Anton Paar

GOOD

SINCE 1967

DENSITY MEASUREMENT™

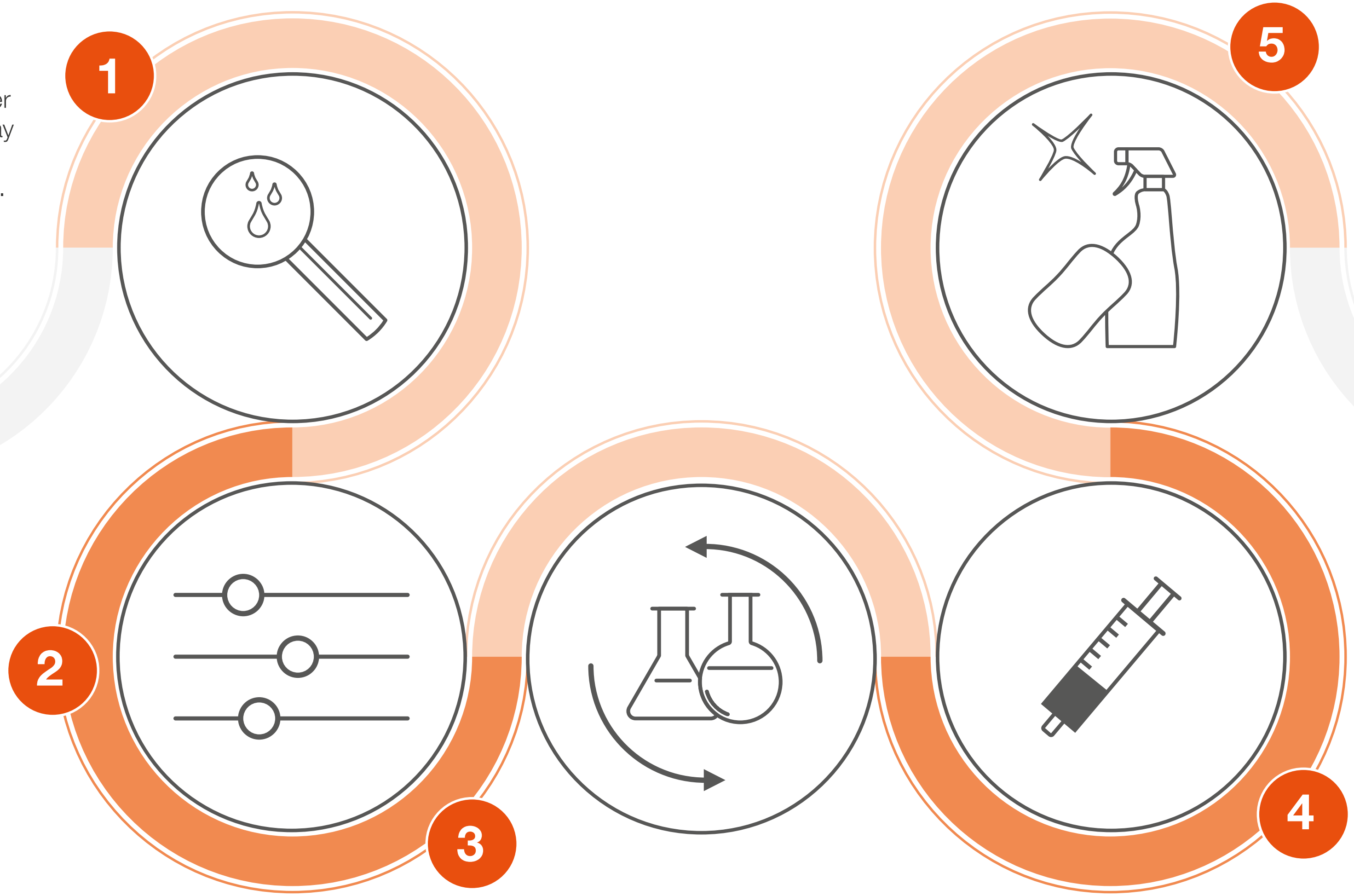
GOOD DENSITY MEASUREMENT REQUIRES CARE AND ATTENTION IN FIVE BASIC AREAS:

THE WATER CHECK, ADJUSTMENT, SAMPLE PREPARATION, SAMPLE FILLING, AND CLEANING.

Since 1967 Anton Paar GmbH has specialized in providing highly accurate and reliable density meters for research and industry.

This brochure sums up our experience and insights into measurement practice gained in over 50 years.

Follow these guidelines and you will be well on your way to accurate and reproducible density results.



WATER CHECK

Perform a water check every day prior to your measurements.

ADJUSTMENT

If the water check fails and cleaning does not help, perform an air/water or water adjustment.

SAMPLE PREPARATION

To get reproducible results prepare your samples with care and the same way every time.

SAMPLE FILLING

Fill the measuring cell carefully and without bubbles.

CLEANING

Remove the sample from the measuring cell right after the measurement, and clean your instrument regularly.

Perform a **water check** every day before your measurements.

If you carry out density checks at regular intervals you can ensure the high and stable accuracy of your density and concentration measurements.

The water check fails if the measured density value is not within a required tolerance range. The tolerance range depends on the application and is more stringent in the pharmaceutical industry than in the soft drink industry, for instance.

WORKFLOW

- Fill ultra-pure (e.g., bi-distilled or deionized), freshly degassed water into the measuring cell.
- Start a measurement.
- Compare the determined density with the reference value

EXAMPLE

A common tolerance limit for soft drinks is ± 1 x 10^{-4} g/cm³. This means the water check is positive if the determined density is between 0.9981 g/cm³ and 0.9983 g/cm³.

IF THE WATER CHECK FAILS, TRY THE FOLLOWING:

Use fresh ultra-pure water.

- Repeat the water check.

IF THE WATER CHECK STILL FAILS:

- Clean the measuring cell thoroughly.
- Repeat the water check using fresh ultra-pure water.

IF THE WATER CHECK STILL FAILS:

- Perform an air/water or water adjustment.

MY WATER CHECK:
THE TOLERANCE LIMIT FOR
MY WATER CHECK IS

If the water check fails and cleaning does not help, perform an **adjustment**.

An adjustment changes the instrument constants. For the consistency and comparability of results an adjustment should only be performed if the water check fails and using fresh water and cleaning the measuring cell does not help. Poor cleaning is the cause of the majority of measuring errors – an adjustment should be seen as a last resort. Instruments without a reference oscillator, such as DMA 501 or DMA 1001, might require adjustments after a temperature change, for highly accurate measurements.

WORKFLOW

- Common adjustment media are dry air and ultra-pure (e.g., bi-distilled), freshly degassed water.
- Follow the automatic adjustment procedure on your instrument.
- Make a record in your adjustment logbook.

CAUSE	EFFECT	INFLUENCE ON DENSITY
Aggressive cleaning	Volume of the measuring cell is increased	Artificial density decrease
Ineffective cleaning	Volume of the measuring cell is decreased	Aritificial density increase

REASONS WHY THE SIDE EFFECTS OF CLEANING NEED TO BE COMPENSATED BY AN ADJUSTMENT

!

IN THE PAST IT WAS RECOMMENDED TO PERFORM AN ADJUSTMENT ONCE A WEEK, BUT THIS IS NO LONGER THE CASE. ADJUST YOUR INSTRUMENT ONLY IF IT IS OUT OF RANGE.

MY ADJUSTMENT MEDIA ARE

Adjustment medium 1 ______________________

Density 1 ______________________

Adjustment medium 2 ______________________

Density 2 ______________________

Adjustment medium 3 ______________________

Density 3 ______________________

To get reproducible results **prepare** your **samples** with care and the same way every time.

YOUR SAMPLE CONTAINS GASES.

There are different methods for the degassing of liquid samples. The best method for your application depends on the kind of sample, the kind of gas, and the amount of gas that is dissolved in the sample. Be aware of the fact that you may slightly change the composition of many samples during sample preparation due to evaporation of volatile components.

STIRRING

- Stir your sample vigorously for 2 to 15 minutes (depending on the stirring equipment) until no more bubbling occurs.
- You can also pour the sample through a paper filter after stirring to get an even more efficient degassing effect.

ULTRASONIC BATH

- Put your sample into an ultrasonic bath for approximately 5 to 10 minutes until the bubble formation stops.

BOILING

- Boil the liquid for several minutes to remove dissolved air.
- Fill a clean glass flask full with the boiled liquid and cover it.
- Wait until the liquid has cooled down to the approximate measuring temperature.

USING A SYRINGE

- Fill the syringe* with the sample and place a finger on the opening.
- Pull the piston to create a vacuum and release finger to discharge the gas.
- Repeat this procedure at least three times to make sure that no gas is left in the sample.

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*The syringe needs to be large enough to leave some space for creating the vacuum. Only up to two thirds of the syringe should be filled.

YOUR SAMPLE IS AGGRESSIVE.

- Observe all safety regulations regarding the handling of the samples, cleaning, rinsing and waste liquids (e.g., use of safety glasses, gloves, respiratory protection, etc.).
- Check the chemical resistance of all materials which come into contact with the sample before starting the measurement.

YOUR SAMPLE IS VISCOUS.

- Heat up your sample to get lower viscosities.
- For highly viscous samples use a heating attachment to prevent sample freezing in the sample inlet and outlet.
- If you use an automated sample changer, check whether the viscosity corresponds to the given specifications.

YOUR SAMPLE IS VOLATILE.

- Close the sample vials with caps.
- Gently swirl the vials to bring condensed droplets back into the bulk liquid.
- For highly volatile samples use a sample filling unit which supports sample filling under pressure.

DO NOT BOIL FLAMMABLE LIQUIDS BECAUSE OF A HIGH RISK OF FIRE.

IF YOUR SAMPLE CONTAINS VOLATILE COMPOUNDS THAT ARE TOXIC, ALWAYS HANDLE THE SAMPLE IN AN APPROPRIATE ENVIRONMENT, LIKE A FUME HOOD.

Contact your local Anton Paar representative to find out the best way of preparing your sample.

Fill the measuring cell carefully and without bubbles.

AUTOMATIC FILLING WITH SAMPLE FILLING UNITS

Using sample filling units is the only way of eliminating filling errors due to the operator. As sample filling units repeat measurements in the same way every time, this is the best way to get repeatable results.
Even critical samples, like highly viscous samples or samples with volatile components, are filled smoothly. Some sample filling units additionally support automatic cleaning.

WORKFLOW

- Fill your samples in the corresponding sample vials and/or prepare the magazine.
- If your sample unit supports automatic cleaning, make sure that sufficient cleaning liquid is available.
- Empty the waste container before starting a series of measurements.
- Check the instrument settings.
- Prepare the sample list for your instrument.
- Start the measurement.

MANUAL FILLING WITH SYRINGE

Using a syringe is the traditional way of filling a sample into a benchtop density meter. It requires some training to achieve repeatable results and to avoid bubbles in the measuring cell.

WORKFLOW

- Press the plunger smoothly and slowly without stopping.
- Check whether the measuring cell is filled without bubbles.
- Check the instrument settings.
- Start the measurement.

For paste-like materials, always use a syringe. If the samples have a very high viscosity, you can fill them into the syringe by pulling the plunger completely out of the syringe, filling it from the back using a spoon and then inserting the plunger again.

⚠

BEFORE FILLING ANY SAMPLE INTO THE DENSITY METER, MAKE SURE THAT ALL WETTED PARTS ARE RESISTANT TO IT.

MY SAMPLE FILLING

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Remove the sample from the measuring cell after the measurement, and **clean your instrument** regularly.

CLEAN AND DRY THE MEASURING CELL AT LEAST ONCE AFTER EACH WORKING DAY OR WORK SHIFT.

CLEANING MORE FREQUENTLY MAY BE NECESSARY WHEN

- you perform adjustments,
- you measure a sample that is not miscible with the previous sample (e.g., water after a petrochemical sample),
- you want to use a minimum sample amount for your measurement,
- you measure a sample that could chemically react with the previous sample.

The best way to clean your instrument is by using sample filling units which support automatic cleaning. In this case make sure that the applied cleaning liquids suit your samples.

WORKFLOW

- Clean the measuring cell using two cleaning liquids:
  - Cleaning liquid 1: Cleaning liquid 1 dissolves and removes sample residues in the measuring cell. It needs to be a good solvent for all sample components.
  - Cleaning liquid 2: Cleaning liquid 2 removes cleaning liquid 1 and is easily evaporated by a stream of dry air in order to accelerate drying of the cell. Cleaning liquid 2 needs to be a good solvent for cleaning liquid 1.
- Dry* the measuring cell by activating the internal air pump.
- Check whether the cleaning and drying was successful by measuring the density of air (= air check).
- The instrument automatically compares the measured value with the reference value.

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* Handheld instruments do not need to be dried.
The DMA 35 should not be dried.

⚠

BEFORE FILLING ANY CLEANING LIQUID INTO THE DENSITY METER, MAKE SURE THAT ALL WETTED PARTS ARE RESISTANT (CHECK IN THE INSTRUCTION MANUAL).

MY CLEANING LIQUIDS ARE

Sample ______________________________

Cleaning liquid 1 ______________________________

Cleaning liquid 2 ______________________________

Sample ______________________________

Cleaning liquid 1 ______________________________

Cleaning liquid 2 ______________________________

More tips on good density measurement.

USE A ROBUST LABORATORY BENCH.

ASSURE A CLEAN ENVIRONMENT.

GET YOUR INSTRUMENT ISO 17025 CALIBRATED ONCE A YEAR.

PREVENT DIRECT SUNLIGHT OR AIRFLOW DUE TO VENTILATION.

AVOID A HEAT SOURCE IN THE VICINITY OF 2 METERS.

ARRANGE REGULAR MAINTENANCE BY SERVICE TECHNICIAN.

PERFORM REGULAR CALIBRATIONS WITH A WELL SPECIFIED STANDARD.

Notes

List of **typical samples** and suggested cleaning liquids

SAMPLE	SUGGESTED CLEANING LIQUID 1	SUGGESTED CLEANING LIQUID 2
AFTER-SHAVE, PERFUME	Alcohol	-
BEER	Water, enzymatic lab cleaner*	Ethanol
BEER WORT	Water, enzymatic lab cleaner*	Alcohol
FUEL	Petroleum naphtha	Acetone, alcohol
LIQUID SOAP & DETERGENT	Water	Alcohol
LUBRICATING OIL	Petroleum naphtha	Acetone, alcohol
MILK, CREAM	Water, enzymatic lab cleaner*	Alcohol
MOTOR OIL	Petroleum naphtha	Acetone, alcohol
ORANGE JUICE	Water	Alcohol
SCHNAPPS	Alcohol	-
SOFT DRINKS	Water	Alcohol
SALAD DRESSING, MAYONNAISE	Petroleum naphtha	Alcohol
SHAMPOO	Water	Alcohol
SUNTAN LOTION	Petroleum naphtha	Alcohol
WOOD PROTECTION/ WHITE SPIRIT-BASED (WATER-BASED)	Petroleum naphtha (water)	Alcohol

* Using enzymatic lab cleaner is recommended for special cleaning. After using the lab cleaner you need to rinse the measuring cell with water.

GLOSSARY

DENSITY ("TRUE DENSITY")

The density ρ is defined as mass divided by volume:

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

ρ — density
m — mass
V — volume

The unit of density is kg/m³ or g/cm³. 1 g/cm³ = 1000 kg/m³.

Mass is independent of external conditions, such as buoyancy in air or gravity. It corresponds to weight in vacuo.

True density of liquids and gases is measured with the oscillating U-tube method.

The density of liquids and gases is highly temperature-dependent. Therefore, density measurement always requires accurate temperature measurement or control. Typically, density decreases with increasing temperature as the individual molecules require more space due to their thermal motion.

Note: Water is a unique liquid. The density maximum is reached at a temperature of 3.98 °C with ρ = 0.999972 g/cm³.

APPARENT DENSITY

The apparent density ρ_{app} of a sample is defined as weight in air divided by volume:

$$\rho_{app} = \frac{W}{V}$$

ρ_{app} — apparent density
W — weight
V — volume

Units applied for apparent density are typically kg/m³ or g/cm³. Please note that the values of (true) density and apparent density differ. Apparent density is smaller than true density.

Apparent density can be calculated from true density by taking into account the buoyancy in air of the sample and the weight and density of a reference weight. Steel is nowadays defined as the material of choice for the weights. Earlier, brass was used.

$$\rho_{app} = \frac{\rho_{true,\ sample} - \rho_{air}}{1 - \frac{\rho_{air}}{\rho_{steel\ or\ brass}}}$$

ρ_{app} — apparent density
$\rho_{true,\ sample}$ — true density of sample
ρ_{air} — true density of air
$\rho_{steel\ or\ brass}$ — true density of brass or steel
With: $\rho_{brass} = 8.4$ g/cm³ and $\rho_{steel} = 8.0$ g/cm³

SPECIFIC GRAVITY

The specific gravity SG (sometimes referred to as relative density D) is calculated by dividing the density of a sample ρ_{sample} by the density of pure water ρ_{water} at defined temperatures:

$$D^{20}/_{4} = SG^{20}/_{4} = \frac{\rho_{sample} \text{ at } 20\ °C}{\rho_{water} \text{ at } 4\ °C}$$

$D^{T1}/_{T2} = SG^{T1}/_{T2}$ — specific gravity related to given temperatures
ρ_{sample} — density of sample
ρ_{water} — density of pure water
At 4 °C: $\rho_{water} = 0.999972$ g/cm³
At 20 °C: $\rho_{water} = 0.998203$ g/cm³

The specific gravity is dimensionless, which means it has no unit.

APPARENT SPECIFIC GRAVITY

The apparent specific gravity SG_{app} (sometimes referred to as apparent relative density D_{app}) is calculated by dividing the apparent density of a sample $\rho_{app,\ sample}$ by the apparent density of pure water $\rho_{app,\ water}$ at defined temperatures:

$$D_{app}{}^{20}/_{20} = SG_{app}{}^{20}/_{20} = \frac{\rho_{app,\ sample} \text{ at } 20\ °C}{\rho_{app,\ water} \text{ at } 20\ °C}$$

$D_{app}{}^{T1}/_{T2} = SG_{app}{}^{T1}/_{T2}$ — specific gravity related to given temperatures
$\rho_{app,\ sample}$ — apparent density of sample
$\rho_{app,\ water}$ — apparent density of pure water

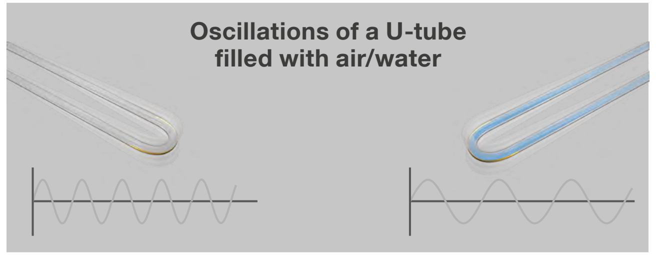
The apparent specific gravity is dimensionless, which means it has no unit.
For measurements with the pycnometer the apparent specific gravity can be determined in the following way:

$$D_{app}{}^{20}/_{20} = \frac{\text{weight}_{\text{sample+bottle}} - \text{weight}_{\text{bottle}}}{\text{weight}_{\text{water+bottle}} - \text{weight}_{\text{bottle}}}$$

	AIR AT T = 20 °C, P = 1013 MBAR	**WATER AT T = 20 °C**
TRUE DENSITY ρ	0.00120	0.99820
SPECIFIC GRAVITY $SG^{20}/_{20}$	0.00120	1
SPECIFIC GRAVITY $SG^{20}/_{4}$	0.00120	0.99823
APPARENT SPECIFIC GRAVITY $SG_{app}{}^{20}/_{20}$	0	1

OSCILLATING U-TUBE METHOD

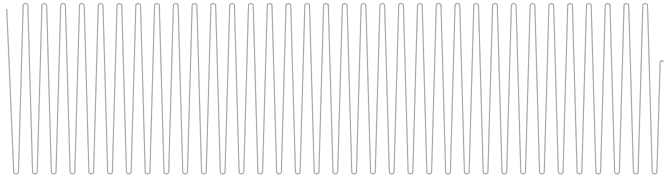
The oscillating U-tube method is used to measure the true density of fluids. The sample is introduced into a U-shaped tube that is electronically excited to oscillate at its characteristic frequency. The characteristic frequency changes depending on the density of the sample. Via a precise determination of the characteristic frequency and an appropriate adjustment, the density of the sample is determined. Due to the high temperature dependency of density, the measuring cell has to be accurately thermostatted.


Oscillations of a U-tube filled with air/water

Modern high-precision density meters additionally provide:	**Viscosity correction** to enable accurate results over a large viscosity range **Reference oscillator** to enable accurate results over a large temperature range following just one adjustment

FORCED OSCILLATION METHOD

Since the launch of the digital density meters a constant oscillation was state of the art. This technology has reached its limits.

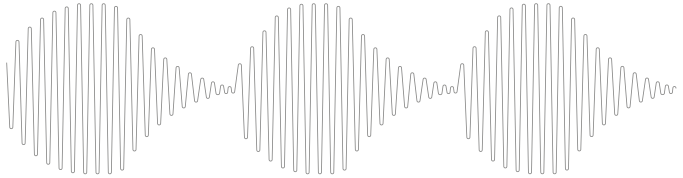


Pulsed Excitation Method

Patented technology exclusively by Anton Paar (Patent AT 516420 B1)

The “Pulsed Excitation Method” describes the fact that the U-tube is excited by impulses to oscillate. Once a constant amplitude is achieved, the pulse sequence is stopped. The U-tube’s oscillation is measured while it fades out freely and unaffected by any influences. Excitation and fade-out alternate periodically.

The advantages are:	– The user obtains more information compared to conventional methods. – The viscosity correction is improved. – The “Pulsed Excitation Method” offers improved repeatability and reproducibility.



CONCENTRATION MEASUREMENT

The concentration of a mixture of two components (binary mixture) can be determined by means of density measurement. Mixing two samples with known densities A and B gives a sample whose density lies between value A and B. The exact value depends on the mixing ratio and therefore on the concentration.

Concentration measurement is also possible for so-called quasi binary mixtures:

- Mixtures containing two major components. Some additional ingredients exist in small concentrations, but due to the small impact on the bulk density, these components can be ignored.
- **Example:** The major components of regular soft drinks are water and sugar. All other ingredients can be ignored when measuring the sugar concentration (°Brix).
- Mixtures containing several components, but only the amount of one component varies. All other ingredients are kept precisely constant.
- **Example:** For the production of infusions several base ingredients are precisely weighed according to a receipe. In a second step this mixture is diluted with water. The concentration can be controlled by means of density measurement.

CALIBRATION

A calibration is the comparison of achieved measurement results with a standard reference value. A calibration is performed to validate the quality of measurements and adjustments. The standard reference value is given by the certificate of density standard liquids, for instance. The standard’s uncertainty and reference method are crucial to keeping the quality of measurements as high as possible.

Recommendation: Perform 1 to 2 calibrations per year with a density standard, preferably certified according to ISO 17034 and specified as 3x better than the instrument.

FACTORY CALIBRATION

Every instrument that leaves Anton Paar’s production centers is factory calibrated. It comes with a factory certificate, is ready to measure on delivery and yields highly precise and accurate measuring results.

ISO 17025 CALIBRATION

A calibration according to ISO 17025 is traceable to international SI units and serves as a reliable and internationally recognized reference during audits.

ADJUSTMENT

An adjustment is the modification of instrument constants to enable correct measurements and eliminate systematic measurement errors. An adjustment is carried out after a calibration, unless the stated deviation is within the tolerance range.

For the adjustment the density meter uses the density values of the standards and the measured oscillation periods to calculate the instrument constants. Usually two standards are required for an adjustment, like dry air and pure (e.g., bi-distilled), freshly degassed water.

ISO 17034-CERTIFIED REFERENCE MATERIAL

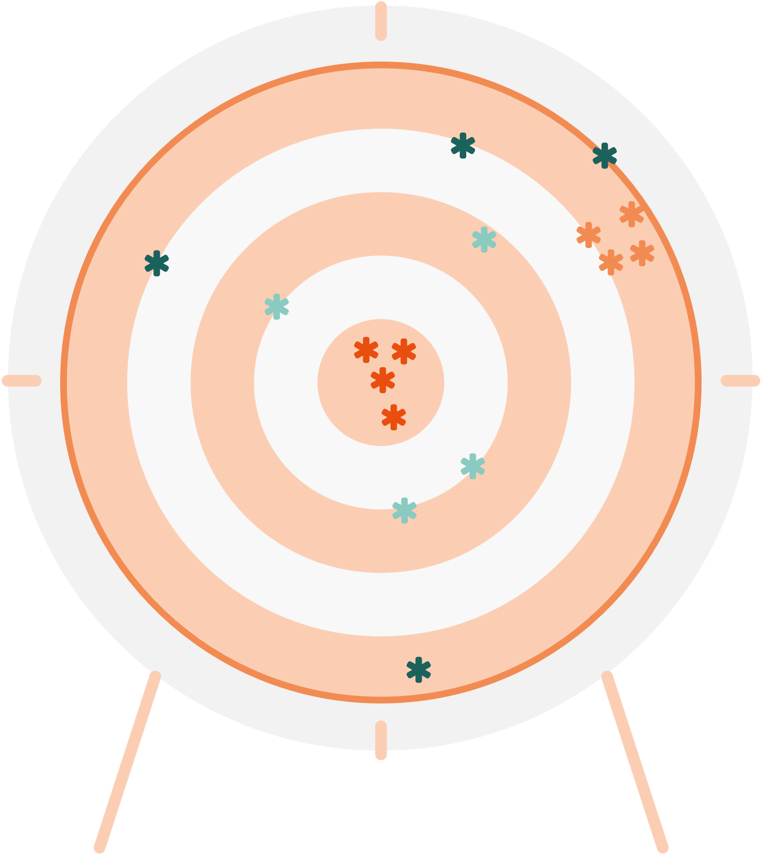
For ISO 17034-certified density standards, specified reference values are valid throughout the standard’s lifetime due to continuous monitoring. Further, they are traceable to SI units.

ACCURACY

Accuracy expresses qualitatively how close the measurement result comes to the true value of a measurand.

In contrast, the quantitative measure of accuracy is uncertainty of measurement.

Accuracy and precision states:	✱ Not accurate, not precise ✱ Accurate, not precise ✱ Not accurate, precise ✱ Accurate, precise



PRECISION

Precision expresses qualitatively how close the measurement results come to each other under given measurement conditions. Precision can be stated under repeatability or reproducibility conditions.

UNCERTAINTY OF MEASUREMENT

The uncertainty of a measurement specifies an interval within which the true value of the measurand is expected. Uncertainty of measurement includes instrumental measurement uncertainty (arising from the measuring instrument), uncertainty of the calibration standards and uncertainty due to the measurement process (sample preparation, sample filling, etc.).

The standard uncertainty can be determined in accordance with the "Guide to the expression of uncertainty in measurement" (GUM), JCGM 100:2008.

REPEATABILITY

The repeatability is the closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement.

Such ideal conditions lead to a minimum dispersion of measurement results.

The repeatability conditions are:	– The same measurement procedure – The same operator – The same measuring instrument, used under the same conditions – The same location – Repetition over a short period of time

Repeatability may be expressed with the repeatability standard deviation. This standard deviation is calculated from measurements carried out under repeatability conditions.

REPRODUCIBILITY

Reproducibility is the closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement.

Such conditions lead to a maximum dispersion of measurement results.

These reproducibility conditions may include:	– Measuring principle – Measuring method – Operator – Measuring instrument – Reference standard – Location – Conditions of use – Time

The changed measurement conditions have to be stated.

Reproducibility may be expressed with the reproducibility standard deviation. This standard deviation is calculated from measurements carried out under defined reproducibility conditions.

MEASUREMENT ERROR

The measurement error is a measured quantity value minus a reference quantity value. Random measurement errors and systematic measurement errors can be distinguished.

RANDOM MEASUREMENT ERROR

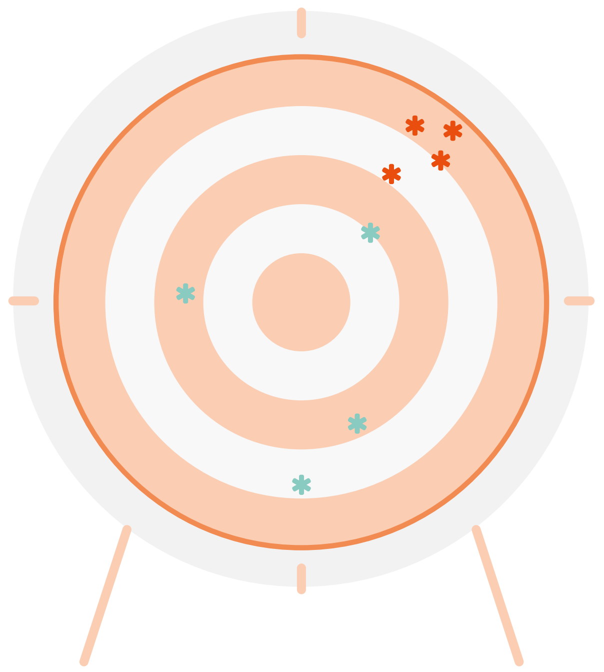
The random measurement error is the component of a measurement error that varies in an unpredictable manner in replicated measurements. Many measurements have to be carried out to eliminate random measurement errors. The mean value of these measurements tends towards the true value.

SYSTEMATIC MEASUREMENT ERROR

The systematic measurement error is the mean value that would result from an infinite number of measurements of the same measurand carried out under repeatability conditions, minus the true value of the measurand.

Systematic measurement errors, and their causes, are either known or unknown. A correction can be applied to compensate for a known systematic measurement error.

Measurement errors:	✱ Random measurement error ✱ Systematic measurement error



RESOLUTION

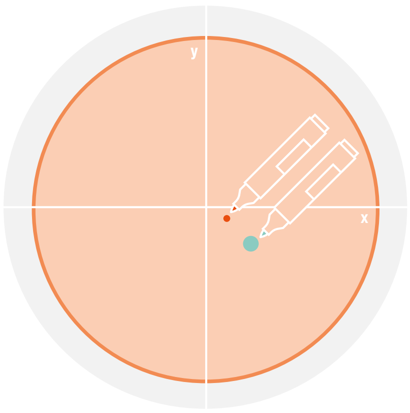
Resolution is the ability to resolve differences, i.e. to draw a distinction between two things. High resolution means being able to resolve small differences. In a digital system, resolution means the smallest increment or step that can be taken or seen. In an analog system, it means the smallest step or difference that can be reliably observed.

The most common mistake is the assumption that instruments with high resolution give more accurate results. High resolution does not necessarily mean high accuracy.

The accuracy of a system can never exceed its resolution!

● **Allegory for fine resolution**
With a fine marker it is possible to draw small dots.

● **Allegory for coarse resolution**
With a thick marker it is not possible to make fine drawings.



ARITHMETIC MEAN VALUE

The arithmetic mean value x_0 is the sum of the measurement values divided by the number of measurements n:

$$x_0 = \frac{1}{n}\sum_{i=1}^{n} x_i = \frac{x_1 + x_2 + \ldots + x_n}{n}$$

x_0 ____________ mean value
x_i ____________ measurement value of the i^{th} measurement
n ____________ number of measurements

The mean value does not give any information about the scattering of measurement results.

Example:

A series of density measurements gives the following results: Arithmetic mean value (with n = 6): $x_0 = 0.9982037$ g/cm³	$x_1 = 0.998203$ g/cm³ $x_2 = 0.998203$ g/cm³ $x_3 = 0.998204$ g/cm³ $x_4 = 0.998203$ g/cm³ $x_5 = 0.998204$ g/cm³ $x_6 = 0.998205$ g/cm³

Tip: In Microsoft Excel you can use the function AVERAGE (number1, number2, ...)

EXPERIMENTAL STANDARD DEVIATION (S.D.)

For a series of n measurements of the same measurand, the experimental standard deviation s characterizes the dispersion of the results. It is given by the formula:

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - x_0)^2}$$

s ____________ experimental standard deviation
n ____________ number of measurements
x_i ____________ measurement value of the i^{th} measurement
x_0 ____________ arithmetic mean value

The mean value is often quoted along with the standard deviation. The mean value describes the central location of the data, the standard deviation describes the scattering.

The example from the arithmetic mean value is used to calculate the experimental standard deviation:

$x_0 = 0.9982037$ g/cm³
n = 6

$$s = \sqrt{\frac{(x_1-0.9982037)^2 + (x_2-0.9982037)^2 + \ldots + (x_6-0.9982037)^2}{5}}$$

s = 0.000001 g/cm³

Tip: In Microsoft Excel you can use the function STDEV.S (number1, number2,...)

All in all, what makes for good density measurement?

AWARENESS OF THE ENTIRE MEASUREMENT WORKFLOW, FROM START TO FINISH – FROM THE MOMENT YOU START WORKING IN YOUR LAB TO THE MOMENT YOU ARE CLEANING YOUR EQUIPMENT. JUST KEEP YOUR EYES TRAINED ON THE FIVE BASIC AREAS – AND YOU'RE WELL ON YOUR WAY …

FIND OUT MORE

www.anton-paar.com/density