields that exert influence on each other, we can obtain the balance reaction in the form of:

- Increasing indication drift, when the charges are reverse, they attract one another;
- Decreasing indication drift, when the charges are the same, they repulse one another;

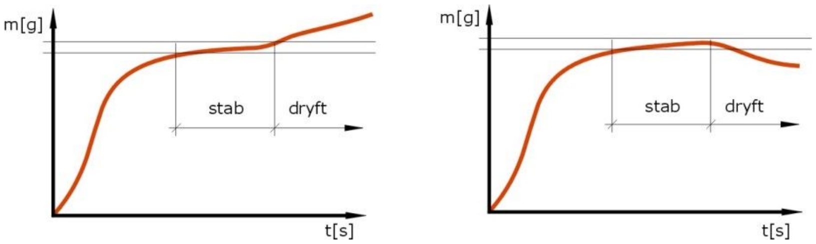


Fig. 63. Indication drift resulting from electrostatic interaction

Electrostatic interactions do not usually take place in the workplace. When the, phenomenon takes place, it is usually because of the sample characteristics and low humidity. In order to prevent it, it is necessary to know that:

- When a negatively charged object comes in contact with an electrically neutral object, the electrons excess will be divided into two objects. As a result, both objects are electrified with the same charge.

- When a positively charged object comes in contact with an uncharged object, a part of electrons will be electrically transferred from the electrically neutral object to the electrically charged object whose positive charge will be decreased. As a result of the loss of a part of electrons, the uncharged object will be charged positively.

In the phenomenon of electrification by contact, the objects will be charged with the same charge. Therefore, it is impossible to obtain a neutrally charged object.
Electrostatic charges might form as a result of:

- Transmission of non-compensated charge from the air;
- By rubbing two non-conductive objects;
- A hand touch.

The assessment of phenomena related to electrostatics as quite complicated, as we can only see the phenomenon effect, not the phenomenon itself.

As it is impossible to remove the source, we try to eliminate or compensate unwanted charges. The solution offered by RADWAG is the ionizer, which neutralizes electrostatic charges.
This device generates ions whose electric charge is opposite than the charge we would like to remove. It compensates the charge on the operator's hand and in the weighing chamber during opening the draft shield. In the stable conditions the speed of ionization equals the speed of recombination , which keeps ionization of the medium on the same level.

XA 60/220.3Y balance with ionizing frame

13.4. Air movement

There are a lot of publications about ergonomic solutions in the laboratory, but they do not concern the specific needs of electronic balances.

The influence of air on the weighing process is meaningful for the balances with reading unit d ≤ 0,1 mg. In practice it does not concern other balances. We will not analyze the balances in the close vicinity of production lines. Generally speaking, the issue of air influence on mass measurement gets down to two things. The first one is laboratory area with a natural air flow, which is sometimes forced by air conditioning. Air flow and air temperature in air-conditioned room is shown below:

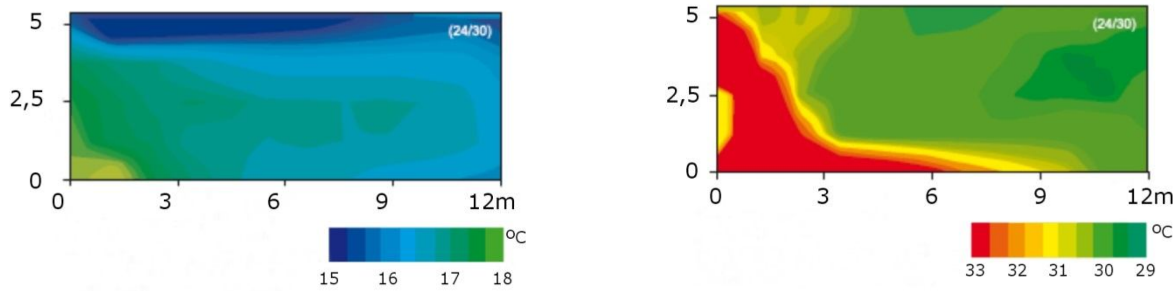


Fig. 64. Distribution of temperature and air flow typical of air conditioning

A different temperature distribution forces a certain pattern of air flow. A typical air conditioning is not the most favorable solution, especially for microbalances with d=1 µg.

Another thing is the balance construction: the weighing module, weighing chamber, weighing pan. The leakproofness and construction of these elements should limit the air flow and its influence on the weighing result. Therefore, the grid weighing pans are used for balances with reading units d ≤ 0,1 mg. Another solution is glass shields installed on the balance construction. Below the instance of UMYA 2 balance:

Grid weighing pan, external shield of the microbalance

The noticeable influence of air movement is the balance instability of indications. The weighing time prolongs, it is possible to oscillate around the stable result. The following relation is true: the bigger pan size, the stronger the effect. The weighing pan behaves like a sail catching the wind. It is a physical phenomenon and concerns all balances. As this disturbance considerably worsens indication repeatability, the following construction relation is used:

The smaller reading unit [d], the smaller diameter of weighing pan

Therefore, there is no balance whose reading unit d=0,001 mg and weighing pan e.g.⍰⍰ 80 mm. It is possible to construct, but there is no guarantee of accuracy. The exception is the balance for weighing filters, but it is totally different than regular weighing pans.

MYA 0.8/3.3Y microbalance weighing pan

the weighing pan shield in the mass comparator

For certain weighing processes special solutions protecting the pan must be used. Like in case of mass comparators, where accuracy matters more than a free access to the pan or the measurement speed. Unfavorable working conditions do not mean losing accuracy. It is regulated by the balance resistance, namely the ability to show the accurate results at the disturbances.

13.5. The ground vibrations

There have been many theories concerning this effect. However, we are not going to describe it, but focus on its influence on the electronic balances. Weighing mass is determining the force it is attracted by the Earth. The balance generates force F_C counterbalancing gravity force F_G, which makes a balanced weighing system. Buoyancy force F_W is neglected in this case:

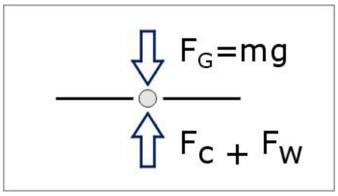


Fig. 65. Weighing process - the system of forces

The vibrations cause the system to lose the balance, which is reflected as the indication instability. The whole measuring signal filtering analysis is not analyzed, and it also influences the indication. Vibrations might be man-made (machines, devices, transport), as well as natural (seismic shakes).

What is the solution?

On the one hand, using special balance constructions; on the other hand using anti-vibration tables. These constructions feature special vibration isolators which effectively suppress the ground vibrations, e.g. SAM/M anti-vibration table with a granite top (for the microbalance) or a concrete SAL/STONE console (for all balance types).

Components absorbing vibrations are installed also for typical laboratory tables. Steel frame and two stone tops closed in a stylish MDF-made jacket provide professional workstation, which has been equipped with two lockers, providing option for installation of computer and USP power supply or power strip, and a pull-out shelf intended for the keyboard and the mouse. Needless to say, monitor rack adds to workstation ergonomics.

As previously noted, the vibrations might be caused by seismic shakes. Their nature might be very different. Therefore, anti-vibration protection can prove ineffective. The below example is a case of seismic shakes registered on 11th April, 2012 at 08:38 UTC. It was an earthquake on the Indian Ocean, approx. 600 km west from the northern part of Sumatra.

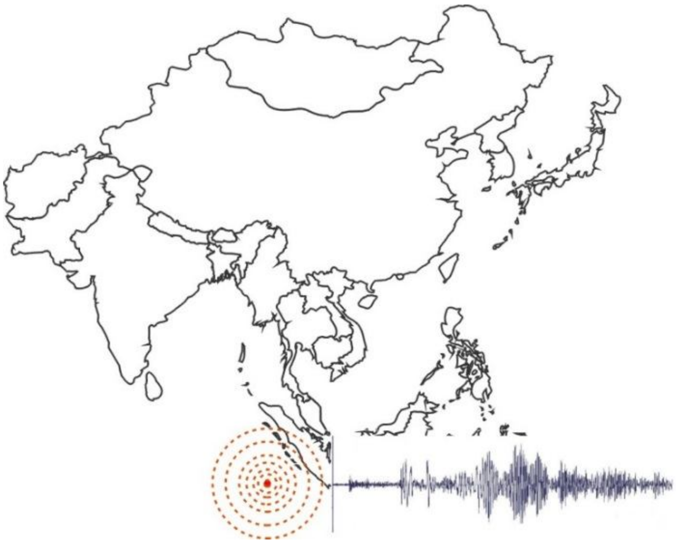


Fig. 66. Seismic shakes - Sumatra

The below diagrams show the earthquake influence on the microbalance indications:

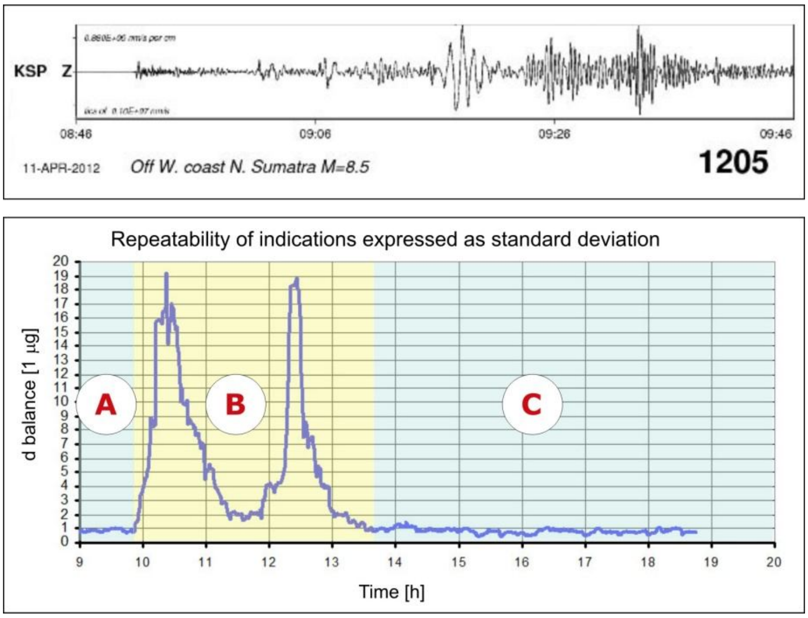
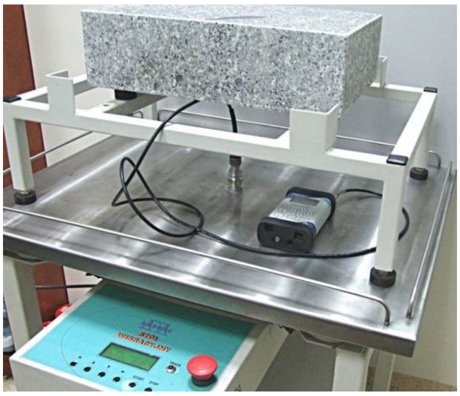


Fig. 67. The shakes influence on the balance repeatability

The first diagram shows the reading of seismograph in South Poland which registered the first shakes at 08:50. The shakes are the strongest between 8 and 9 UTC. From March to October the local time in Poland is UTC + 2 hours.

The other diagram shows the balance repeatability of indications. Before the shakes it is 1 sd, during the shakes it is almost 20 sd. This phenomenon impact is impossible to eliminate on the level of software, because of its nature (the shakes deformed by the Earth crust). The issue is problematic in areas of high seismic activity.

Vibrations from different sources can be quite efficiently eliminated using proper software or mechanisms. RADWAG solutions are the outcome of a long research. We check not only the level of construction vibrations suppression, but also the behavior of a balance subject to vibrations. Below the example of the test. A granite slab was placed on a special construction. The shock absorption elements are the same as in a typical anti-vibration table SAL/M. This construction was installed on a vibration table and we registered the indications of vibrations detector on the vibration table and the granite slab.



Testing vibrations of vibration table

Testing vibrations of a granite slab

The test revealed that for vibration amplitude ½Max, the anti-vibration table suppresses 65% - 92% (depending on the frequency).

13.6. Electromagnetic interference

Every operating device is a source of electromagnetic interference. It can be stated that a workplace is an electromagnetic place where:

- All devices are subject to electromagnetic interference emitted by other devices,
- All devices emit electromagnetic interference

Therefore, we can talk about electromagnetic compatibility: the balances and other electronic devices ability to work properly in electromagnetic environment. In practice it means that the balance:

- Emits electromagnetic interference that does not distort the work of other devices,
- Is resistant to interference emitted by other devices.

Electromagnetic disturbance

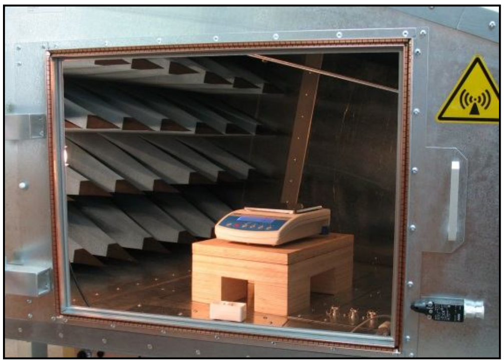
it is every electromagnetic effect that might negatively influence the balance operational parameters. It includes a signal emitted by another device operating in the same environment, electromagnetic noise, transient state in electric circuits., etc.

Electromagnetic disturbance might cause:

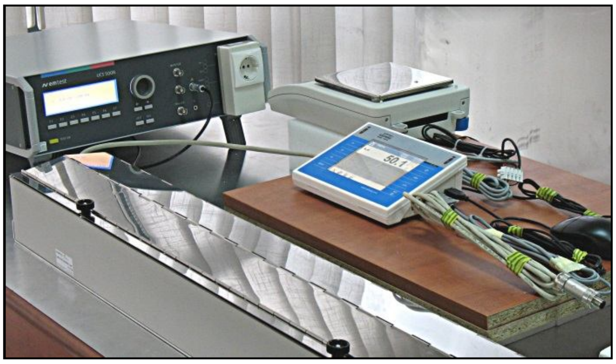
- Unstable states;
- Turning off or restart of internal programs,
- The display hibernation,
- Introduction of systematic error to the test result,
- Permanent failure.

In case of electromagnetic compatibility, declaration of conformity only with PN-EN 45501 norm is not sufficient. This norm includes only balance resistance tests, it does not include emission tests.

Therefore, it is necessary to carry out additional tests confirming that the balance is conformable with PN-EN 61326-1 norm. This would provide the legal basis to mark the balance with CE sticker or M for verified balances. Those tests are carried out in RADWAG Electric Laboratory.

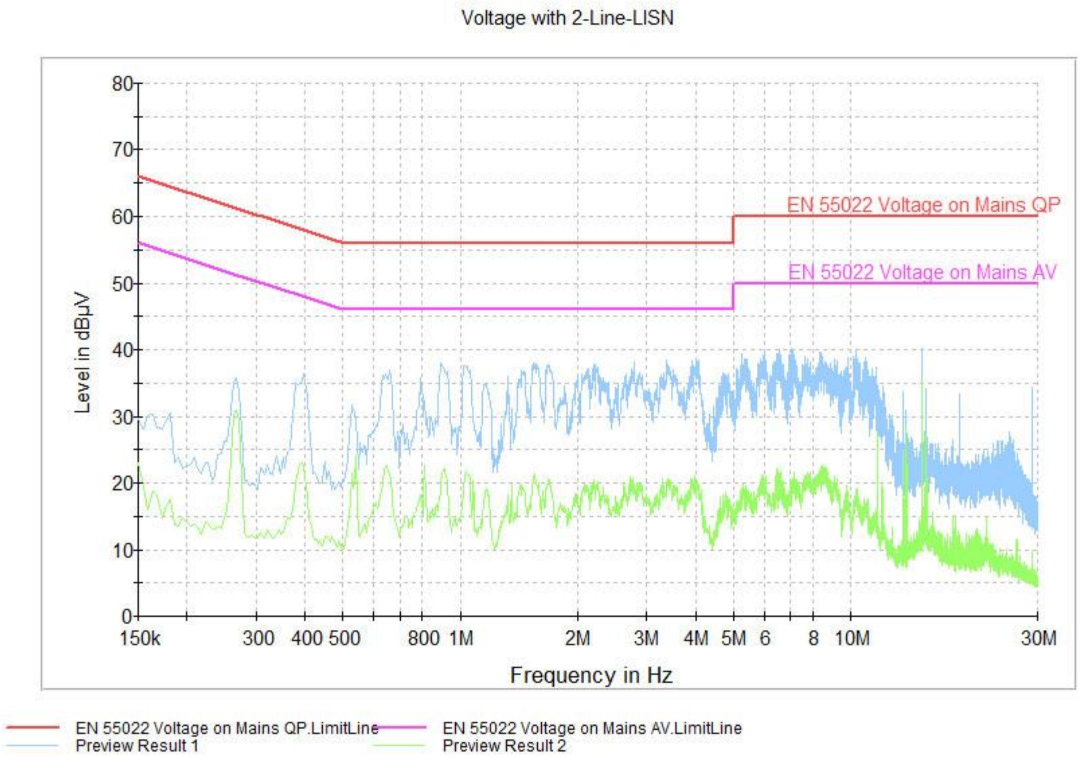


Testing the balance resistance in GTEM chamber

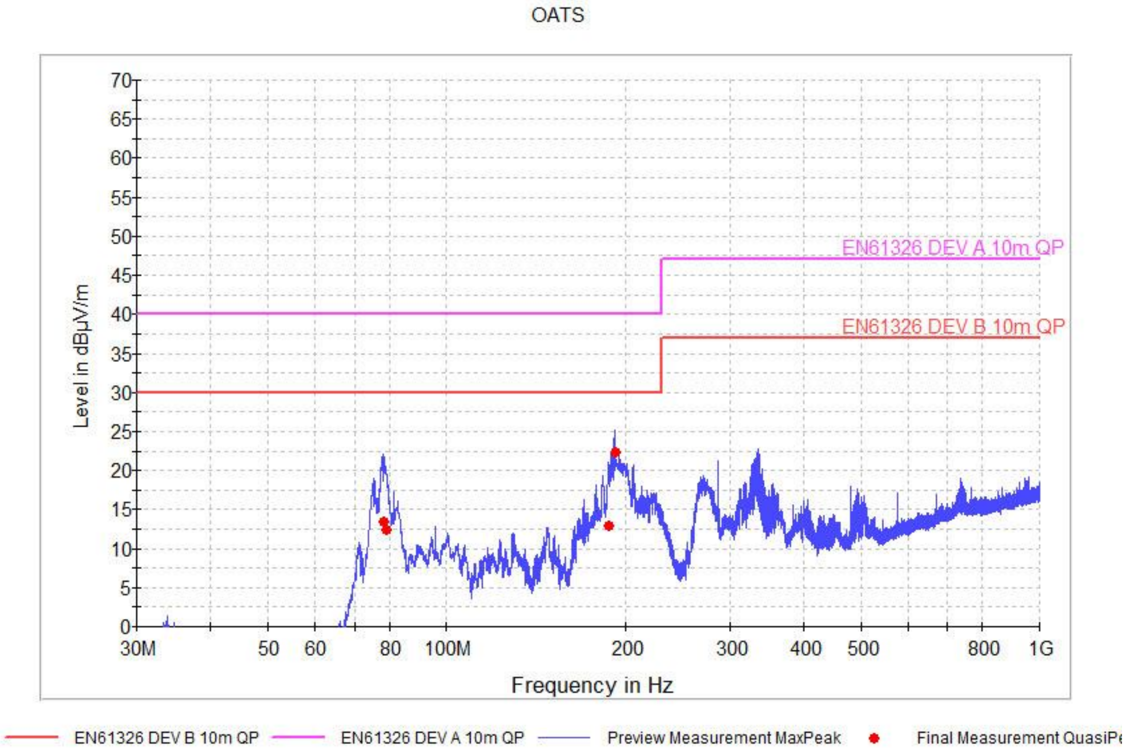


Testing the balance resistance to interference

Testing conducted emission for AS 310/C/2 balance:



Testing radiation emission of AS 310/C/2 balance:



RADWAG also includes this parameter in the balances. The test results are used also to improve electronic balances construction.

14. Semi-automatic procedures of balance control

Obtaining measuring data in case of electronic balances requires the operator's interference. Fully automatic systems are not commonly used probably because of the cost, complicated construction, the sampling method, etc. The same concerns the balance control: we need to plan, prepare standards. Sampling does require human interference, but the balance control might do without it. We can use the balance systems of internal adjustment to control it. This solution is offered in most RADWAG balances.

14.1. GLP report

The function's task is the automatic determination of the balance indication repeatability in the operational conditions. Repeatability is calculated out of a series of 10 weighments of the internal adjusting weight. In this procedure we additionally obtain information concerning the deviation of Max capacity from the expected (real) value. It is at the same time Max indication error for this mass value. Repeatability is calculated from the below equation:

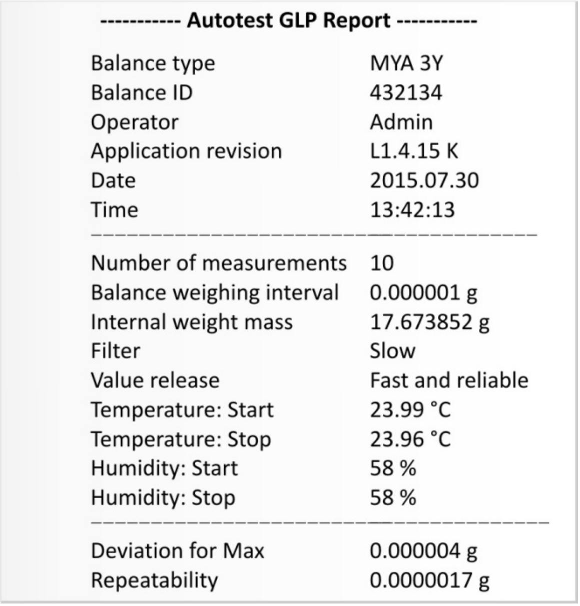
$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}} \qquad (87)$$

where: s – *standard deviation*
x_i – *another weighment*
$\overline{x}$ – *arithmetic mean from a series of weighments*
n – *number of repetitions in a series of weighments*

The operator activates the function which is fully automatic. The final result is displayed and possible to print out (report) or to export to the external memory through a USB port.

The report has been presented in the later sections of this publication. It includes three fields:

- The balance identification data and test performance time. The balance is identified by a unique serial number;
- Information on ambient conditions for which the test was carried, and on the most important balance parameters;
- The test final results which when subjected to analysis let assess stability of indications over time and standard variation of indications;



```
---------- Autotest GLP Report ----------
Balance type                MYA 3Y
Balance ID                  432134
Operator                    Admin
Application revision        L1.4.15 K
Date                        2015.07.30
Time                        13:42:13
------------------------------------------------
Number of measurements      10
Balance weighing interval   0.000001 g
Internal weight mass        17.673852 g
Filter                      Slow
Value release               Fast and reliable
Temperature: Start          23.99 °C
Temperature: Stop           23.96 °C
Humidity: Start             58 %
Humidity: Stop              58 %
------------------------------------------------
Deviation for Max           0.000004 g
Repeatability               0.0000017 g
```

14.2. Autotest Filter

Most modern balances have several filters and other settings allowing to optimize the balance adaptation to operational conditions. Effective use of those possibilities requires practical skills and numerous tests. Therefore, most users do not use those functions. Technical aid is necessary; diagnostic function autotest filter available for Y series balances.

This function **automatically** tests repeatability of indications and determines the measuring time for every for all possible combinations of settings: filter → *result confirmation.* The user has 5 levels of filtering and 3 levels of result confirmation to choose from. The test cannot be carried out manually as it would be too time-consuming.

Weighment time is calculated as the average of 10 measurements of internal mass. This parameter is an approximation of real time, as the time algorithm starts counting the time since the moment of selecting ‘put weight’ function. The measurement end is the stable state achieved according to the determined criteria (user menu).

The measurement time is determined with certain approximation because:

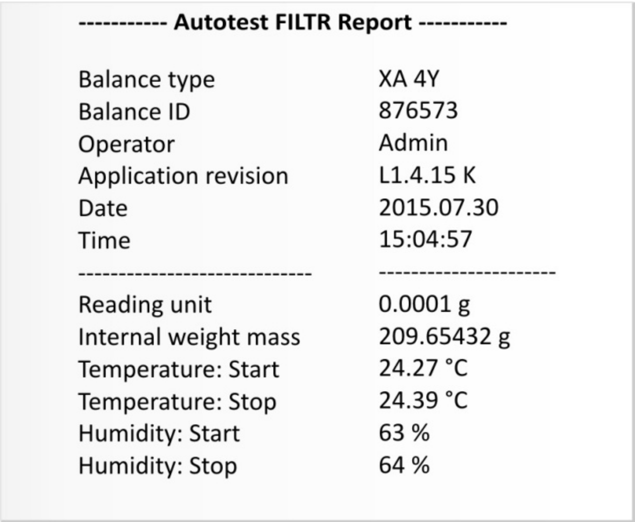
- The tests are carried out automatically by the balance internal mass, so the putting conditions are 100 % repeatable; in practice it is hardly possible to achieve – surges on the weighing bench might appear during the test;

- In practice mass measurement concerns objects like flasks, sinks, weighing vessels, etc. of different size, external conditions might influence the test.

Analyzing report results you can select optimal settings for a particular workplace considering the test duration time or determined repeatability.

After completed procedure the balance displays results which help the user to decide which setting is the one that provides an optimal result:

- the shortest time for measurement
- the best repeatability

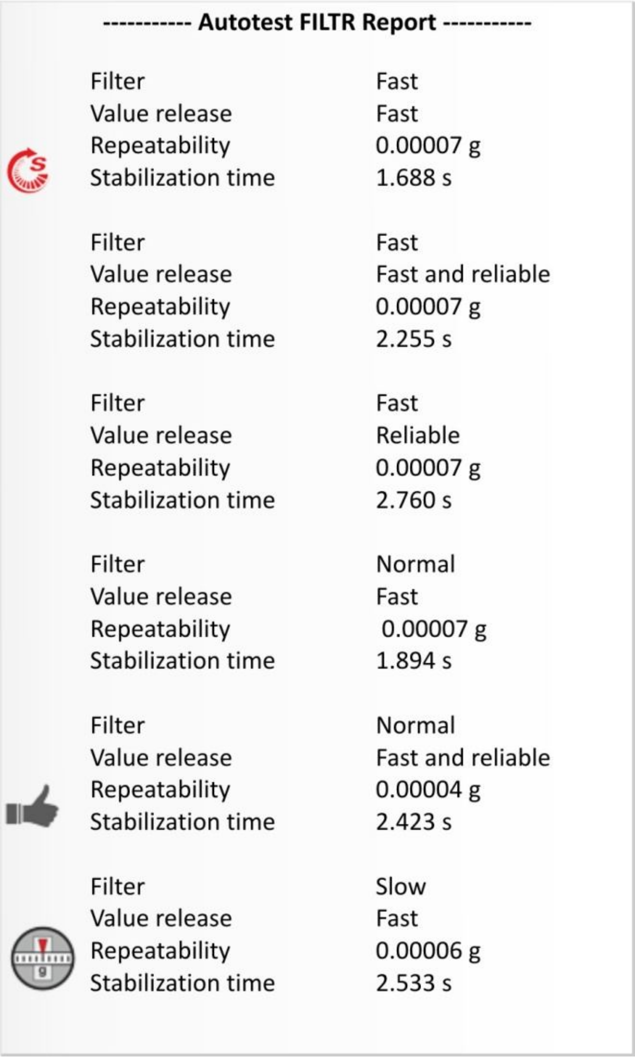


```
----------- Autotest FILTR Report -----------

Balance type                  XA 4Y
Balance ID                    876573
Operator                      Admin
Application revision          L1.4.15 K
Date                          2015.07.30
Time                          15:04:57
-----------------------------  ----------------------
Reading unit                  0.0001 g
Internal weight mass          209.65432 g
Temperature: Start            24.27 °C
Temperature: Stop             24.39 °C
Humidity: Start               63 %
Humidity: Stop                64 %
```

First part of the report contains data on a balance and working conditions parameters.

The other part includes results obtained within the test. Current balance settings are marked with a tick. In order to swap to other settings one shall click a respective option.



```
----------- Autotest FILTR Report -----------

Filter                   Fast
Value release            Fast
Repeatability            0.00007 g
Stabilization time       1.688 s

Filter                   Fast
Value release            Fast and reliable
Repeatability            0.00007 g
Stabilization time       2.255 s

Filter                   Fast
Value release            Reliable
Repeatability            0.00007 g
Stabilization time       2.760 s

Filter                   Normal
Value release            Fast
Repeatability             0.00007 g
Stabilization time       1.894 s

Filter                   Normal
Value release            Fast and reliable
Repeatability            0.00004 g
Stabilization time       2.423 s

Filter                   Slow
Value release            Fast
Repeatability            0.00006 g
Stabilization time       2.533 s
```

Fig. 71. Autotest FILTER - results

The shortest time

The best of repeatability

Optimal parameters

15. Differential weighing in practice

The idea of differential weighing has been known for years: it implies determination of the same object at least twice. The test checks the sample stability in time or the sample mass change after some processes like heating, burning, contamination absorption, etc. We should consider what factors influence the test accuracy. The processes the sample goes through is a separate issue and will not be described in this unit.

Several sources of elements influence the differential weighment accuracy; they result mainly from the sample size. Let us consider only two values: a very small sample weight and a very big sample weight (in relation to the balance Max capacity).

15.1. Differential weighing of small sample weight

As discussed in the previous units, the only meaningful parameter for weighing small samples is the balance indication repeatability, because we weigh at the beginning of weighing range. The accuracy of weighment will be the result of repeatability – the better repeatability, the higher accuracy.

Usually when a load is taken off the weighing pan, the balance indication comes back to zero [0.0000]. Another weighment starts with so called ‘exact zero’ and the result might be afflicted only with repeatability error (determined for small sample weight). It is known that balance accuracy depends on balance sensitivity. For mass standard of 5g weight, the balance indication shall be exactly 5.00000g. Sensitivity is of course regulated by means of an internal adjustment procedure performance – usually within 50% - 75% of maximum balance capacity. The relation is linear in its character therefore insignificant deviations of high weighing range are of no importance when the sample is light (green area). See the below chart.

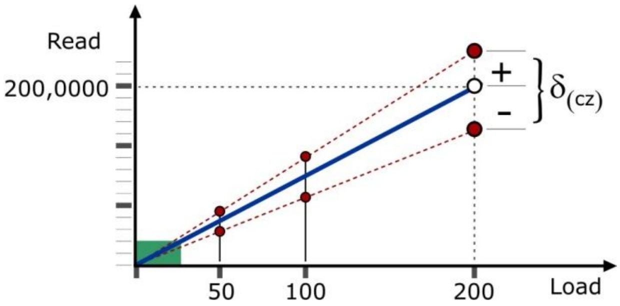


Fig. 72. Deviation of sensitivity for samples of light weight

Note:
The balance sensitivity test which implies weighing a standard of mass similar to the tested sample makes sense. It all depends on the required accuracy of weighing. Despite the automatic adjustment systems, the balance can show slight sensitivity drifts. A test with a standard will detect them. Weighing the standard also causes a spread of indications.

Zero indication drift might negatively influence the weighment accuracy. It might result from inadequate conditions for weighing (temperature, humidity, air movement). It might also be the outcome of the processes the sample was subject to. When you test abrasion resistance, we rub two samples (Schoppera-Schlobach method, Taber-Abraser), which will cause electrostatic problem.

Sometimes the elements used in the weighing process have an unbalanced electrostatic charge, which causes a vast spread of indications. An example of differential weighing of small sample weight is labeled as fraction PM 10 (particulate matter), abrasion testing, surface oxidizing processes, etc.

15.2. Differential weighing of big sample weight

Defining accuracy of this process implies more work as the balance whole weighing range is involved. It is necessary to know a lot about indication repeatability, linearity and sensitivity stability in time (the sample is weighed in time intervals). Testing linearity and repeatability was described before. Concerning sensitivity stabilization, all drifts are eliminated in the balance adjustment process. The procedure is following:

- Carry out adjustment before the first weighment;
- Next test the balance indication with a weight standard similar to the sample weight;
- Weigh the sample;
- Do all the activities connected with the sample;
- Stabilize the sample to the room temperature (when it is different);
- Carry out the balance adjustment before the next weighing, and test the balance indication with a weight standard similar to the sample weight;
- Weigh the sample.

This procedure guarantees that each subsequent weighment of the sample will not be afflicted by error resulting from the balance sensitivity changes. It is justified on condition that the sample weight is big (between ½ balance Max capacity and Max capacity).

15.3. Differential weighing – the sample weight registering

For a single case it is easiest to register the result manually. But for a series of weighments registering the results is crucial. When the process concerns several samples grouped in series taken every day, it starts to be problematic. It concerns both weighing time and identification. Weighing time: the balance construction and parameters are designed for certain purposes. The sample identification implies the use of special programs, like in case of 3Y series balances. The user can:

- Define a series, each of which might contain several samples;
- Define the sample in an alphanumeric name;
- Select a method used by differential weighing (net/gross);
- For every sample select tare value, initial mass, and for 5 subsequent weighments ?
- Print or export to external memory the data concerning the series of weighments.

First of all, you should enter the series to the software database, next, define the samples in a series and edit a given series. Making series is possible from the level of databases.

The program structure of function ‘differential weighing’ uses databases which define both series and subsequent samples. It is only necessary to enter a particular series and sample before the weighment, and carry out weighment. Before the other weighment, again select a series and a sample. After the weighment we will obtain the differential result; it will re automatically registered in the database.

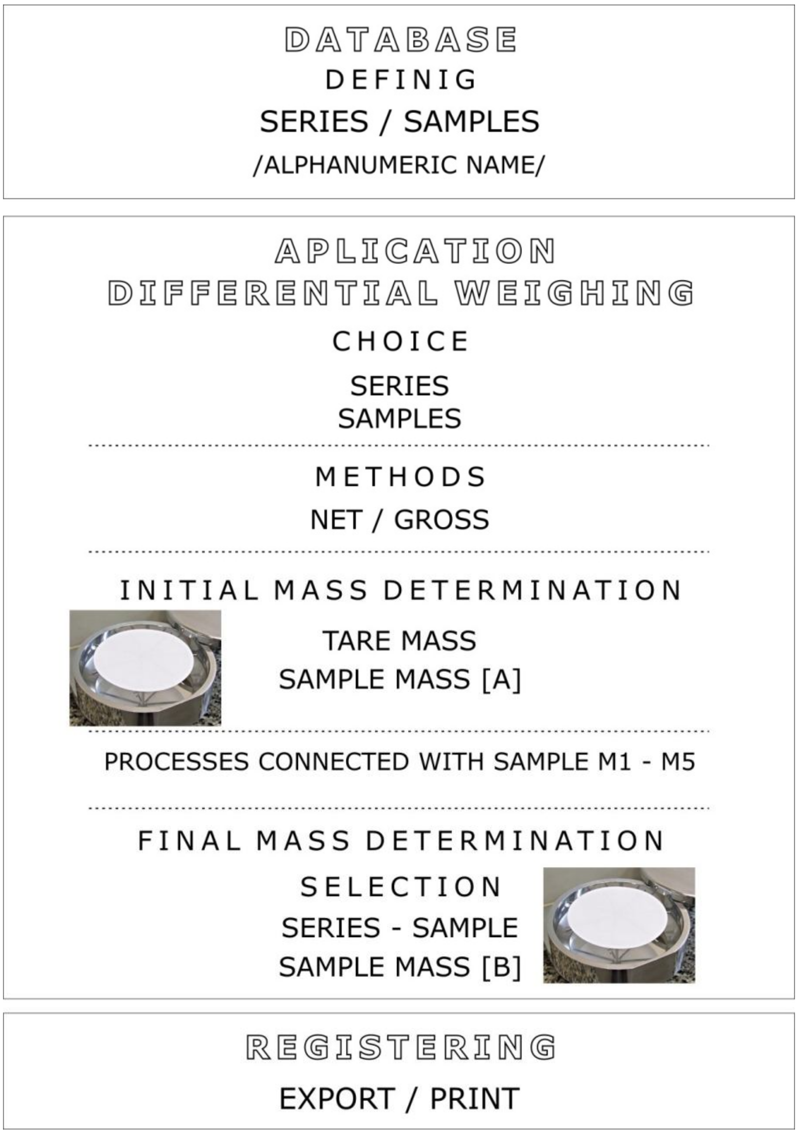


Fig. 73. Structure of application 'differential weighing'

Printing out information connected with differential weighing might be complicated. The fields it will contain are selected by declaring the contents for a standard print-out connected with this function. The print-out for the sample might contain: the sample name, the sample number, status, tare, temperature, humidity, pressure, non-standard print-out. Weighing A contains: date, time, status for leveling, warehouse, product, packaging, universal variable 1…5, net, tare, non-standard print-out. Weighing B might contain the same fields as weighing A and additionally Interval, difference [BA], difference [%], rest [%].

Below you will find a print-out for different stages of the process:

```
----------- Serie: filtr 25 -----------          A
Sample no                  5

Sample                     F-1
Status                 Weighing A
          Weighing A                             B
Date                  2013.08.13
Time                   12:22:25
Net                    0.0543 g

Sample                     F-4                   C
Status                    Tare

Sample                     F-5
Status                 Weighing B
          Weighing A
Date                  2013.08.13
Time                   14:13:41
Net                   0.19648 g
        Weighing B: 1/1                          D
Date                  2013.08.13
Time                   14:15:32
Net                   0.26732 g

Interval             0 d/ 1 h/12 m
Difference               0.07084 g
Difference %              36.05456 %
Rest %                    136.0546 %

Signature                                        E
```

Section A	series name (contains 5 samples)
Section B	sample for which only weighing A was carried out and initial mass determined
Section C	sample for which no weighing has been carried out yet
Section D	sample for which a cycle of differential weighing, weighing [A] and [B] was carried out (time between weighings was determined and a difference and the rest was calculated)
Section E	operator's signature

16. Conformity with regulations

Weighing equipment is applied by various industries (pharmacy, petrochemistry, environmental protection, etc.) worldwide, which means that conditions with respect to geography also vary for a particular device. These two factors, the industry and the geographical location, determine requirements for balance mechanical design and for maximum permissible values of particular metrological parameters.

16.1. Legal metrology and practice

Legal regulations resulting from WELMEC law acts, OIML guidelines and drafts are commonly known mainly due to the fact that WELMEC is a globally operating organization. WELMEC-approved methods and procedures are worldwide spread and used in course of individually performed testing. The said methods and measurements demand defining limit values (MPE). The limit values always refer to verification scale interval e, they include used load m. Example for balances of I accuracy class:

MPE	Load
0,5 e	$0\ e \le m \le 50\ 000\ e$
1 e	$50\ 000\ e < m \le 200\ 000\ e$
1,5e	$200\ 000\ e < m$

Stating that balance complies to legal regulations means that errors occurring while measurement performed by this balance are comprised within specified thresholds. This is just a general information giving no details on reliability of any weighing system. With information that the narrowest verification scale interval is 1 mg and that reading units and MPE values are as follows:

d=0,1 mg	MPE = 5 d
d=0,01 mg	MPE = 50 d
d=0,001 mg	MPE = 500 d (microbalance)
d=0,0001 mg	MPE = 5 000 d (ultra-microbalance),

statement informing that deviation of balance indication is not greater than MPE is no significant fact at all. This is often the reason why most balance users obliged to apply the devices in accordance with legal regulations decide to perform adjustment procedure. The said procedure provides information on errors of the particular balance. It may be concluded that legal metrology regulations are not relevant when it comes to high resolution balances. Still, the testing methodology is of importance and use.

16.2. GMP – metrology for industry

As for the methodology perspective, industrial metrology is based on the same schemes that legal metrology is. The main difference when comparing the former one to the later, is specifying required measurement reliability first, next checking if the requirement has been met. Two problems may be noticed here.

As for the first one, it may be difficult to determine how big the greatest deviation shall be in relation to the real value. It is worth to memorize that for some cases this parameter may be determined only by tests performed by means of a mass standard. Test of eccentricity or repeatability may be carried out using any load of mass constant over time.

The second problem concerns testing methodology, more specifically choice of the most appropriate tests, such ones that:

- are appropriate for the performed measurements range, i.e. only necessary respective tests are selected, this is described in Risk Analysis documentation – QRM process production, formality and documentation shall be adequate to level of risk and it shall be based on knowledge,
- are quick and simple, test of the balance shall not interrupt operating cycle,
- provide basic information allowing to decide on post testing balance use, adjustment or ruling it out

A great help for testing results interpretation is establishment of Warning Limits and Critical Limits.

16.3. Pharmacy

Extraordinary requirements for this branch are mainly a result of the fact that the measuring devices are used for medicine production. Their quality may affect particular drugs characteristics and as a result exert an impact on patient’s health. Apart from legal regulations valid for a particular region also pharmacopoeia guidelines are adhered to. Pharmacopoeia are documents binding for a particular continent, e.g. American , Japanese, European, Russian pharmacopoeia, etc. American pharmacopoeia is the one of the greatest priority.

There are two chapters devoted to requirements concerning balances, <General Chapters, Apparatus for Tests and Assays <41 ,,BALANCES”> and <General Information, <1251 ,,WEIGHING ON AN ANALYTICAL BALANCE”>. The former one describes specification for repeatability and accuracy, the description is as follows:

Repeatability is satisfactory if two times the standard deviation of the weighed value, divided by the nominal value of the weight used, does not exceed 0.10%. If the standard deviation obtained is less than 0.41d , where d is the scale interval, replace this standard deviation with 0.41d

The accuracy of a balance is satisfactory if its weighing value, when tested with a suitable weight(s), is within 0.10% of the test weight value. A test weight is suitable if it has a mass between 5% and 100% of the balance's capacity

Chapter 1251 is not compulsory, it supplies the reader with explanation and definitions of terms that are pivotal when it comes to electronic weighing equipment: sensitivity, accuracy, linearity and eccentricity. In order to comply to regulations of pharmacy industry it is necessary to meet chapter 41 requirements, especially those intended for repeatability of indications. As it is commonly know, it is repeatability that decides on measuring accuracy, i.e. balance reliability. For microbalances this parameter is used for MSW determination.

HOW TO DETERMINE MINIMAL SAMPLE WEIGHT?

In order to determine minimal sample weight one shall:

a. perform series of 10 measurements, using mass standard
b. use mass standard of much greater weight than expected MSW value (USP 1251)
c. calculate standard deviation using the obtained results
d. calculate MSW, to do it standard deviation value must be multiplied by constant value equal 2000

MSW = 2000 sd

e. MSW value depends on repeatability of indication, whereas repeatability depends on balance settings (optimization) and on ambient conditions

NOTE

Having in mind the above information, it may be concluded that in order to obtain as low MSW value as possible it is necessary to provide proper working conditions. The greater resolution, the more demanding requirements for ambient conditions stability.

Apart from metrological perspective there are also functional requirements relating to balance use and safety. They refer to the following aspects:

- multi-levelled system of authorization,
- user logging mechanism,
- record of settings modifications, etc.

For more detailed guidelines refer to 21 CFR Part 11.

16.4. Environmental protection

Balances used for performance of environmentally related processes require conformity to legal regulations binding for a particular region and to regulations of respective standards. As it has been presented before, standards specify quite high MPE values, therefore from the metrological point of view, most balances meet the specified requirements, and there is still some margin. As a consequence of the above it is necessary to subject a given balance to a periodical verification, performed by a respective body.

Particular standards concerning environmental protection, and regulations they provide, define balance by its reading unit. There are no other requirements. It is the user who has to establish how much metrologically important parameters influence the indication.

17. Features of electronic weighing equipment

Modern weighing devices shall be characterized by proper metrologically important parameters and by particular ergonomic and software solutions. Market demands influence the final outcome, i.e. development scope and direction. Users' requests and comments contribute to both, progress and advancement of high resolution balances.

17.1. Speed

Speed approached to as a parameter of electronic balances usually refers to measurement duration, i.e. to amount of time within with the sample weight value is determined. As such, the parameter may be understood differently by independent subjects. It may be defined as follows:

Time of measurement is time period after which sample weighing result falls within a specified tolerance.

This time is relatively short, it may take 2-3 seconds, whereas actual time needed for the result to stabilize takes usually around 6 – 7 seconds. While reading balance data contained within brochures and catalogues, one shall be able to distinguish between marketing content and real balance performance characteristics.

In case of ultra-microbalances and microbalances, time of measurement consists of two cycles. The first one concerns draft shield access procedure, the second one weighing procedure. It takes about 1,2 seconds to open and close the shield. Trying to estimate how long it takes to deposit a load on a weighing pan is quite impossible, it shall not be established here. Time needed for weighing does not depend on sample weight and it normally takes about 6 seconds.

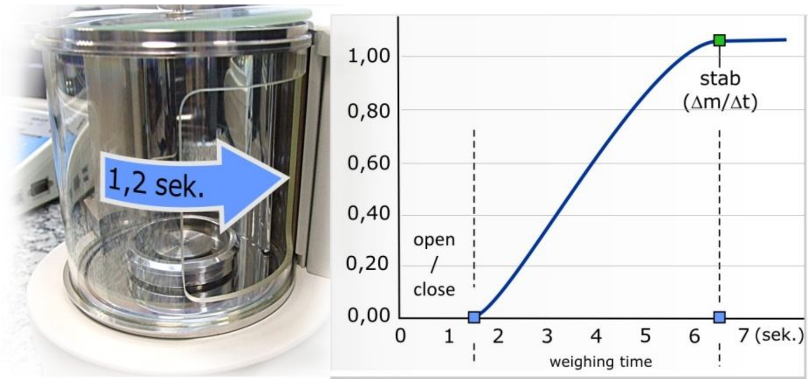


Fig. 74. Speed of measurement for 1 g heavy sample

NOTE

Measurement or dosing of a particular amount of a sample, wherein the resolution is at least 20 million reading unit, shall be approached form accuracy perspective, e.g. 3/20 million., not from the speed of measurement perspective. Most experienced users find this issue clear.

Wherever highly precise accuracy is demanded, it may happen that time needed for measurement performance is intentionally lengthened.

17.2. Touch-free operation

Manual abilities of an operator may be limited by characteristics of a workplace or by a required testing methodology (suit, gloves etc.)

Owing to proximity sensors, RADAWAG microbalances and ultra-microbalances may be operated regardless of the said limitations. These sensors allow the operator to perform various operations: printing, tarring, opening or closing the draft shield, selecting the name of a sample intended for weighing and many more.

Sensors operation power may be adjusted which is useful when there is a need for their activity area optimization.

Fig. 75. Proximity sensors

17.3. Wireless operation

Most balances of modular mechanical design use cables connecting particular components. Such solution is the most common one but not always satisfactory. There are situations when it should be possible to access the draft shield from more than one side. This requires terminal to be located somewhere in a distance. Limited by cable length space between balance and terminal is a serious drawback therefore RADWAG balances use Bluetooth connection allowing to locate the terminal anywhere in a distance (up to 10 meters). This is a convenient solution when placing a balance inside fume cupboard or Glove Box type of chamber.

Internal batteries installed inside the panel provide 8-hour-long, continuous operation.

Fig. 76. Balance-terminal wireless connection

17.4. Safety

It often happens that balance parameters optimization takes place in course of validation process, this is performed in order to provide the best possible settings allowing respective weighing accuracy. These parameters should be used throughout balance lifetime. They are protected against unauthorized modification, few access levels accessible. Some particular options and balance functions are enabled for each operator individually, e.g. weighing, printing, saving data etc. The operator logs in using his own password, after completing particular set of operations he or she logs out. It shall be remembered that all measurements are recorded into so called ALIBI memory, wherein data such as date, time, operator name etc. are specified. The protection is based on a system comprising 4-level access structure, owing to that it ensures:

a. ergonomics (a particular operator takes only necessary actions, which is time-saving advantage)
b. stability of balance parameters that are decisive for accuracy (accuracy guaranteed regardless of the operator's manual skills)

17.5. Customization

Customization is simply a process of fitting balance operation to one's needs. The scope of possible modifications depends on a particular balance program. Microbalances and other balances manufactured by Radwag offer vast range of options and functions that may be customized. For a particular user the following can be personalized:

a. Password
b. Access level
c. Language version for an interface
d. RIF card number
e. Possibility of fitting working environment so that is suited individual preferences.

   One's own profile, referring to used application, shall be created.

   It is possible to preset the following:

   - parameters concerning result stability – menu for readout
   - information displayed in INFO area
   - quick access buttons
   - default profile, run at the start after logging procedure completion
   - required printout type

17.6. Multi-functional working environment

Weighing module of each balance shall provide measurement accuracy. This is guaranteed by internal adjustment systems like in case of Radwag manufactured balances. The measurement may be monitored by means of so called weighing applications. These can be divided into two groups. The first group comprises applications relating to weighing:

a. dosing
b. checkweighing
c. parts counting
d. % control of sample weight
e. formulas
f. density determination

The second group includes Statistics, SQC, Databases which are designed to process and collect information. Simultaneous operation of numerous applications forms multi-functional environment enabling performance of complicated projects.

17.7. Service support – media module

User-friendly interface features touch panel and it seems to be uncomplicated when it comes to operation. Long-term work proves that software mechanisms may turn out to be ambiguous. Any doubts and uncertainty may be resolved by means of user manuals, however one may apply more convenient method, namely MEDIA module which is supported by Radwag balances. The module supplies balance users with instructional videos on various areas of use.

18. SOP for mass measurement

Metrological tests performed periodically for electronic balances call for at least basic level of knowledge on BALANCE related issues (possibilities when it comes to settings and the effect they have on the observed weighing result), MASS STANDARDS (requirements for accuracy and scope of use in course of metrological tests), METHODOLOGY (principles for tests performance), REQUIREMENTS (metrological tests tolerance, particular tolerance values causes) and AMBIENT CONDITIONS (influence on the measurement result).

18.1. Balance

Every single balance type has its own characteristic filter settings that somehow decide on an obtained final indication. By default the filter values are selected in a way providing precise results for standard laboratory working environment. Prior to performing test, it is necessary to check current balance settings. Default settings do not have to be modified while performing tests except for one situation, namely ambient conditions other than optimal. For such an instance, i.e. when there is a need to adjust settings, it is necessary to provide such modification that assures the best accuracy or speed of operation.

a. Thermal stability of a balance – thermal stability is required when balances equipped with electromagnetic converter are tested. This means that balance temperature and temperature of the testing room shall be of the same value. Such situation takes place after so called acclimation time or time of self-heating.

b. Acclimation time – if balance temperature significantly differs from ambient temperature, then the balance shall be plugged to the mains for a specified amount of time. How long does the acclimation take?

   Acclimation time depends on
   - temperature variation,
   - balance mechanical design (reading unit value).

In practice, metrological tests are performed on the following day.

18.2. Mass standards

There is a special code of practice when it comes to use of mass standards, read the following information:

- While performing tests, use external mass standards with valid calibration certificate. It is essential for traceability purposes.
- Mass standards shall be put on a weighing pan with care, when no longer used, they must be placed in a storage box immediately.
- Mass standards shall be stored in the testing room. Temperature difference between mass standards and the balance environment is a major cause of measuring errors.
- Mass standards that WERE NOT STORED in the testing room require acclimation which may take several hours.
- Mass standards shall be handled by means of a special tools such as tweezers, forks, holders or gloves.

Accuracy of mass standards by means of which the balance is to be tested, shall be referred to a balance reading unit. In practice:

- Mass standards with maximum accuracy class allow to check any balance
- Mass standards with greater errors cannot be used for testing balances with high resolution.

A completely different issue concerning mass standards is their maintenance. It is generally know that mass standards are subjected to wear and tear when being frequently used. This in turn influences their deviation values. Mass standards with negative deviation values may lose their accuracy class with time, e.g.

20g (E2) = δ = - 0,06 mg 06.2014

20g (E2) = δ = - 0,09 mg 06.2015

After some period of use, the error starts exceeding E2 accuracy class limits. Realising the above issue, one shall be aware of the fact that it is not always necessary to perform tests by means of mass standards with maximum accuracy class. It is recommended to use weights with accuracy class that is sufficient for a particular test.

18.3. Test methodology

During acceptance tests or while verifying the balance, e.g. after transportation, only some of the balance parameters are controlled, these are linearity, dispersion of indications and eccentricity. This document provides detailed characteristics of tests for the three parameters control. The following questions shall be answered:

a. What does the parameter stand for?
b. What information does parameter value provide?
c. How to determine the parameter?
d. What is the parameter definition according to standards?
e. Is it possible to adjust the parameter value?

18.3.1. ACCURACY OF INDICATION - SENSITIVITY

Accuracy is a broad notion combining many factors that influence the measurement indication. On the said factors list there are errors resulting from linearity, repeatability, eccentricity and from sensitivity variation. Combination of all these may lead to inaccuracy of indication.

a. What Does Sensitivity Stand For

Sensitivity is one of the major balance parameters, it decides how accurate the measurement performance is. It may be associated with calibrating, i.e. with teaching the balance how to provide an accurate indication.

Definition of sensitivity

Quotient of the change of the observed indication (ΔR) and the corresponding change of the measured mass (Δm).

$$SE = \frac{\Delta R}{\Delta m}$$

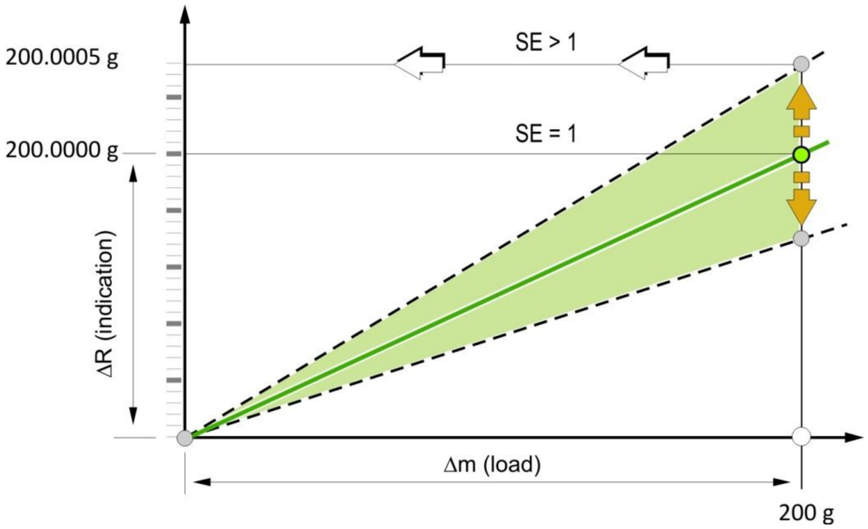


Fig. 77. Sensitivity – interpretation in a graphic form

Analysing the graph it may be concluded that test for sensitivity variation makes sense only for heavy loads and that the error is proportional to weight of a tested sample. Having that in mind it can be stated that:

> *"effect of sensitivity variation IS NOT SIGNIFICANT when small samples are weighed".*

b. Sensitivity And Its Significance In Practice

It is commonly known that appropriate sensitivity calibration is the first factor providing accurate mass measurement. The said calibration is carried out by means of an adjustment procedure, wherein for most balances an internal weight is used. Sometimes the adjustment is performed using an external weight. Upon completion of the adjustment procedure an ideal relation between an indication and a load weight is obtained. For example:

- Test mass standard = 200,0007 g (mass standard error taken into account)
- Balance indication upon putting mass standard on a pan = 200,0007 g
- Sensitivity is correct.

It shall be noticed that for laboratory balances the sensitivity is not stable. As a result of ambient conditions variation and of time flow, the sensitivity changes, which in turn may cause errors of indication. Since dynamics of ambient conditions changes is not known, then only performance of the adjustment procedure provides 100% certainty that the balance sensitivity is proper.

ONE MAY WONDER
How often shall the adjustment procedure be performed?

The answer depends on various factors, but trying to simplify this complex issue, the question may be approached in the following way.

TAKING RESOLUTION INTO ACCOUNT

- If you use a balance of low resolution, lower than 2 million intervals (e.g. all PS series balances), then the adjustments may be performed at the very beginning. The balance itself initiates successive adjustment procedures from time to time.
- If you use balances of high resolution (more than 2 million intervals), then adjustment procedure shall be performed prior to measurements.

TAKING REQUIRED ACCURACY INTO ACCOUNT

- If your measurement does not have to be accurate, it is enough to perform the adjustment prior operation.
- If your measurement requires accuracy and precision, then the adjustment procedure shall be carried out also prior to the measurement, it is necessary to put a sample in the very centre of a pan.

TAKING WEIGHING RANGE INTO ACCOUNT

- If small loads are measured, of weight lower than 10 of maximum capacity, then sensitivity error is insignificant.
- If heavy loads are measured, then sensitivity error may be significant.

Independently from the above information, adjustment is a procedure that corrects balance accuracy. In accordance with GLP it is recommended to perform the adjustment procedure periodically, also prior to measurements.

c. Sensitivity – How To Determine The Parameter

Sensitivity is determined by comparison of mass standard weight measurement indication and an expected value. The test shall take place right after the adjustment process completion. It is recommended to use mass standard of weight close to max capacity of the balance. Since a single measurement is used for the test, then:

- The result is affected by repeatability error of indication, specific feature for a particular series of types,
- The result is affected by eccentricity error of indications, therefore the load shall always be put in the very centre of a weighing pan,
- The result is affected by repeatability error of adjustment, such is balance construction specificity, this parameter value is usually lower than the balance reading unit.

While testing sensitivity remember to use mass standard with a valid calibration certificate. It is necessary to be sure that the deviation stated by a certificate is correct – i.e. that traceability is provided.

d. Sensitivity And Standards

Sensitivity is defined as one of few metrological characteristics of a balance by OIML R 76-1, EN 45501 and NTEP. It is not subjected to assessment tests.

e. Sensitivity – Is It Possible To Adjust The Parameter Value

Balance sensitivity is periodically adjusted by means of an internal adjustment process. Basically there is no need to adjust the sensitivity by other means and operations. Factory adjustment of sensitivity is a completely different issue, here all adjustment process relations are taken into account.

18.3.2. LINEARITY

a. What Does Linearity Stand For

A perfect balance is such one that provides a “precisely accurate” measurement, i.e. balance that displays 100,00000 g. when 100 g mass standard is measured. For 50 g heavy mass standard, the balance shall display 50,00000 g, and for 200 g heavy mass standard, the indication shall be 200,00000 g. This kind of balance is “accurate”, i.e. “perfectly linear” within the whole weighing range.

For balances with high resolution this concept is true only in theory, this is due to the following:

- mass standards used for factory adjustment feature some deviations,
- balance accuracy depends also on repeatability of indications (putting one and the same mass standard on a weighing pan over and over again provides different results)

With the information above it may be stated that there are at least two factors that may affect balance “accuracy”. This is presented by means of graph b. Balance linearity is simply a deviation of the balance indication in relation to the correct (perfectly ideal) value. Catalogues usually provide maximum deviation value, e.g. linearity +/- 0,3 mg.

b. Linearity And Its Significance In Practice

As it has been noticed in the previous subsection (4.3.a), there are some factors affecting linearity. Since it is not known to what extend do the factors affect the indication, then one has no clear idea on what real balance linearity is. It is possible to determine linearity deviations while testing the whole weighing range. For an instance, the weighing result for an ideal mass standard shall be 100,0000 g whereas in reality it is 100,0007 g, the deviation here equals 0,0007 g. In practice it means that a sample weighing about 100 g will be measured with the same error as the mass standard, i.e. 0,0007 g.

Thus, linearity determines error value for determination of sample weight. It is assumed that no external processes interfering the sample measurement takes place.

c. How To Determine Linearity

Linearity is determined by means of weighing a mass standards and reading the indications. Prior to measurements the balance shall be adjusted using an internal or external weight. Right before performance of the proper measurements, the balance shall be loaded with mass standard of weight value close to Max. It is enough to measure such mass standard twice. Upon removing the mass standard, the balance shall be subjected to zeroing. Only thus prepared balance is ready for tests wherein several mass standards are used and the whole weighing range is tested. If the test is to be accordant with EN 45501 or NTEP, then it is necessary to select such measuring points for which MPE value changes. In case of balances with smaller reading units, one shall take mass standard deviations into account. This clearly shows that in order to determine correct balance LINEARITY only mass standards with VALID CALIBRATION CERTIFICATE can be used.

Balance with Max capacity of 220 g, d = 0,1 mg (direct method)

Mass standard	Tare	Mass standard weight	Indication	Deviation of accuracy
[a]	[b]	[c]	[d]	[d - c]
20 g	0	20,0000	20,0001	0,0001
50 g	0	50,0000	50,0002	0,0002
100 g	0	100,0000	99,9998	-0,0002
150 g	0	150,0000	149,9998	-0,0002
200 g	0	200,0000	200,0003	0,0003

/Direct comparison of an indicated value and the mass standard weight value/

Balance with Max capacity of 52 g, d = 0,01 mg (supplementary weights method)

Mass standard	Tare (g)	Mass standard weight	Indication	Deviation of accuracy
[a]	[b]	[c]	[d] = (c+b_i)	[d - c]
10 g	0	10,00005	10,00007	+ 0,00002
10 g	10		10,00001	- 0,00004
10 g	20		9,99999	- 0,00006
10 g	30		9,99998	- 0,00007
10 g	40		10,00002	- 0,00003

/Use of one mass standard of 10,00005 g weight, supplementary weights allow to test linearity for the whole weighing range/

Balance with Max capacity of Max 5 g, d = 0,001 mg (supplementary weights method)

Mass standard	Tare (g)	Mass standard weight	Indication	Deviation of accuracy
[a]	[b]	[c]	[d] = $(c+b_i)$	[d - c]
1 g	0	1,000002	1,000003	+ 0,000001
1 g	1		1,000005	+ 0,000003
1 g	2		0,999999	- 0,000003
1 g	3		1,000004	+ 0,000002
1 g	4		1,000000	- 0,000002

/ Use of one mass standard of 1,000002 g weight, supplementary weights allow to test linearity for the whole weighing range/

Caution: the above examples ***are not*** *real tests results, they serve for test methodology explanation purposes.*

It is assumed that:

„if balance linearity is perfectly ideal for the whole weighing range, then testing of any point for the linearity by means of one and the same mass standard shall provide the same results independently from used supplementary weight."

According to the above assumption, the supplementary weights mass does not have to be determined precisely. It may be easily noticed that for the supplementary weight method, loads of different values can be used for the test. This depends on the used mass standard weight and on Max capacity of the balance, e.g.:

- Max = 5 g / 1 g = 5 measuring points, but
- Max = 5 g / 0,5 g = 10 measuring points

Not too many points are used when it comes to acceptance tests, it takes too much time to perform such a test. Besides, it may happen that loading a weighing pan with many supplementary weights for a long time can result in change of indication (so called "creep under loading") and the balance linearity at the same time.

SUMMARY

Balance linearity may be tested by means of increasing and decreasing loads (method accordant with R 76-1, NTEP). During weighing, the user usually wants to determine increase of the sample weight. Nevertheless there are situations that require determination of a sample weight loss.

d. What Is The Definition Of Linearity According To Standards

Standards do not define linearity as a metrological parameter. Documents such as OIML R 76-1, EN 45501 and NTEP, refer to linearity using “accuracy” term. Each of the said standards provide almost the same test method which consists in comparison of indication value with load weight value when loading and unloading the weighing pan. Supplementary weights are not used and it is required that the error for the test weight was not greater than 1/3 MPE for a particular load. The test shall involve points for which MPE values change. The standards, OIML R 76-1, EN 45501 and NTEP, additionally specify accuracy classes for balances and requirements for MPE. This is a lawful mean of control over weighing equipment such as balance.

e. Is It Possible To Adjust The Linearity?

Linearity visualizes relation between mass standard weight value and the weighing result value. Repeatability of indications, eccentricity and adjustment accuracy are factors that decide on how precisely the linearity can be adjusted. To make it a little bit less complicated let us assume:

- that eccentricity error is insignificant and that it is the very centre of a weighing pan that is involved while weighing, and
- that correct adjustment is maintained, then

LINEARITY of the balance depends on the repeatability of the balance only. If so than we have just one parameter effecting the linearity, however repeatability is influenced by:

- ambient conditions and place of use,
- balance settings,
- test load, for some balance types.

SUMMARY

You can place mass standard on a weighing pan 6 times, determine difference between Max and Min indications, the obtained result is the lowest possible error of linearity. For example:

1. 50,00001
2. 50,00003
3. 49,99999
4. 50,00000
5. 50,00001
6. 49,99998

DIFFERENCE: 50,00003 – 49,99998 = 0,00005 g.

Linearity of indications for weight of 50 g is at least 0,00005 g, assuming that mass standards we use are “accurate”.

Accuracy Of Indications Vs Linearity

Both of the above terms describe the same balance parameter. The former one, accuracy, additionally comprises errors resulting from eccentricity, repeatability and it has to meet requirements for mass standard error (the error must be smaller than 1/3 MPE).

Here the result is referred to MPE criterion (R 76-1). Linearity, on the contrary, does not comprise errors resulting from eccentricity, it uses known mass standard weight and it is affected by error of repeatability of indications and mass standards errors. The result is referred to the manufacturer’s requirements.

18.3.3. DISPERSION OF INDICATIONS

a. What Does Dispersion Of Indications Stand For

Dispersion of indications may be referred to darts or any other target shooting competition. No matter how much the competitors try it is very rare for them to hit the bull’s eye every single time they shoot. The competitors score various points: 6, 7, 8, 9, 4, 10, 8 etc. The dispersion of their hits is 4 to 10, i.e. 6. Exactly the same relation takes place when it comes to electronic balance. Nobody shoots the target here, nevertheless putting one and the same load in a likewise manner gives different indications. Dispersed results are an effect of both, target shooting and weighing. The dispersion of indications is a parameter that by name shows how much the indications of measuring series performed with one and the same load are dispersed.

b. What Information Does The Parameter Value Mean In Practice

A particular value of dispersion of indications parameter, e.g. R=0,006 g, means that a deviation of this value may be expected while weighing a given sample. If the measured sample weighs 68,762 g then the maximum possible result to be obtained while weighing it, is 68,768 g. It may be rightly concluded that repeatability is determined in order to find out what the maximum possible error is when performing sample measurement. Of course all GLP guidelines must be followed.

Dispersion of indications may be given alternatively as a standard deviation of series of measurements. When it comes to standard deviation, it is recommended to subject one and the same load to 6-10 measurements. Generally it is said that standard deviation value is 3 times lower than value of dispersion of indications. This assumption gives us the following equations, R = 3xsd or sd = R/3. Standard deviation informs on how much the weighing result deviates from a mean value. An example of series of measurements:

1	2	3	4	5	6	7
100,0003	100,0005	100,0001	99,9999	100,0006	100,0002	100,0000
R = 100,0006 – 99,9999 = 0,0007 g						
Mean value of measurement series = 100,00023 g						
Standard deviation (σ) = 0,000256 g						

This sample weight is contained within a following range:

100,00023 g	+ 0,000256 g – 0,000256 g	68 % (1sd) probability
100,00023 g	+ 0,000512 g – 0,000512 g	95,5 % (2sd) probability
100,00023 g	+ 0,000768 g – 0,000768 g	99,7 % (3sd) probability

The above relation proves that it is not possible to determine weight of a sample with 100% certainty. The assessment is affected by an error od dispersion of indications. Having determined value of standard deviation it is possible to define, with a certain probability, the sample weight value. Three-sigma rule is applied for the below relations:

- 68% probability that the weight is contained within ≤ 1σ range limit from the expected value
- 95,5% probability that the weight is contained within ≤ 2σ range limit from the expected value
- 99,7% probability that the weight is contained within ≤ 3σ range limit from the expected value.

These relations are interpreted by means of the below graph.

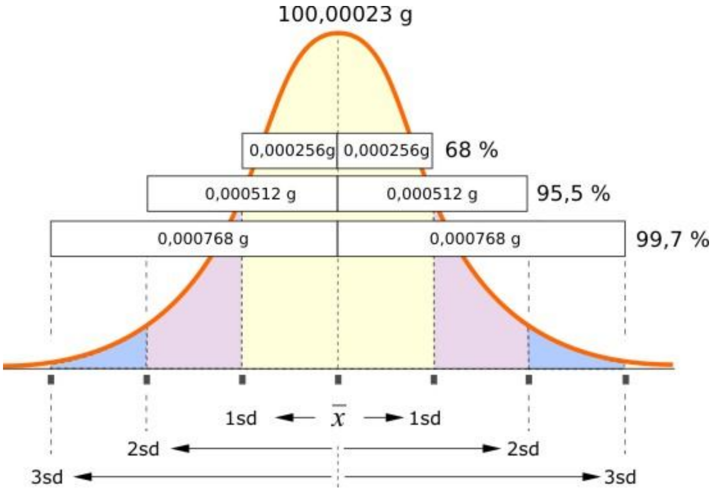


Fig. 78. Repeatability as standard deviation

For this very instance it can be assumed with 99,7% probability that weight of the tested sample is 100,00023 ± 0,000768 g.

c. How To Determine Repeatability Of Indications?

Series of measurements is performed using one and the same load, wherein the load is put in a repeatable manner in one and the same spot of a weighing pan (i.e. in the very centre of a weighing pan). Mass standard accuracy is not important for this test since it is the difference between measurements or standard deviation that is tested. For laboratory balances, series of 6-10 measurements is used. Prior to test performance it is necessary to carry out few preliminary measurements, adjustment is not necessary. Calculate dispersion of indications, i.e. Max – Min or standard deviation using results of the measurement series. This value may be determined by means of equation Sd = R/3. More precise value, if needed, shall be calculated in accordance with the following formula:

$$sd = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1}}$$

where: sd – standard deviation

x_i – next measurement

$\overline{x}$ – measurement series mean

n – number of measurements within a series

Generally, repeatability is tested using loads of ½ Max or Max capacity of a particular balance, however it is permissible to use other loads, e.g. 5% of Max capacity.

d. Repeatability And Standards

Methods for testing repeatability are described by all standards (R-76-1, EN 45501, NTEP, USP etc.). EN 45501 and NTEP provide information on maximum permissible errors of test loads. Manufacturers of balances specify their own criteria for repeatability. The repeatability test aims to check compliance with the specification supplied by the manufacturer. While testing repeatability, one must be aware of the fact that test conditions significantly influence the test result.

e. Is It Possible To Adjust The Repeatability Value

Repeatability is one of the characteristic balance (balance series) parameters and it cannot be adjusted. As it has already been noticed, repeatability is affected by repeatability test conditions and by balance settings.

18.3.4. ECCENTRICITY

a. What Does Eccentricity Stand For

Not only logic but most of all Good Laboratory Practice make one put a load in the very centre of a weighing pan while performing the measurement. Reality shows that it is not easy to meet this seemingly simple requirement, especially when the loads that are to be weighed are asymmetrical when it comes to their shape. Eccentricity, more precisely its deviation, is understood as difference between indication obtained for a load placed in the weighing pan centre and indication obtained for the same load placed anywhere but in the centre.

b. What Does The Eccentricity Value Mean In Practice

In practice eccentricity deviations may lead to a right conclusion: if the load is placed elsewhere than the weighing pan centre, then the indication may be affected by an error, value of which shall not be greater than the eccentricity deviation itself. For example:

- Eccentricity deviation is 0,0005 g,
- Measured weight of a sample placed in the centre is 123,7654 g,
- Measured weight of a sample placed outside the centre is 123,7659 g.

It has to be mentioned that eccentricity deviation value depends on the load. In practice it means that the greater test load value, the greater the deviation. Owing to this relation there are some standard procedures specified for determination of eccentricity deviation. A logical conclusion may be reached from the above statements, namely, there is practically no error of eccentricity when small loads are weighed. It is considered that these are loads weighing maximally 20% of maximum balance capacity.

c. HOW TO DETERMINE ECCENTRICITY DEVIATION?

Eccentricity deviation is determined by means of mass standards. As it has already been stated, there are some certain procedures specified for determination of eccentricity deviation, they are described by standards R 76-1, EN 45501 and NTEP. According to the said documents, eccentricity is tested using weight of 1/3 of Max capacity, wherein the weight is to be put in a specified spots of ½ of a weighing pan surface. The figure below presents the test in a graphic form.

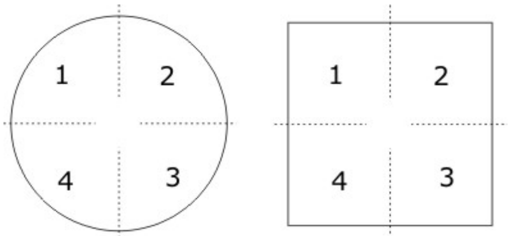


Fig. 79. Eccentricity testing points R- 76-1

Weighing result, for a mass standard measured when placed in points 1-4, shall not exceed errors specified by standards and the manufacturer.

d. Eccentricity And Standards

Eccentricity test method is provided by OIML R 76-1, EN 45501 and NTEP. In accordance with the instruction, the deviation of indication obtained for points 2 – 4 is compared with permissible tolerance.

e. Eccentricity – Is It Possible To Adjust The Parameter Value

Eccentricity is adjusted during the manufacturing process and sometimes upon transportation that takes long time. Scope of actions to be taken and a detailed description is provided by a user manual. Accuracy of eccentricity adjustment shall not be greater than repeatability of indications that is obtained while weighing a particular load.

18.3.5. GENERAL TEST GUIDELINES

Metrological tests shall always be performed when stable ambient conditions are provided. In practice an insignificant temperature or humidity variation over time is acceptable (ideally perfect stable conditions do not exist). The balance shall be located on an even surface that is not subjected to any perceptible vibrations. Prior to tests the device must be in a thermally stable condition (already mentioned). It is necessary to perform levelling.

Since mass standards are used for the test therefore there is no interference of sample electrostatics origin. Mass standard as a small load is not susceptible to air drafts. Air drafts are source of problems for balances featuring big weighing pans. Test procedures are commonly known, they are often enforced by applications. Prior to tests it is advised to perform some preliminary measurements using different loads and observing both, stability of indications and returning of indication to zero point.

It is needless to say that in course of tests the balance shall be a completely equipped device. Some manual skills may be an issue when it comes to weighing, ability of placing the load without shocks on a weighing pan is of great importance here. While making the balance judgment one shall be objective. In case of any doubts when it comes to obtained test results, the tests must be performed again.

19. Weighing Modules – versatile weighing solutions

Thinking of typical laboratory mass measurement brings particular balance image to one's mind, which is nothing unusual since we have been getting used to a given scale model for years. The brand new design does change significantly, nevertheless its characteristic mechanical components remain the same (housing, weighing pan, cover etc.). The modification would not take place if it was not for the constant development of technology. An ongoing progress and growing needs, when it comes to research and automatic control engineering, bring about changes of electronic scales design. In consequence, it often happens that popular forms are replaced with versatile weighing workstations that can become a component of any mechanical structure. With this, it is possible to make customized weighing stations that work on the basis of automatic or semi-automatic cycles offering option of so called feedback.

At the first glance the module differs a lot form the balance, in contrast to the balance it does not feature components such as draft shield or display. This may be strongly discouraging for the user but it should not be so since the module readability and the standard balance readability are likewise. See the comparison provided below.

Standard PS 6000.R2
Max 6 kg , d=0,01 g, IP 32

MPSH 6000 module
Max 6 kg , d=0,01 g, IP 67

Weighing modules are used for various applications as one of many components of the whole unit. They are often built-in elements so the user has strictly limited possibility to observe them. Nevertheless he or she can watch its operation results, i.e. measurement, calculation based on the indication, graphic interpretation of changes being an effect of the whole system variations. Read sections 19.1 – 19.3 to find out where weighing modules are especially praised.

19.1. Thermogravimetry

Thermogravimetry is a method by means of which, with application of either weighing chamber or thermobalance, one can measure temperature or time flow dependent weight of particular substance. The method is quite simple – first you need to place a particular platinum or aluminium trioxide sample in a container, next put the container in a heater connected with the thermobalance. Heat the sample until it reaches specified, even up to 1600 ^{o}C, temperature. It is obvious that technical infrastructure shall be isolated from heat source. In order to provide the said isolation, certain mechanical design and fireproof materials are applied. Internal temperature is continually analysed by means of thermoelement located in a close vicinity of a sample. There are many various thermobalance sets on a market, some of them arranged vertically, others horizontally.

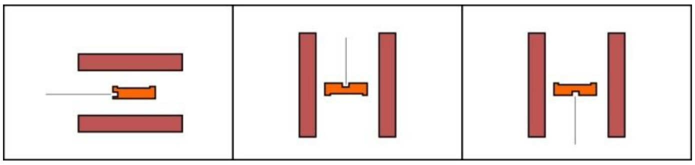


Fig. 80. Thermobalances Arrangement

Sample weight measurement requires use of weighing module that is characterized with particular resolution and reading unit. RADWAG installs weighing modules in microbalances (d=1 mg) and ultra-microbalances (d=0,1 mg). The modules comprise rigorously selected mechanical components, electromagnetic converter of optimal parameters and electronics of high resolution (80 million reading units). The weight converter is equipped with complex digital mechanism for optimization of measurement process. With the said mechanism it is possible to adapt any measuring system to any technical and IT infrastructure of other devices. Owing to long experience, RADWAG can provide you with support and advice as for the above.

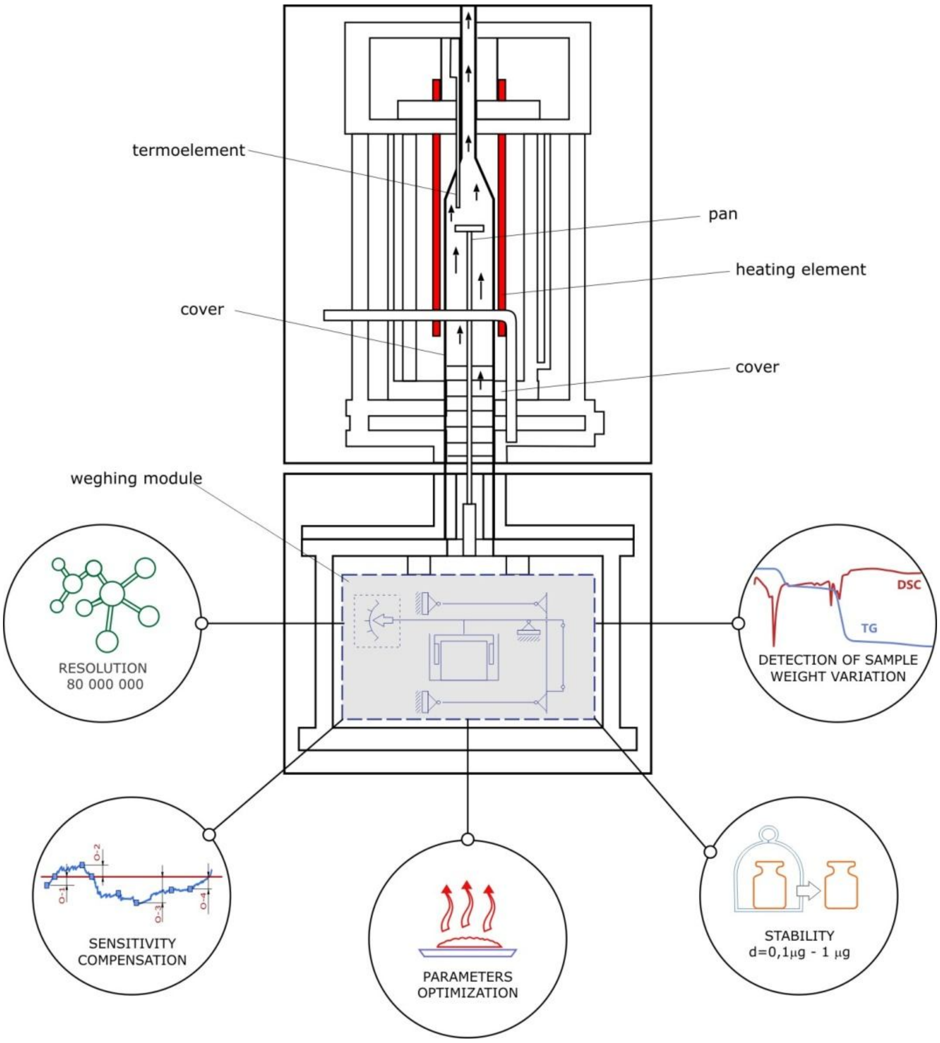


Fig. 81. TGA Device with Weighing Module – Schematic Drawing

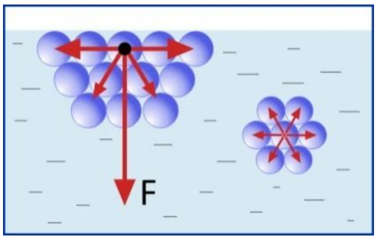
Technical Specifications of MYA Module (d=1 µg)

Max capacity	2 g ÷ 52 g
Readability [d]	0,1 µg ÷ 10 µg
Tare range	2 g ÷ 52 g
Repeatability	0,4 µg ÷ 1,0 µg
MSW (USP 41)	3 mg
Weighing chamber dimensions	ø 90 × 90 mm
Stabilization time	5 s
Weighing pan dimensions	ø 26 mm or any other fitting the design
Operating temperature	+10 ÷ +40 °C
Power supply	13,5 ÷ 16 V DC
Adjustment	internal
Display (option)	5,7'' (touchscreen)
Interface	2 × USB, 2 × RS 232, Ethernet, Wi-Fi, 4 ins / 4 outs
Power consumption	700mA (wireless terminal - 1A)

It is possible to provide such setup and metrological parameters for the module that match other devices design.

19.2. Tensiometer method for testing surface tension of liquids and solutions

Process of asymmetrical interference between intermolecular forces occurs for practically each liquid. As a result of this process, molecules exposed to a surface are drawn away from it. Downward force exerted on the surface molecules causes certain pressure referred to as surface pressure. Additionally, tangential force being an effect of cohesion process (surface tension) is present within surface layer of the liquid. It is defined as tangent force per length unit or as a mechanical work needed to increase the surface by one unit. Surface tension unit for SI system is N/m or J/m^2.



Rys. 82. Interaction between molecules

There are numerous surface tension measurement methods, the most commonly used are: Capillary Rise Method, Stalagmometric Method (weighing and reading a drop of liquid), Ring or Plate Method and Bubble Pressure Method. For measurement of surface tension metal plates are used. The measurement consists in estimation of force F applied in order to detach plate of known perimeter from the liquid surface. Surface tension is calculated using the following formula:

$$F = F_n + Q$$

$$where:$$

$$F_n = 2\sigma(l + d)\cos\gamma$$

$$\sigma = \frac{F_n - Q}{2(l + d)} = \frac{F_n - Q}{2l}$$

Q – plate weight
Fn – force being an effect of Surface tension
σ – Surface tension,
l – immersed plate part length
d – plate thickness,
γ – contact angle between plate surface and surface tangent to the liquid surface

If value of plate thickness *d* is low when referred to edge length *l*, then plate thickness can be neglected.

Figure illustrating the measurement

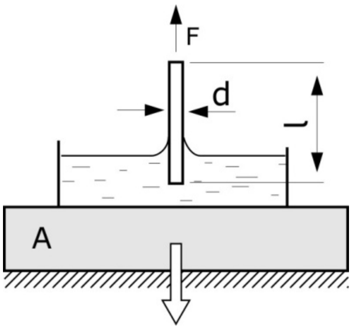
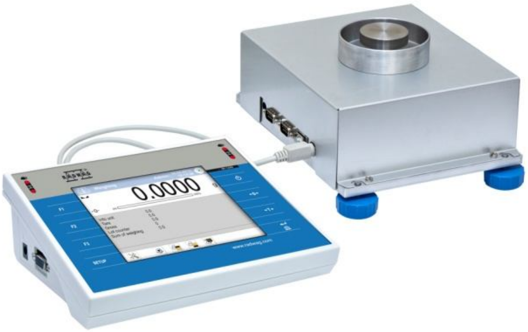


Fig. 83. Parameters Arrangement for Tensiometer Method

Tensiometer method shall be carried out by means of precise weighing module with the highest possible reading unit d=0,1mg. The most important module’s parameter is sensitivity, i.e. ability to detect even insignificant variations of measured sample. Naturally, most weighing modules can be adapted to prevailing conditions, this means that their operation can be optimized. RADWAG products operate on a basis of two-level system which guarantees almost 100% successful adjustment of a particular weighing module to a used measurement methodology. In order to provide device that would be right for performance of tensiometer method, RADWAG has designed MAS series module. The said module is equipped with converter characterized with tens of millions of reading units and highly stable electronics providing fast and precise measurement. Using the module one must remember to adapt it to his/her testing workstation requirements. Fortunately, the adaptation is an extremely simple process. For metrological parameters of MAS module read the table below:

MAS series with terminal



Max capacity	220 g
Readability	0,1 mg
Tare range	-220 g
Start load	22 g
Repeatability	0,1 mg
Linearity	± 0,2 mg
Stabilization time	3,5 s
Weighing pan dimensions	ø 42 mm
Adjustment	internal
Operating temperature	+10 ° - +40 °C
IP rating	IP 32
Power supply	12 ÷ 16 V DC
Housing	aluminium

In course of measurement the tensiometers may work using computer software designed to provide automatic record of weight variation. The measurement indications may also be stored in a weighing module memory. Learn that it is not a rare practice to use a typical balance for the measurement, but remember that for such a case plate motion is carried out by means of an external device.

19.3. Automatic cycle operation

Automation of mass measurement process calls for such weighing applications that provide fast measurement. It is measurement methodology that specifies requirements for a particular weighing device. Aforementioned fast measurement is a need when it comes to analysis of large amount of samples. For this kind of measurement it is often determined whether sample weight value is contained within specified high and low tolerance thresholds. Measurement carried out periodically for certain small amount of samples may require much greater readability. There is always a compromise between measurement speed and accuracy and it is not a secret to metrology specialists designing their own weighing workstations. It is not always easy to decide which device would be the most suitable one, manufacturer's experience and advice may turn out to be priceless when it comes to planning stage.

19.3.1. Weighing modules installed in automatic scales

Nature of some industry branches, e.g. cosmetic industry or pharmaceutical industry, requires detailed control of all manufactured products. It is conditioned by safety reasons on one hand and by economical aspects on the other hand. For heavy products, weighing about few kilograms, the control process may be performed by means of automatic controlling scales operating on the basis of load cell. The problem arises when light loads are to be subjected to measurement or when maximum measurement accuracy is required. Solution to thus challenging demand are RADWAG-manufactured high resolution modules.

Manufacturing process of high resolution modules is much more complex in comparison to manufacturing process of load cell scales. It is not possible to provide successfully operating high resolution module without wide knowledge and years-long experience. Resolution is the main difference between weighing module and mechanical design based on load cell operation. Load cells provide resolution of 3 000 – 6 000 reading units. When it comes to weighing systems the reading units quantity may be increased to 10 000 providing that respective measurement method is applied. However, most users require certified devices, therefore resolution of 3 000 reading units is a limitation, since it is not possible to provide certified weighing equipment of resolution higher than resolution of load cell being a base component. Note that the said resolution of 3 000 reading units is characteristic for most load cells. As for load cells operation, it has been described by numerous publications. In general it consists in measurement of resistance variation being a result of elastic deflection of the load cell (read section 4).

In contrast, typical weighing module featuring electromagnetic converter provides one order of magnitude better resolution. Right at start there are 60 000 – 2 000 000 reading units available. In order to obtain repeatable results it is necessary to reduce the resolution (which may be conditioned by measurement method) but even when reduced, the resolution still stays high. The above described procedure is used for scales measuring very light loads with respectively high accuracy, e.g. MAS or MPSH series modules.

Another important issue is reaction to a signal, i.e. how long it takes to obtain result contained within specified high and low tolerance thresholds. This is especially important when large amount of samples has to be controlled in a relatively short period of time.

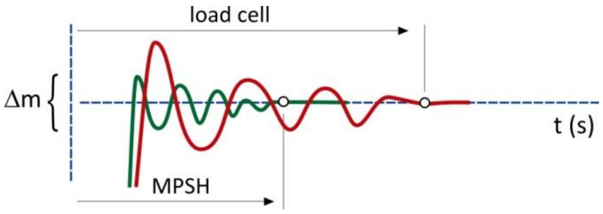


Fig. 84. Stabilization rate for a weighing module

Systems designed to perform selection or separation are of great importance. MWMH series modules with IP 67 are applied when it comes to performance of the aforementioned operations on heavy samples. Device with max capacity reaching even 30 kg (d=0,1 g) is a perfect solution that can be an in-built component of any manufacturing line.

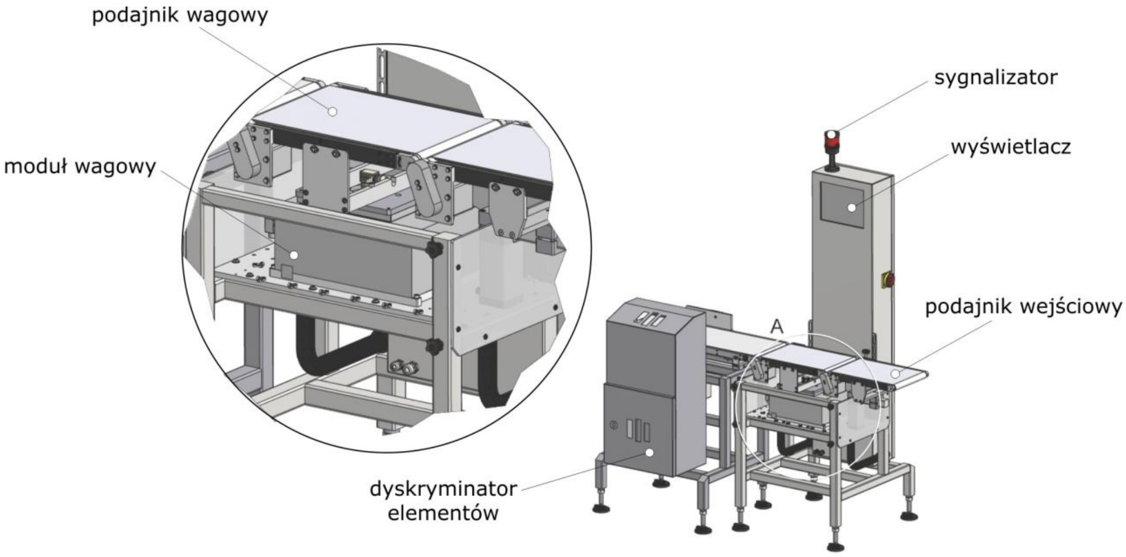


Fig. 85. Dynamic scale equipped with a weighing module.

19.3.2. Automatically performed powder dosing

Precisely dosed amount of particular substance is a key demand of many processes, research and studies among them. The processes add to development of industries such as pharmacy, cosmetics and petrochemistry. Manually performed dosing operation is a method that shall be avoided due to the fact that it can provide neither required accuracy nor repeatability. Automation of dosing cycle could be accepted as a solution here. Automation usually refers to measurement of certain amount of particular product, e.g. cachets, which are placed in special containers. Next net and gross weight of each cachet is measured. The weight measurement is a pivotal stage of the dosing process. Quick weighing module reaction and right metrological parameters are expected.

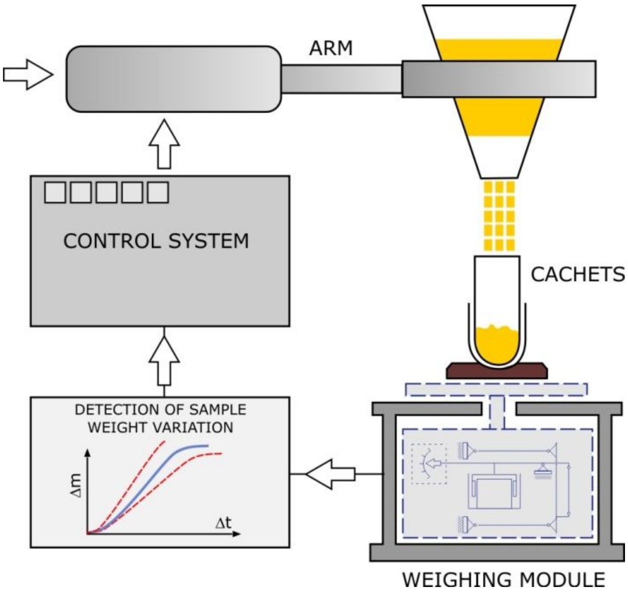


Fig. 86. Weighing module as a component of dosing system

In order to select weighing module that meets dosing operation requirements it is necessary to consider the following: dosed portion amount, gross weight and repeatability of indications. The necessary technical specification of weighing modules is provided by catalogues. For the most important data read the table below.

	MYA SERIES	MAS SERIES
Max capacity	2 g ÷ 52 g	220 g
Readability	0,1 µg ÷ 10 µg	100 µg
Tare range	2 g ÷ 52 g	220 g
Repeatability	0,4 µg ÷ 1,0 µg	100 µg
Satbilization time	5 s	3,5
Operating temperature	+10 ÷ +40 °C	
Interface	2 × RS 232, 2 × USB, , Ethernet, Wi-Fi, 4 ins / 4 outs	

Supplement - Directions of development of scientific and industrial metrology

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Horizontal character of metrology

As a study about measuring and measuring applications, metrology integrates practically all experimental sciences. It plays a crucial role also in all branches of industry, particularly in high technology sector. Metrology is applied in retail trade, and it is even more important in wholesale and international trade. The range of blanches where measuring is subject to metrology restrictions is constantly growing: medicine, pharmacy, agriculture, environment protection and safety are only the most common examples. As applications of metrology concern a lot of fields that are connected with one another, metrological issues are often regulated by law. The key role in so many different, complex and integrated fields requires to adjust this discipline to the constant changes. A big acceleration of science, technology, industry and trade as well as growing social expectations imply changes in metrology which must meet the modern demands.

Metrology in breaking the technical and administrative barriers in trade

Technical and administrative barriers in trade have always been a serious problem for international economy. The problem implies the necessity for the manufacturers and salesmen to adjust to legal regulations abiding in particular countries. A lot of barriers have already been removed (e.g. substituting legal demands for declarations of conformity issued by the manufacturers). However, all the time new barriers are created as one of domestic economy defence processes against cheap imported goods.

Practice shows that creating administrative and technical barriers makes the negative selection, as it hits most of all the countries and companies obeying the rules in production and trade. However, this mechanism is ineffective regarding the organizations which do not obey the rules. Effective control of the domestic market is a necessary requirement for the functioning of open economy, which is a difficult problem even for the highly industrial countries to deal with.

The necessity of repeating the same metrological tests was a serious problem even a few years ago: manufacturers and salesmen incurred the cost connected with it (covered by the clients) and wasted time for carrying out the same tests and obtaining analogical documents in many countries. This problem has been solved by the directors of BIPM and CIPM, who negotiated to acknowledge the certifications and calibration certificates in the countries that joined Mutual Recognition Arrangement CIPM (MRA or CIPM MRA) signed in Paris in 1999.

This arrangement is not international, but it is an agreement of NMI directors of member countries. The arrangement is obeyed even though there are no formal sanctions for not obeying it. Violating this rule by a member would question this member’s credibility, which is the key in economy. Apart from that, recognizing the documents issued by NMI countries-members of CIPM MRA is not automatic; every NMI member must show its measuring skills in a given field, successively taking part in the key comparisons, supplementary and international comparisons, which is registered in the database (KCDB) kept by BIPM. CIPM MRA arrangement is regularly modified in order to adjust the agreements to the changing situation and the latest trends in economy and science.

International cooperation in metrology

Submitting more and more branches of science and economy to metrology demands creates the necessity to develop metrological infrastructure. Only the biggest and the richest countries can meet all the requirements posed by developing metrology. This issue is clear in Europe where metrological infrastructure is significantly fragmented.

It takes years to develop mechanisms of research coordination. Cooperation of European countries regarding metrological research was successfully implemented in international research programs like MERA, iMERA, iMeraPlus, and recently EMRP. The program of coordinated research in metrology will soon be continued in another undertaking: European Metrology Programme for Innovation and Research, EMPIR). The programme budget of 600 mln € will be half supported by UE. It is a big opportunity for the smaller and poorer European countries, as they can take part in research consortiums doing scientific researches they would not do on their own for a number of reasons.

International cooperation in metrology at present has mainly regional, European dimension. However, there are already international projects integrating NMI from different continents, e.g. International Avogadro Coordination, a project whose scope is to determine the Avogadro constant; members from Europe, America, Asia and Australia take part in it. Intercontinental cooperation has long been a standard in scientific researches; also in this respect metrology resembles other academic disciplines.

The SI reform

Up to the middle of 20th century definitions of physical values and their units were purely operational: they defined how to measure a given value. It directly concerns definitions of mass and length adopted on the First Conference CGPM in 1889: the measurement implied direct and indirect comparison with the definition-described reference standard. Reference standards of a kilo and a metre in shape of a platinum-iridium artifact have a lot of disadvantages: they were selected in an arbitrarily manner, they are subject to slight but meaningful changes in time (drifts), they are not accessible everywhere, and in case of their damage it would be impossible to recreate them.

Defining physical units by means of atom properties proposed by Maxwell before the Metre Convention, is also operational. Measuring implies a comparison of a measured value with its atom, equivalent, e.g. the length of emitted wave, frequency or mass. The idea of definition atom standards was realized only in 1960 when a metre was defined as the wavelength in vacuum of the radiation corresponding to a transition between specified energy levels of the krypton 86 atom. The interferential definition was following. It should be emphasized that a metre atom standard and the length measurement using this method was created by Michelson in years 1892-1893. Time unit was also defined by means of atom standard. In years 1967-1968 CGPM decided that a second should be linked with the frequency of radiation emitted by cesium atoms. The cesium definition standard is today the basic time definition. In 1980 there was a breakthrough in the approach to defining basic SI units, as it was noticed that a unit might be unambiguously defined by determination of numeric value of a physical constant. The first unit defined in this way was a meter connected with a numeric value of light speed in the vacuum c, which as calculated to be c = 299 792 458 m/s (exactly): as c is constant, defining its numeric value, namely $\{c\}$ = 299 792 458, we clearly determine the unit value $[c]$ = m/s.

As a second was defined previously, we defined the length unit, a meter, at the same time.

Applying the same method of understanding to other basic SI units will be the basis of the future reform of the SI, most commonly called the New SI. Determining the numeric value of the Planck constant h = 6.626 069 57 kg m^2 s^{-1} we define a kilo mass at the same time. When $h = \{h\}\,[h]$ is constant, defining the numeric value $\{h\}$, we define the unit value $[h]$ = kg m^2 s^{-1}. As a metre and a second were described previously, defining h value defines a kilo value. This approach can be applied to other SI units. The New SI will define 4 basic SI units: 1) the mass unit, a kilo, will be defined by determining the Planck constant h; 2) the thermodynamic temperature value, kelvin, will be defined by determining numeric value of the Boltzmann constant k_B; (3) mole , a unit to express amounts of a chemical substance, will be defined by determining numeric value of the Avagadro constant N_A; (4) ampere, the unit of electric charge, will be defied by determining numeric value of elementary charge e.

The other three SI units will be reformulated so that their structure of the seven definitions stays the same. Defining measure units by determination numeric values of physical constants is highly abstract and requires a specific realization (*mise en pratique*) of those units. There is more than one method to do it; today realization of a second admits using several spectral lines, not only hyperfine transition in the cesium atom.

The reform of SI, called the New SI, has been put off twice. The main obstacle in the reform introduction is technical, namely the necessity to obtain the assumed accuracy of the initial realization of the unit (e.g. ~2×10^{-8} in case of a kilo), conformity of the measurements acquired by different methods (e.g. conformity of results of Alvogadro project, IAC, with the results of Watt balance project in case of a kilo redefinition), and a possibility of the initial realization of the unit with the assumed accuracy in different research centres, so that the independent verification of measurements would be possible (in case of realization of a kilo using Watt balance, currently only NIST is successful).

Conclusion

The key condition of the economic growth is the high level of metrology. Where the production requires the technological regime or the products must meet the legal standards, metrology plays a crucial role. Poor measuring skills in some field might be meaningful for production plants whose products will not be introduced to the market in the planned time.

The awareness of modern economy dependence on metrology was there in time of creation of the first national metrological institutes (NMI) on the threshold of 20th century. PTB, NPL and NIST were the first scientific institutes supported by the state, even though they were founded in the countries of purely free market economy. Supporting domestic trade and industry by financing the metrological research is today one of the few acknowledged (namely legal) methods of supporting domestic economy. Most other methods if support is illegal because it would violate the rule of free market. Competitiveness of our economy requires that the meaning of metrology should be appreciated as well.

Linking metrology with economy also has a different aspect; it goes about the meeting of science and industry, about dealing with difficult practical problems that industry has today. Scientists are usually accused of living in their ivory towers in conditions of splendid isolation, dealing with pure science with no links to reality. At the same time, industrial circles are accused of low innovativeness and inability to absorb the latest developments in science. Both accusations are partly true, those dilemmas are appear also in the most developed countries.

This issue was recognized already several dozen years ago in the USA and the proper means were taken, e.g. founding (financing) research consortiums grouping the state laboratories (including NIST), academic institutions and industrial companies. The biggest concerns in the IT branch (ITM), telecommunication (ATT), energetics (GE), aeronautics (Boeing), chemical industry (Du Pont) and other hi-tech branches have their own laboratories, usually more developed than the state laboratories.

Thanks to a global competition in the sector of high technologies, differences between the research and application are quickly fading. However, it is different than economic politicians expected in the previous political system in Poland. Scientists did not give up their research to work in the factories, but quite the opposite: high tech industry came so close to the scientific research that the differences between science, technology and production are only symbolic. Work in the industrial laboratories means not only financial benefits, but gives a scientific prestige as well. Fading borderlines between pure science and hi-tech industry is common, independently on a geographical region.

Appendix A - metrological terms index

The idea behind the index connected with this publication implies explanation of particular metrological terms. Copying dictionary or legal definitions is groundless, they can be found in certain publications. It is important to understand what the term means in practice.

A ADIUSTMENT

A sequence of activities that bring the weighing instrument to operation according to its purpose. In relation to electronic balances it means correcting the balance sensitivity by comparing the weighing result of the standard (usually built in inside the instrument) with the standard's reference value. Those comparisons are carried out in automatic cycles (controlled by the changes of temperature and time) or in semi-automatic cycles (by the operator).

Adiustment report
The procedure which implies printing, registering and exporting of the adiustment result. It might obtain a short or a more elaborate form; in the processes of monitoring over the weighing instrument might be used to test the balance efficiency.

Adiustment weight
A weight used in the process of the balance indication accuracy determination; it is essential to know the weight class and its error.

Automatic scale
A fully automatic scale which weighs without the operator's interference. They are usually used for dynamic weighing – weighing mass of a load in motion, conveyer scale, automatic dozers.

Accuracy of indication
Closeness of an agreement between a measured quantity value and a true quantity value of a measurand – VIM 2010. Generally speaking, a measurement is accurate when a difference between a measured quantity value and a true quantity value is very small.

Accuracy of measurement
Closeness of an agreement between a measured quantity value and a true quantity value of a measurand. Generally speaking, a measurement is accurate when a difference between a measured quantity value and a true quantity value is very small. This parameter depends on repeatability of indications and the balance linearity and might be dependent on a sensitivity drift. For samples placed in the centre of the pan, centricity might be disregarded.

Accuracy class
A symbolic division of balances that takes into consideration a number of the balance reading units and intends to keep measurement errors or instrumental uncertainties. There are 4 classes of accuracy: Special, High, Average, Low

The value of errors depends on the accuracy class and the load (PN-EN 45501). These relations are used during tests connected with e.g. the balance subsequent verification. The division and the implied errors are often used for the user's criteria determination.

C CALIBRATION

A number of operations that determine (in certain conditions) a relation between the measured value (indicated by the weighing instrument) or values represented by the standard or reference material, and particular values represented by standards.

Calibration range

A range in which indication error is determined for particular weighing points; there can be a weighing range from 20 g to 150 g in several weighing points, weighing points values are usually similar with the tested sample mass.

Calibration certificate

A document issued usually by national metrological institutes, measurement administrative units, district councils, accredited or not accredited measuring (calibrating) laboratories. The document contains results of the weighing instrument calibration and confirms that the instrument meets the determined metrological standards. Calibration certificate is one of the basic documents allowing to maintain measuring traceability.

CE mark

By affixing the CE mark, the manufacturer declares that the marked instrument conforms to all applicable European Directives.

Certification

Process of testing the balance technical parameters which tests the balance indications comparing them with their MPE (PN-EN 45501). The test is correct if all the tests are positive. Certification is the basis to issuing the certificate (type approval) for the tested balance (type and series) manufacturer.

Coverage factor

A numeric factor used for multiplying the expanded uncertainty uc(y) in order to determine a a size of a range around the corrected weighment result enclosing the measured value with certain uncertainty. Marked as *k*

Conformity assessment

The process preceding the product introduction to the market. It implies any activity to determine, directly or indirectly, that a process, product, or service meets relevant technical standards and fulfills relevant EU requirements.

D DECLARATION OF CONFORMITY

With a declaration of conformity, the manufacturer confirms that the European Directives applicable to the respective products are fulfilled.

Deviation

Commonly speaking, it is the balance (moisture analyzer) indication value minus the reference value. Deviation might be applied to the balance control processes or to the sample

Drift

Continuous change over time in indication of a measuring instrument.. in case of electronic balances, it implies very small changes of indications when the weighing pan is unloaded and during the weighment. It also applies the balance sensitivity, therefore, balances have automatic systems of internal adjustment.

Drying temperature

Temperature in which the sample mass changes in time is tested. For reference methods it is usually 105^{o}C, for moisture analyzers this temperature depends on the tested sample specificity.

Drying profile

In case of moisture analyzers, it is a manner of drying temperature dynamics control which is in the drying chamber from the moment of startup until the automatic or manual end of the process

E ELECTROMAGNETIC CONVERTER

The converting system whose essential element is the coil positioned in the magnetic field of the converter; the weighing pan is connected with the system straight-line mechanism, its load does not cause elastic deformations but a slight deflection of straight-line mechanism element, this deflection is registered by the position sensor and compensated by the force coming from the coil in the magnetic field.

EC verification

The procedure according to which the Notified Body checks and confirms that the balance parameters are compatible with the type described in the Type Approval Certificate EC and comply to NAWI directives.

EX mark

Official symbol for marking products intended for use in hazardous areas. By affixing the EX mark, the manufacturer declares that the product complies with ATEX Directive 94/9/EC.

Expanded uncertainty of measurement

Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand. Expanded uncertainty of measurement is usually shown by the symbol U

G GLOBAL APPROACH

According to philosophy of Directives of New/Global Approach there are certain requirements for products designed and made and the procedures of type approval thanks to which the manufacturer is responsible for identification and meeting requirements concerning the product design and making. The manufacturer who shows that his product is compatible with the norms, uses the procedures of type approval listed in the directive, selects the ones to his requirements. When he selects harmonized norms, the procedure is simpler and the manufacturer declares compatibility with the legal directives. By affixing the CE mark, the manufacturer declares that the marked instrument conforms to all applicable European Directives.

GLP – Good laboratory Practice

In Poland it is introduced by The Minister of Health Directive on 4th June 2003 regarding the criteria that should be met by units testing chemical substances and controlling the fulfillment of these criteria.

"(...) It is a system of quality assurance testing, setting rules for the organization of research units engaged in non-clinical safety studies and human health and the environment, particularly the chemical substances required by the Act, and the conditions under which these studies are planned, performed, monitored, and the results are recorded, stored and given in the report (...)”.

Good Laboratory Practice (GLP) embodies a set of principles that provides a framework within which laboratory studies are planned, performed, monitored, recorded, reported and archived. These studies are undertaken to generate data by which the hazards and risks to users, consumers and third parties, including the environment, can be assessed for pharmaceuticals (only preclinical studies), agrochemicals, cosmetics, food additives, feed additives and contaminants, novel foods, biocides, detergents etc.... GLP helps assure regulatory authorities that the data submitted are a true reflection of the results obtained during the study and can therefore be relied upon when making risk/safety assessments.

GMP - Good manufacturing practices

Good manufacturing practices (**GMP**) are production and testing practices that helps to ensure a quality product and origin of raw materials. GMP standards were worked up for pharmaceutical manufacturing, now they are used by some cosmetic companies, nutritional supplements, etc.

Gravimetric method of pipette calibration

The method of testing the volume of piston pipettes by means of electronic balances. The liquid is ejected to the balance weighing vessel which is weighed. Knowing the liquid density and the ejected liquid mass we can determine the sample volume, which is assigned to the pipette volume. Conversion of the weighment result for the volume is a quotient of the sample mass and volume

$$V = {}^{m}\!/_{\rho}$$

I INITIAL VERIFICATION

The procedure carried out since 1st May 2004, currently not used. Carried out by the Weights and Measured Office officers to check a given balance parameters before introducing it to the market.

Industrial metrology

Part of metrology which deals with measuring in different branches of science and industry, except the normative area (legal metrology).

L LEGAL METROLOGY

Part of metrology relating to activities which result from statutory requirements and concern measurement, units of measurement, measuring instruments and methods of measurement and which are performed by competent bodies.

Linearity

Ability of a weighing instrument to follow the linear relationship which describes the ideal balance. However, there are no ideal balances, the balance characteristics is not a line, we only aim to achieve this characteristics.

M MAXIMUM CAPACITY

Upper limit Max of the weighing range without consideration of an additional maximum tare, i.e. the maximum capacity whose weight can be determined on a balance.

Minimum capacity

lower limit Min of the weighing range, below which the weighing results may be subject to an excessive relative error (PN-EN 45501

Measurement average value

Measurement average value is a quotient of a sum of n digits and n (n is a number of added digits), so it is a quotient of a sum of all weighments result of a given sample and a number of weighments; this parameter is used during the indication repeatability testing

Measurement error in a control point

Error of a measuring instrument or measuring kit at a certain value of a measurand. An good example is the balance calibration in selected control points. The balance is regularly tested (usually after adjustment) with a standard. it is also determination of error in a control point, which should be similar to the tested samples mass

Metrology

A study concerning the methods of carrying out the measurements and the principles of the obtained results interpretation. It can be divided into legal, scientific and industrial metrology. The term is a compound of two words: *Metros* – measure and *Logos* – science.

M mark
A green square with an M letter is an additional marking declaring that non-automatic balances whose application demands it, comply with the basic requirements of 'Non-automatic weighing instruments' Directive 90/384/EEC.

Measuring range
A set of measurands values for which it is assumed that the weighing instrument error is enclosed in certain borders

MPE
Maximum positive or negative difference value permitted by the law between the value indicated by the instrument and the real value; the term coms from the legal requirements for balances (PN-EN 45501) and this mechanism (dependence of error and load) was used for making our own standards.

Measurement error
Difference between the value indicated by the instrument and the real value is commonly called measurement error.

MID - Measuring Instruments Directive
A directive by the European Union, which seeks to harmonise many aspects of legal metrology across all member states of the EU. Its most prominent tenet is that all kinds of meters which receive a MID approval may be used in all countries across the EU. The directive includes the following balances:

- Automatic scales for a single load;
- Batching automatic scales;
- Weighing automatic scales;
- Conveyor scales;
- Railway bridges.

N NAWI DIRECTIVE - NON-AUTOMATIC WEIGHING INSTRUMENTS
This Directive aims at harmonising the rules which apply to non-automatic weighing instruments in order to ensure their free movement in the internal market and to protect the public against the consequences of incorrect weighing results. The directive determines the requirements for non-automatic balances regarding the construction, research and MPE.

Non-automatic balance
A balance requiring the operator interference in the weighing process, placing the load on the pan, taring, clearing, etc.

Notified body
In the European Union, it is an organization that has been accredited by a Member State to assess whether a product meets certain preordained standards. Assessment can include inspection and examination of a product, its design and manufacture.

O OIML INTERNATIONAL ORGANIZATION OF LEGAL METROLOGY

OIML is an intergovernmental organization to promote the global harmonization of the legal metrology procedures that underpin and facilitate international trade.

One and two-step verification

- One-step verification applies to the balances that feature the mechanisms correcting the influence of gravitation force changes on the result; these balances contain automatic adjustment systems.
- Two-step verification applies to the balances that do not feature these mechanisms. In order to achieve their operational accuracy, we need to determine the balance sensitivity in a new place:

$$SE = \frac{\Delta R}{\Delta m}$$

It results from the electronic balances operation practice. When gravitational force ‘g’ changes, the balance needs to be adjusted again.

P PISTON PIPETTE

Measuring instrument used for measuring determined liquid volume, used in certain branches of industry. Because of the construction, there are single channel and multichannel pipettes, because of volume there are fixed and adjustable volume pipettes.

Precision of measurement

Closeness of agreement between independent measurement values obtained under stipulated conditions.

R RANDOM MEASUREMENT ERROR

Component of measurement error that in replicate measurements varies in an unpredictable manner. It results from different random factors (e.g. temperature changes, air drifts). Uniqueness of the same value measurement is the result of random error (testing the balance indication repeatability).

Reading unit [d]

Expressed in units of mass, the difference between the values corresponding to two consecutive scale marks, for analog indication or the difference between two consecutive indicated values, for digital indication.

Reference method

Testing method enclosing the following elements: sampling, measurement, the data analysis, acceptation criteria. This method produces accurate and repeatable results; this method result is the reference point for optimization of e.g. drying parameters (of moisture analyzer).

Repeatability of measurement

It is the precision of measurement in conditions of repeatability of measurement. Repeatability is high when weighing the same sample produces the same result or the differences are small, e.g. several reading units.

Reproducibility

Reproducibility is a degree of the results compatibility of the same value measured in the changed conditions. The following conditions can be changed:

- The weighing principle;
- Weighing method as a logical chain of operations,
- The observer,
- Weighing instrument,
- Weighing standard,
- The place of weighing,
- Ambient conditions (temperature, humidity, drafts, vibrations, etc.),
- Time.

Reproducibility might be expressed quantitatively or by means of the results spread characteristics

Resolution

The smallest increment of weight which the numeric display can indicate. For electronic balances it is expressed in the relation Max / d, so e.g. 220 g / 0,1 mg = 2 200 000 reading units; the internal resolution of the balance converter is much bigger

Risk analysis

A sequence of activities that reveal the elements connected with the weighing process that generate the biggest errors. You can analyze your own competence regarding e.g. the sample preparation, weighing skills, optimal use of the balance. Another aspect is the balance parameters assessment. Depending on the value of the weighing mass, we can talk about the influence of repeatability (small samples) and linearity on the weighment result.

S SAMPLING TIME

In case of balances, a period of time in which the balance indication is analyzed in order to obtain the measurement result, the converter in a continuous manner tests (samples) the measuring signal, which is converted by the filtering systems. In case of moisture analyzers the mass sampling time implies also analyzing the drying sample mass stability in a certain time period, e.g. 25 seconds.

Sensitivity drift

Small changes in the measuring kit indication which result from the characteristics of electronic systems and changes in the balance mechanism. These deviations are eliminated by the balance adjustment systems.

Sensitivity

Quotient of the change in an indication of a measuring system (ΔR) and the corresponding change in a value of a quantity being measured (Δm).

$$SE = \frac{\Delta R}{\Delta m}$$

Self-heating time
Time counted from the moment of the balance plug in until the moment when the balance errors are smaller than MPE (the norm). The balance is practically not plugged out, so the effect of self-heating takes place during the first use.

Scientific metrology
Part of metrology which deals with maintenance and development of standards and values connected with them.

Standard uncertainty of measurement
Uncertainty of the result of a measurement expressed as a standard deviation, usually shown by the symbol uc (y). In general, Standard uncertainty of measurement means type A and type B uncertainties.

Standard deviation
A measure of the value of the mean distribution of a measurand about its mean value. The smaller deviation value, the bigger concentration of results about its mean value, so better repeatability. When all the measurements in a series are the same, standard deviation equals zero, but because of rounding the results off, it is assumed as 0,4 x the balance reading unit.

Subsequent verification
Checking the balance basic parameters comparing them with their MPE (MPE listed in PN-EN 45501). Subsequent verification is carried out regularly due to the current legal procedures. The obligation of subsequent verification rests upon the user. The balance errors are related to their MPE. Therefore, before subsequent verification it should be checked if the balance indications are lower than MPE. The balance is accurate when its indication errors do not exceed 2xMPE.

Systematic measurement error
component of measurement error that in replicate measurements remains constant or varies in a predictable manner. It results from the imperfection of weighing instruments. Systematic errors should be taken into consideration introducing a correction to the result. It can be a correction, multiplier or a value form a table. An example of systematic error is a standard error listed in the calibration certificate.

T TRACEABILITY
Property of a measurement result, or value of a standard, to be related to suitable other standards, usually international or national standards, through an unbroken chain of comparison measurements, each of them has certain uncertainties

Tensometric converter
The converter which measures a deflection of the measuring element (extensometer),a change in the extensometer resistance ΔR is proportional to the mechanical stress.

Thermogravimetric analysis
A method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. The sample is weighed before and after heating, and the difference between the masses is calculated. The term is a compound of three Latin words: *Thermo* – hest, *Gravi* – weight, *Metry* – method.

Type approval
Decision of legal relevance, based on the evaluation report, that the type of a measuring instrument complies with the relevant statutory requirements and is suitable for use in the regulated area in such a way that it is expected to provide reliable measurement results over a defined period of time (VIML 2.6.).

U Uncertainty of measurement
Non-negative parameter characterizing the dispersion of the quantity values being attributed to the measurand, based on the information used.

Uncertainty budget
All possible elements that influence the weighing process. Usually the balance parameters are analyzed, however, it also might apply to other factors if they matter. It is not necessary to focus on all, but on the key elements, namely the elements that contribute to the uncertainty budget.

Uncertainty of measurement determination type A method
The method implies the analysis of a statistical series of observations. Uncertainty in this case means standard deviation, so it requires a large number of repetitions. It is applied when it is possible to carry out a large number of repetitions of the same value in identical conditions.

Uncertainty of measurement determination type B method
The method is determined by means of a scientific analysis based on all possible data concerning the variability of the initial value. This data might include the previously obtained weighing results, experience, parameters of particular materials and weighing instruments.

V Verification
In quality management systems, it is the act of reviewing, inspecting or testing according to Good manufacturing Practice, in order to establish and document that a product, service or system meets regulatory or technical standards.

Verification unit [e]
Value, expressed in units of mass, used for the classification and verification of an instrument. The details are enclosed in norm PN-EN 45501. For accuracy class III balances d=e, for other balances d≠e

W Weight

An object of clearly determined mass, shape and tolerance used for scaling and balance testing. The weights should meet the metrological requirements of OIML R 111. Frequently a weight is used as a mass standard.

Weighing instrument testing

The procedure which tests a weighing instrument for possible errors and general efficiency. The instrument is then admitted to use or rejected. The testing procedures are made taking into consideration the balance working range.

Weighing instruments approval criterion

Legal (or our own) requirements that are the basis to determine that the balance fulfills the given criteria. They usually concern the measurement accuracy, but sometimes also functionality and weighing time.

Qualification of weighing instruments

One of the validation processes. It might apply to:

- Design Qualification (DQ)
  A process that shows the equipment is fit for purpose.
- Installation Qualification (IQ)
  Aim to ensure if the right balance type has been delivered (checking parameters, documentation, descriptions, etc.).
- Operation Qualification (OQ)
  Aim to ensure that devices function correctly after installation.
- Performance Qualification (PQ)
  The documented evidence that the system, equipment or process is capable of consistently producing a safe product of high quality.

Weighing instrument

An instrument used for weighing, on its own or connected to other devices.

Working temperature

The temperature range indicated by the bottom and top value within the balance works according to the manufacturer declaration, namely the balance accuracy is correct. The temperature dynamics is essential.

Weighing range

A range between the Min and Max balance capacity (the norm), in practice a minimal sample weighing threshold might be bigger – it is determined by requirements connected with weighing accuracy (MinWeight)

Appendix B – Distilled water density

	0 °C	**10 °C**	**20 °C**	**30 °C**
0 °C	0,99984	0,99970	0,99820	0,99565
+ 1 °C	0,99990	0,99961	0,99799	0,99934
+ 2 °C	0,99994	0,99949	0,99777	0,99503
+ 3 °C	0,99996	0,99938	0,99754	0,99470
+ 4 °C	0,99997	0,99924	0,99730	0,99437
+ 5 °C	0,99996	0,99910	0,99704	0,99403
+ 6 °C	0,99994	0,99894	0,99678	0,99368
+ 7 °C	0,99990	0,99877	0,99651	0,99333
+ 8 °C	0,99985	0,99860	0,99623	0,99297
+ 9 °C	0,99978	0,99841	0,99594	0,99259

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