Good practice guide

for the measurement of the density of liquids in industry

rhoLiq

EMPIR EURAMET

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The EMPIR project "Establishing Traceability for Liquid Density Measurements" (EMPIR 17RPT02 rhoLiq) is a European project focused on the establishment of the degree of equivalence in liquid density measurements in Europe. This good practice guide was written as a part of activity A4.1.5 of the project and is meant to enhance the quality of density measurement results obtained by laboratories and industries employing oscillation-type density meters for liquids, to achieve the traceability of the derived quantity, liquid density, back to SI base units. For more information of the project, please visit www.rholiq.org or https://www.ptb.de/empir2018/rholiq/home/.

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1 Introduction

European economy is dependent on high-value liquids such as wine, olive oil and fuel, however, only a few European National Metrology Institutes (NMIs) currently possess the appropriate expertise to perform liquid density with a level of accuracy and uncertainty that meets the national and international needs. This means that the traceability chain of liquid density measurements to the user level, such as test, calibration, and research laboratories as well as industry is often compromised in less experienced European countries. This was the major need that was addressed in this EURAMET 17RPT02 rhoLiq –project by developing the metrological capacity in liquid density metrology in European NMIs.

This project allow the progress of the national and international metrology capacities in liquid density metrology by developing the capacities of the participating NMIs on the primary and secondary level. The robustness of liquid density measurements has been studied by studying the effects of surface tension and viscosity to the measurement results. In addition, studies on measurement of liquid density of non-Newtonian liquids have been performed. In addition to this good practice guide, three guides that will be submitted as EURAMET technical guides have been written as part of this project.

This “Good practice guide for the measurement of the density of liquids in industry” is the result of activity A4.1.5 in the EURAMET 17RPT02 rhoLiq –project. This activity builds on the results from activities A1.2.6, A3.3.4 and A4.1.3. This guide is meant to be more problem specific guide directed towards industries, whereas there are three other guides written as part of this project that are more scientifically detailed guides. [1], [2], [3]

This guide has been compiled by JV and is based on the information and experience gathered from all the project partners: IPQ, BEV-PTP, BRML, CMI, DMDM, GUM, IMBiH, PTB, TUBITAK, INM and Anton Paar GmbH.

1.1 Scope

This guide is written to address some of the most asked questions and possible problems associated with liquid density measurements on the industrial level. The purpose of this guide is to give a general overview of the basic method for liquid density measurements with oscillation-type density meters.

As mentioned earlier, this guide is not meant to be a detailed scientific guide on the measurement method, and therefore, does not dive deep into the theories behind the measurement principles. This guide is more directed towards the liquid density measurements on the industrial level.

This guide gives a starting point for a more in depth look at liquid density measurement principles. It gives references to dive deeper in the theory if needed. However, the main point is to provide solutions from more experienced laboratories to certain problems that arises during liquid density measurements on different substances.

1.2 Terminology

Density	Derivate unit regarding to SI defined as its mass per unit volume. The unit of the density is kg/m^3.
Reference Temperature	Temperature at which the sample density value will be reported. For example, this temperature value may be 15 °C or 20 °C
Reference pressure	101 325 Pa
Adjustment of a measurement system	Set of operations performed on a measurement system so that it provides prescribed indications, corresponding to given values of the magnitude to measure. The measurement system includes setting of zero, adjust the offset and amplitude of scale. The adjustment should not be confused with calibration. The calibration should be repeated after adjustment process.
Calibration	Series of operations in which, under specified conditions, a relationship is established between the magnitude values and measurement uncertainties provided by the measurement standards in the first stage and the corresponding indicator values. The relevant measurement uncertainties, and in the second stage, this information is used to derive the measurement result from the indicator.
Metrological Traceability	Property of result linked to a reference by an interrupted and documented chain of calibrations with the uncertainty contributions.
Reference Material (RM)	Homogeneous and stable material or substance which produced for the measurement of one or several properties.
Certified Reference Material (CRM)	Material accompanied by a certificate (ISO Guide 31) with the metrological traceability and validated procedures (ISO 17034, ISO Guide 35).

1.3 Symbols

LATIN CHARACTERS

f	frequency [Hz]
k	coverage factor (JCGM 100:2008)
m	mass [kg]
p	pressure [0,1 MPa =1 bar]
t	temperature [ºC]
u	standard uncertainty (JCGM 100:2008)
u_c	combined standard uncertainty (JCGM 100:2008)
U	expanded uncertainty (JCGM 100:2008)
V	volume [m^3]

GREEK CHARACTERS

ρ	density [$kg \cdot m^{-3}$]
ω	angular velocity (rotation), angular frequency (oscillation) [rad/s], [s^{-1}]

1.4 Abbreviations and Acronyms

BEV-PTP	Federal Office of Metrology and Surveying - Physico-technical testing service (the Austria's NMI, in German: *Bundesamt für Eich- und Vermessungswesen -Physikalisch-technische Prüfdienst*)
BRML	*Biroul Roman de Metrologie Legala* (the Romania's NMI)
CMC	Calibration and Measurement Capability
CMI	*Ceský metrologický institut* (the Czech Republic's NMI)
(C)RM	(Certified) Reference Material
DMDM	*Ministarstvo privrede Direkcija za mere i dragocene metale* (the Serbia's NMI)
EMPIR	European Metrology Programme for Innovation and Research
EURAMET	European Association of National Metrology Institutes
GUM	Guide to the Expression of Uncertainty in Measurement
GUM-NMI	GUM Central Office of Measures (the Poland's NMI, In Polish: *Główny Urząd Miar*)

IMBiH	*Institut za mjeritejstvo Bosne i Hercegovine* (the Bosnia and Herzegovina's NMI)
INM	*I.P. Institutul National de Metrologie* (the Republic of Moldova's NMI)
IPQ	Portuguese Institute for Quality (in Portuguese, *Instituto Português da Qualidade*)
ISO	Internal Organization for Standardization
JRP	Joint Research Project
JV	*Justervesenet* (the Norway's NMI)
NMI	National Metrology Institute
OD	Oscillation-type density meter
PRT	Platinum resistance thermometer
PTB	*Physikalisch-Technische Bundesanstalt* (the Germany's NMI)
MSDS	Safety Data Sheet
SI	International System of Units (in French, *système international d'unitées*)
SMOW	Standard Mean Ocean Water
TUBITAK	*Türkiye Bilimsel ve Teknolojik Araştırma Kurumu* (the Turkey's NMI)
VIM	International Vocabulary of Metrology (in French, *Vocabulaire International de Métrologie*)

2 Oscillation-type density meters

The operation of oscillation-type density meters is not described in great details in this document and more detailed description can be found elsewhere. The basic operation principle is presented in this chapter and the following chapters focuses on good practice for density measurements.

2.1 Basic principle

The simplest way to represent the measuring principle of an oscillation-type density meter is through a simple harmonic motion as depicted in Figure 1.

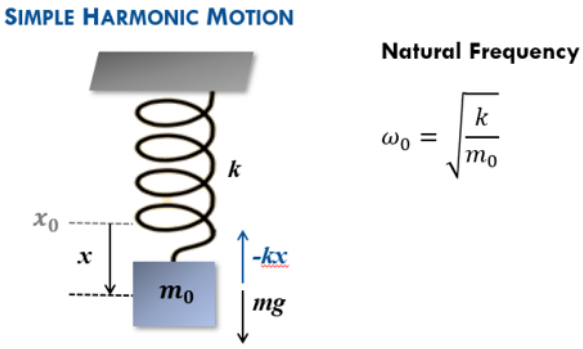

Figure 1 Schematics of the simplest way to represent measurement principle behind the oscillation-type density meter. The figure includes some symbols that are not explained in this good practice guide. [1], [4]

In this schematic, the mass m_0 attached to a spring which has a stiffness (spring constant) of k is displaced from the equilibrium x_0 by an external force. Therefore, the system is subjected to a force that pulling towards the equilibrium and is proportional to the displacement at a given time $x(t)$. ω_0 is the natural frequency of this system, which is dependent on the spring constant and mass of the system.

A measurement cell of one type of oscillation-type density meter is depicted in Figure 2.

Figure 2 Photo of a measuring cell of an oscillation-type density meters (courtesy by Anton Paar)

When empty, the internal glass tube, which is represented by the light blue color in the Figure 2, has a mass corresponding to m_0, a spring constant k and is made to oscillate at a frequency ω_0. The oscillation can be induced for example electrically or mechanically. When the tube

with volume V, is then filled with a test liquid with density ρ, the total mass m of the system changes to $m = m_0 + \rho V$. Assuming that the spring constant of the system is unaffected, the oscillation frequency f changes.

The oscillation period τ of the previously described system can be obtained from the oscillation frequency f. In most of this type of instruments, the density of the measured liquid is obtained by a second order empirical relation with the square of the oscillation period according to equation (1).

$$\rho(t,p) = A(t,p)\tau^2 - B(t,p) \quad (1)$$

Where t and p, are temperature and pressure, respectively. Without going more into the details [1], these instrument constants A and B, are defined by using two known reference densities, i.e., reference liquids.

A more detailed and in-depth description of this principle is described in the Guideline on liquid density measurement using oscillation-type density meter. [1]

As one can imagine, there are several things that need to be considered to ensure reliable and repeatable measurements. In the next chapters, we go through some of the most common sources of error and suggest how to correct for or avoid these errors.

3 Sample preparation

All the samples and (certified) reference materials (CRMs/RMs) is recommended to be stored in a dark and cool place, lower than 20 °C, if not otherwise specified by the producers. To ensure the stability of the liquids, it is also recommended to avoid temperature cycling as much as possible.

One of the most important things while performing this type of measurements is to know your samples. First and foremost, the samples can be harmful to health and environment, or harmful to the instruments. Getting to know the sample by reading the material safety datasheet (*MSDS*) and following the guidance of the MSDS is the first step.

To know the samples is also relevant since (the material of) the measuring cell needs to be resistant to the sample. Usually, these tubes are made of borosilicate glass which tolerates quite large variety of liquids, however care needs to be taken with liquids that can be slightly more aggressive, such as solutions containing acids.

In addition, the sample also need to be removed from the instrument after the measurements are done. It might sound like a trivial problem, however if the wrong solution is used to clean the instrument afterwards, in the worst case, the sample can harden and damage the instrument beyond repair. The best way to avoid this is to have a small amount of the sample on a glass plate (or metal, depending on the design of the instrument) and try different cleaning solutions. Usually, it is beneficial to use two solutions, the first to remove the sample and the second to remove the first cleaning solution. The second solution should also be easily evaporated, and therefore, it is usually either alcohol or acetone.

3.1 Syringes

Usually, the sample liquid is transferred to the measuring cell with the help of syringe. This means again that the syringe should be made of a material that is not harmed by the sample, and which does not contaminate the sample. The most common syringes are plastic or glass syringes, depending on the properties of the sample. The general guidelines for syringes are [1]:

- **Plastic syringes:** For accurate measurements use 2 mL or 5 mL syringes unless a syringe holder is available. Do not re-use plastic syringes to avoid the risk of carryover. Please bear in mind that plastic syringes for medical purposes contain a lube to allow the plunger to easily flow, meaning that your sample (for instance, ethanol solutions ≥ 40 %V/V) can be contaminated if you do not clean the syringe prior to the use. For this purpose, ethanol can be used. Allow the syringe to dry completely before you use it.
- **Glass syringes (with glass, Teflon or metallic tip and plunger):** very useful for solvent liquids, like dodecane, ethanol and tetrachloroethylene. For sulfuric acid use an all-glass syringe. Thorough cleaning of glass syringes is important before re-use. Usually, you can use the solvents used to clean the density meter cell to clean the syringe. Again, allow the syringe to dry properly before you use it. Keep in mind that glass

syringes are much more expensive than the plastic ones, so you may reserve set of syringes by type of liquids (for instance: one set for water-based liquids and other for organic liquids). Be aware that glass syringes with glass plungers have no grip and your sample may be discharged by the effect of gravity.

The size of the syringe is important for accurate measurements. While more repetitions can be done without refilling or change the syringe, a larger syringe can cause stress to the measuring cell due to weight of the syringe. It is therefore recommended to not use syringes over 5 mL without a support accessory for the syringe.

3.2 Degassing of the sample

After the safety side of liquids is taken care of, the next step is to find out how to prepare the sample. Different liquids require different type of preparation. The sample should be degassed, if (and only if) the purpose of the measurement is to measure a liquid without dissolved gases. Bear in mind that degassing will change the density and sometimes the composition of sample by losing its more volatile components. There are several methods for degassing liquids [1]:

- Degassing can be performed by stirring the sample vigorously or agitating the sample until no more bubbles occur. However, care must be taken that the stirring/agitation does not introduce gas into the sample. This way of degassing can be enhanced by pouring the sample through a paper filter after stirring.
- Using an ultrasonic bath until no more bubbles occur. Usually between 5 and 10 minutes.
- The liquid can also be heat up for several minutes (around 30 minutes – if more you may risk losing your sample by evaporation) to remove dissolved air. For water, 80 °C is enough. After heating, the liquid should be poured into a clean flask with a lock. The sample needs to be let to cool down close to the measurement temperature, before transferring the sample into the measuring cell. Samples that can change composition during the heating should not be subjected to heat. **DO NOT BOIL FLAMMABLE LIQUIDS!**

With all these methods, the risk of evaporation and toxicity of the samples need to be considered. Always handle the samples according to the instructions in the MSDS.

Even if a sample is degassed, gases (air) can dissolve back to the sample while transferring the sample from the flask/container to syringe. Therefore, liquids like water can be left in the syringe to stabilize for 30 minutes before injecting the sample into the measuring cell. During this time, the remaining air gathers to small bubbles to the walls of the syringe and these bubbles can be “eaten” by a bigger bubble, which then can be pushed out of the syringe before injection.

3.3 Samples with high viscosity

If the sample has a very high viscosity, it might be difficult to transfer the sample into the syringe and from the syringe to the measuring cell. In such cases, it is possible to pre-heat the sample to make it lower viscosity and easier to handle. However, a great care needs to be taken that the heating does not change the sample composition. It is also not recommended to go much above the measuring temperature.

4 Instrument preparation

As with all electromechanical instruments, the temperature of the device and its environment can affect the measurements. It is therefore recommended that the instrument is kept under stable environment and turned on few hours before starting the measurements. Also, the location of the instrument should be chosen carefully to avoid heaters, air conditioners or direct sunlight.

4.1 Environment control

The environment should be as stable as possible during the measurements and inside the parameters given by the manufacturer. Usually these are around 20 °C and 30 – 60 %RH.

Limiting the exposure to dust and particles is also an important aspect. Each particle from the laboratory air that ends up into the sample, or into the measuring cell, will affect the measurement result and will contaminate the sample. The more accurate the measurement needs to be, the less dust and particles should be allowed in the air.

The air pressure is usually not controlled; however, it affects the density of the sample. For accurate density measurements, the air pressure should be measured, and a correction should be applied to the indicated density reading. The magnitude of this correction will be dependent on sample's compressibility, that for this reason should be known.

4.2 Water check

To ensure that the instrument is in condition to perform accurate measurements, it is important to perform water check at least every day before starting the measurements. This is important since it is possible that the natural oscillation frequency of the system or volume of the measurement cell changes over time. This drift can be caused by physical changes in the measurement cell, such as stress or that the measurement cell is not cleaned properly.

The method for the water check is usually given in the user manual of the instrument and it is best to follow the procedures given there. It is common to use bi-distilled or deionized, freshly degassed water for this purpose. The sample preparation and measurement for the water check should follow the same good practice as any other measurement that is performed with the instrument.

Even though the measurements can be done in a wide temperature range, the water check is usually performed at 20 °C. The producers also often suggest tolerance for the density check; however, it can vary depending on the need for accuracy. A common tolerance limit for example for soft drinks is ± 1×10^{-4} g/cm^3. This means that if the result from the water check, performed with bi-distilled, freshly degassed water at 20 °C, needs to be between 0,9981 g/cm^3 and 0,9983 g/cm^3, otherwise the water check fails. See the user manual of the instrument for how to set the tolerance for water check. [5]

One of the most common reasons for a failed water check is insufficient cleaning or the quality of the water that is used for the water check. Therefore, the first stage after a failed water check is to run the water check with a new sample of freshly degassed bi-distilled (or ultra-pure) water at 20 °C. The use of a new clean syringe and flask may be also advisable, as they can be contaminated, and therefore causing these differences of the water density results. If the water check fails again, then proceed to clean and dry the measuring cell and perform the water check again. If the water is pure and fresh, the cell is clean and the water check fails, an adjustment is needed. [1], [5]

4.3 Air and water Adjustment

Adjustment of the instrument should be performed only if the water check fails and it is made sure that the measuring cell is clean. When the adjustment is performed, the instrument constants A and B in equation (1) are changed, and therefore, unnecessary adjustments can cause inconsistent or incomparable results.

The adjustment should be performed according to the producer's procedure. This is usually done with air and bi-distilled or deionized, freshly degassed water. The new values for the instrument constants should be stored, either in the instrument itself, or in a separate logbook. This information can be used to monitor the instrument and discover possible problems or identify special situations that cause a drift in the system. [6]

5 Measurements

All measurements are subjected to random and systematic errors. For good measurements, both types need to be considered. In this chapter we go through some of the most common sources for both random and systematic errors.

An example of a very simplified measurement procedure can look something like:

1. Water check -> Needs to pass. If not, see chapter 4.2 and 4.3;
2. Make sure the right cleaning agents (1 and 2) are available;
3. Sample preparation according to the needs;
4. Sample injection to the measuring cell (make sure to use a proper syringe and when inserting the sample, ensure that you have an un-interrupted sample column from the inlet to the outlet of the measuring cell – make sure that there are no air bubbles);
5. Temperature stabilization;
6. Measurement;
7. Inject at least 1,5 mL of new sample;
8. Repeat point 5 forward. Eventually change to new filled syringe if needed, until there is enough data to meet the needs;
9. Cleaning the instrument with cleaning agent 1;
10. Cleaning the instrument with cleaning agent 2;
11. Drying the instrument by passing dry air (most of these instruments are supplied with a pump and a silica cartridge);
12. Check instrument, if failed, repeat points 9 to 12.

5.1 Injection of the sample

The filling of the measuring cell with the sample causes a random error. Each operator injects the sample slightly differently. Variations comes from, for example: the force applied when inserting the syringe into the measuring cell entrance and the rate of injection. These can vary also in measurements performed by the same operator.

These types of errors cannot be eliminated without automatization of the sample injection and measurements. However, these can be minimized by training and good procedures:

- Use consistent and just enough force to insert the syringe;
- Press the plunger smoothly and slowly without stopping, when injecting the sample into the measuring cell.

Inserting the syringe into the entrance of the measuring cell with too much force can cause stress in the measuring cell. This stress can be seen in accurate measurements and relaxation time of several hours, up to days can be required for the measuring cell to relax back to normal state.

Also, choice of the right size and type of accessories (syringes, hoses, waste container etc.) can help to reduce the variations due to operator.

For most liquids, viscosity is decreasing when the temperature of the liquid increases. The same applies here as for the sample preparation. The sample can be heated up before injection to reduce the viscosity and making the sample easier to handle. However, care needs to be taken to avoid permanent changes of the sample due to the heating.

5.2 Bubble control

Right after the injection, the measuring cell should be checked for possible air bubbles. Bear in mind that air bubbles, besides being elastic, will also reduce the actual volume of the sample and therefore causes a random error in the measurement. If there is a bubble in the measuring cell, a new sample should be injected. However, not all the liquids are equally prone to bubble formations. If you want the density of a water sample above 40 °C you need to degas it, otherwise it will be impossible to measure it without the formation of air bubbles.

The bubble formation is greatly reduced with a proper degassing of the liquid and if the sample has had enough time to stabilize in the syringe. Also, slow, and stable injection rate reduces the bubble formation. Injection temperature slightly above the measurement temperature decreases the chance of bubble formation during stabilization time [1].

5.3 Temperature stabilization

The density measurements are always performed at specific temperatures, even if it is “room” temperature. When the sample enters the measuring cell, it always has slightly different temperature than the target temperature. This is due to air temperature being different than the measuring cell temperature, the hand of operator who touches the syringe are warmer than the measuring cell temperature and so forth. Also, the temperature is typically controlled by a Peltier element, which has a controller. This type of heaters/coolers tends to overshoot the target temperature and then slowly oscillate towards the target temperature.

Since density is a function of temperature, more accurate results are obtained if the sample has enough time to stabilize. So, the stabilization time varies depending on the temperature difference between the injected sample and the temperature where measurement is performed. However, for accurate measurements, the stabilization time should be at least 30 minutes, but can be up to 24 hours.

However, portables density meters do not possess such Peltier elements that allow to set the sample at the target temperature. In these situations, you may cool down the sample by using ice bath or heating up the sample with a hot water bath and leave the sample to reach the desired temperature inside the density meter cell. Other possibility is to know (and or determine) sample’s temperature coefficient and to correct the density values to the target temperature afterwards. Some density meter models allow to insert this value and give the density results already at the desired temperature.

5.4 Non-Newtonian Liquids (Viscoelastic samples)

Viscoelastic materials are always showing viscous and elastic behavior simultaneously. The viscous portion behaves according to Newton's law and the elastic portion to Hooke's law. So, depending on their rheological behavior, viscoelastic materials may behave as viscoelastic liquids or viscoelastic solids. The viscoelastic properties of a fluid can influence the resonant frequency of the oscillator of a vibrating tube density meter. On the one hand, additional harmonic forces act on the oscillator due to the elastic portion of the fluid, leading to an apparent increase in the elastic constant of the oscillator (Δk) (Figure 3). On the other hand, the viscous portion of the fluid leads to an increase in the inert mass (Δm) of the oscillator due to the movement of the fluid layers in the boundary layer which is in phase with the oscillator (Figure 3).

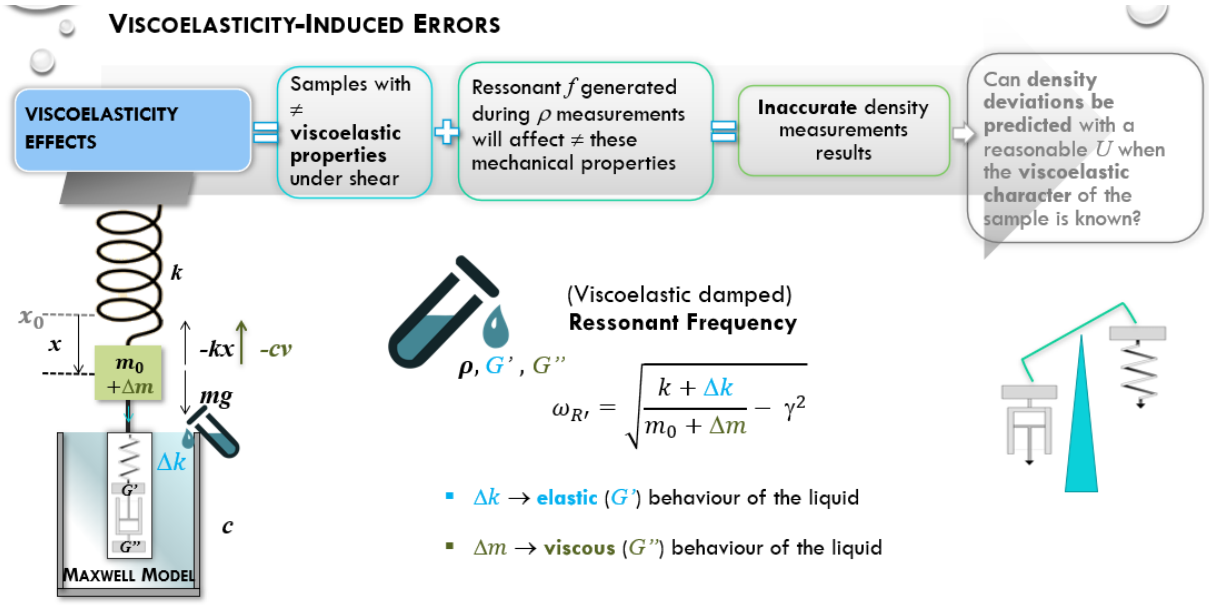

Figure 3 Causes of the viscoelasticity effects in density measurements performed with oscillation-type density meters (adapted from [4])

Several studies found that the viscosity calibration curve performed with Newtonian samples should not be used for non-Newtonian liquids, as it does not account for the elasticity effects (that will lead to density decreasing by attenuation of viscous damping by the elastic part). It is advisable to use an alternative density measurement method, such as hydrostatic weighing or pycnometer to be used as reference method.

6 Cleaning the instrument

One of the most important good practices in liquids density measurement is to keep your instrument clean. In accordance with Chapter 3, cleaning of the instrument starts already at the sample preparation by making sure that the cleaning agents available can remove the sample from the measuring cell. When the cleaning agents are chosen, one needs to find out if the cleaning agents can be disposed into the same waste or should they be collected separately.

Two different cleaning agents should be chosen; the first one to remove the sample residuals and the second one to remove the residuals from the first cleaning liquid. The second one should also be volatile to help the drying process of the measuring cell.

The following cleaning process is suggested:

- Pass 3 x 10 mL of the cleaning agent 1 through the measuring cell. Purposefully introducing bubbles increases the effectiveness for the cleaning due to greater abrasiveness;
- Pass 3 x 10 mL of the cleaning agent 2 through the measuring cell. Purposefully introducing bubbles increases the effectiveness for the cleaning due to greater abrasiveness;
- Dry the measuring cell at least for 10 minutes by passing dry and clean air through the measuring cell. Usually, the instruments have an integrated pump for this purpose;
- Measure the air density to verify that it agrees with air density. Reference value for air density is 0,001199 g/cm^3 for 20 °C and 1013,25 mbar. However, corrections need to be applied if temperature and pressure deviates from these values. Water check can also be performed. If so, follow the guidelines for water check;
- If the air density check, or water check fails, pass ethanol through the measuring cell and dry and test the system again.

There are some general guidelines for the choice of cleaning liquids, however it is good practice to test the cleaning agents before inserting the sample into the measuring cell. This is easily done by having a drop of the sample on the surface of a piece of glass (e.g., microscope slide) and rinsing the glass with the chosen cleaning agent. It is important to rinse only, no physical agitation or abrasion. The cleaning agent is suitable if the glass becomes clean by rinsing only.

The best cleaning agents are often liquids that are similar to the samples and some general suggestions can be found in Table 1. Following this rule, the best cleaning agents for aqueous (polar) samples are polar liquids like water, alcohol, and acetone. For organic samples like oils, fuels and lubricants, organic liquids such as petroleum naphtha, petroleum ether, toluene and n-nonane can be used.

In some cases, to remove the sample, it might be necessary to replace first cleaning agent with several cleaning cycles with alternating cleaning agents. This can be the case with some

samples that are mix of organic and aqueous components, such as mayonnaise. The same rules apply and an aqueous and organic cleaning agents are alternated after which the "Cleaning Agent 2" is used after the sample is completely removed.

Table 1 General guidelines for cleaning agents according to the type of sample, taken from [1].

Sample		Cleaning Agent 1	Cleaning Agent 2
Hydroalcoholic Solutions	Without organic content	Alcohol	Alcohol
	With organic content	Ultrapure water, enzymatic cleaner	Alcohol
Hydrocarbons		Petroleum ether	Acetone
Sugar solutions (sucrose, glucose, fructose)		Ultrapure water	Alcohol
Fat solutions		Petroleum ether	Alcohol
Sugar and fat solutions		Ultrapure water, enzymatic cleaner	Alcohol

Even though the Table 1 gives the general suggestions, there are some cases where one needs to be very careful. For example, samples containing proteins should never be cleaned with alcohol since the alcohol can cause denaturation of the proteins causing the proteins to coagulate and precipitate to the glass walls of the measuring cell.

It is not usually necessary, however, when water is chosen as the Cleaning Agent 1, the effectiveness can be increased using standard laboratory cleaners. If some proteins have been building up on the surface of the measuring cell during, for example prolonged measurements of beer wort, enzymatic cleaners can be used. Always follow the instructions of the manufacturer concerning dosage and duration of application, if used.

Any "heavier" cleaning should be used with care. For example, strong alkaline lab cleaners (pH over 10,5) can cause etching of the glass surface upon prolonged exposure and at higher temperatures. If you must use strong alkaline lab cleaner, keep the exposure short and below 25 °C.

When measuring paints and varnishes, some pigments may stick to the wall of the measuring cell. One proven cleaning method is to pass a solvent mixture through the cell by using a water jet pump, for example. If there is a valve in the suction line upstream of the density meter through which air can also pass, the cleaning effect will be particularly intense owing to the air entrained. Some pigments still may remain in the cell. [1]

It is recommended to avoid the use of very aggressive substances and they should be used as a last resort, if at all due to the risks for both the instrument and health. For example, hydrofluoric acid etches glass and hence, can damage the measuring cell. Chromic acid, which used to be popular cleaning agent, is a risk to health due to its high carcinogenic potential.

7 Results

The result on the display of an oscillation-type density meter is not necessarily the most exact, and some corrections may need to be applied. We go through the most common corrections in the chapter below. A more detailed explanations of the corrections can be found in [1].

7.1 Applying Corrections

To obtain the actual density of the sample from the display reading on the oscillation-type density meter, the equation (2) is used. [1]

$$\rho(t_0, p_0) = [\rho_{mean}(t,p) - \varepsilon_{MS}] \cdot [1 + \alpha_{fluid}(t - t_0)] \cdot [1 - \gamma_{fluid}(p - p_0)] + \varepsilon_{res} + \varepsilon_{rep} + \varepsilon_{Rep} + \varepsilon_{fluid} \quad (2)$$

Where:

- $\rho(t_0, p_0)$ is the density value at the target temperature, t_0 and target pressure, p_0.
- $\rho_{mean}(t,p)$ is the mean measured density value, at measured temperature, t and measured pressure, p.
- ε_{MS} is the measurement error related with the measuring system, including the error due to: density indication $\varepsilon\rho$; temperature εt; pressure εp; viscosity of the sample $\varepsilon\eta$; viscoelasticity of the sample εVE. Correction for this error is achieved by performing a calibration with certified reference materials (CRMs).
- ε_{res} is the error due to the finite resolution of the device. This error has zero average value but has a contribution value in uncertainty.
- ε_{rep} is the error due to the repeatability of the device. This error has zero average value but has a contribution value in uncertainty.
- ε_{Rep} is the error due to the reproducibility of the device. This error has zero average value but has a contribution value in uncertainty if known.
- ε_{fluid} is the deviation coming of the unknown air saturation of the liquid and other features that may affect density.
- α_{fluid} is the cubic thermal expansion coefficient of the liquid.
- γ_{fluid} is the isothermal compressibility of the liquid.

Depending on the required accuracy of the measurement, some of the terms in the equation 2 can be negligible and may be omitted.

7.1.1 Temperature

It is not always possible to measure the sample at exactly the correct temperature, and therefore the correction term $[1 + \alpha_{fluid}(t - t_0)]$ in equation (2) is used scale the measured density to the density at the target temperature. However, this requires that the cubic thermal

expansion coefficient (α_{fluid}) of the sample is known or determined by means of equation (3), by knowing the density of the sample at two temperatures (t_0 and t).

$$\alpha_{fluid} = \frac{\rho(t)-\rho(t_0)}{t-t_0}\rho(t_0)^{-1}, \text{ in } °C^{-1} \quad (3)$$

7.1.2 Pressure

Since the pressure is not usually controlled in laboratories, or in the measurement cells, the error due to pressure deviation from the reference pressure 1013,25 mbar needs to be corrected. This is done by the term $\left[1-\gamma_{fluid}(p-p_0)\right]$ in the equation (2). In a similar fashion this requires that the isothermal compressibility (γ_{fluid}) of the sample is known. This is highly sample dependent, however just for a reference, the density deviation of water between 970 mbar and 1013,25 mbar is approximately 0,002 kg/m^3 [1]. If it is practically possible, the isothermal compressibility can be calculated from equation (4).

$$\gamma_{fluid} = \frac{\rho(p)-\rho(p_0)}{p-p_0}\rho\left(p_0\right)^{-1}, \text{ in mbar}^{-1} \quad (4)$$

7.1.3 Viscosity

High viscosity of the sample causes an extra dampening of the oscillation, and therefore the measured density is an overestimation. Many of the current oscillation-type density meters on the market, has some preinstalled algorithms that can be used to correct the results. See the user manual from the manufacturer to see more details on the specific correction methods. [1]

If a specific viscosity range is interesting, it is possible to derive algorithms to calculate the correction for the viscosity when the instrument is being calibrated with viscous CRMs with known value for both density and viscosity. [1]

In density indications without viscosity correction, it can be found a linear relation between the density deviation $\Delta\rho$ and the squared root of the dynamic viscosity $\sqrt{\eta}$ up to a maximum of around 365 mPa.s, and then a plateau where the density deviation reaches a maximum value, and it is no longer dependent on dynamic viscosity.

Bear in mind that the corrections and the plateau are dependent on the oscillator characteristic, so be sure to perform a proper calibration to your density meter if you need to obtain accurate density values.

7.2 Uncertainty

One important part of a traceable measurements is the uncertainty of the measurement. The same way as every measurement has errors, every measurement has uncertainties. These uncertainties rise from small deviations of conditions and processes, which can not necessarily be controlled. The uncertainties are divided into two categories: Type A and B [7]. Type A uncertainty is based on the statistical evaluation of the measurement data itself, for example the standard deviation of the mean. The type B uncertainty includes the uncertainties that arise from all the conditions during the measurement and from the instrument itself. Examples for Type B uncertainty are resolution of the reading, environmental conditions, and uncertainty from the calibration of the instrument. However, these are only examples and the real uncertainty contributions need to be evaluated for each specific measurement method.

The measurement result itself is not a point, but a range where within the real result can be found with a certain probability, called confidence interval. In standard metrology, a ~95,5 % confidence interval (corresponds to k = 2) is usually used and the corresponding uncertainty is called expanded uncertainty, U. The expanded uncertainty consists of the combined uncertainty, u_c, and a coverage factor, k:

$$U = k\, u_c(y) \tag{5}$$

where y is the quantity to be measured (measurand) [7].

However, the confidence interval used is dependent on the branch of industry. For example, medicine and health industry uses even higher confidence interval (~99,7 %, corresponds to k = 3), due to the severity of consequences in case of an error in the measurement.

The measurement result, *Y*, is reported as

$$Y = y \pm U \tag{6}$$

An example of an uncertainty budget for density measurement with oscillation-type density meter can be found in Table 2. The details of uncertainty analysis are not explained here, however, more details on the uncertainty can be found in [1], [7].

The size of the contributions mentioned in the Table 2 varies and since not all the measurements require the most accuracy, some of them can be neglected from the daily use uncertainty calculations. It is usually the few largest contributions that dominate the uncertainty; however, all the contributions should be evaluated and if a contribution is neglected, a justification should be provided.

Table 2 A generic example of an uncertainty bugdet for a high accuracy density measurement with an oscillation-type density meter. The table includes symbols which are beyond this guide and are not explained here. For more information on the uncertainty budget see [1].

Source of uncertainty	Standard uncertainty	Type of evaluation	Distribution	Degrees of freedom
Density ρ				
Resolution of the density meter	$\frac{\rho\ resolution}{\sqrt{12}}$	B	Rectangular	50
Calibration and drift	$u_{\rho_{cal\ \&\ drift}}$	A	Normal	*n*-1
Repeatability	$\frac{\sigma_\rho}{\sqrt{n}}$	A	Normal	*n*-1
Reproducibility	$\frac{\sigma_\rho Rep}{\sqrt{n}}$	A	Normal	*n*-1
Temperature *t*				
Resolution of the density meter	$\frac{t\ resolution}{\sqrt{12}}$	B	Rectangular	50
Calibration and drift	$u_{t_{cal\ \&\ drift}}$	A	Normal	*n*-1
Temperature hysteresis of the oscillator	$u_{hyst.oscillator}$	B	Rectangular	50
εt	εt	B	Rectangular	50
Pressure *p*				
Resolution of the pressor transducer	$\frac{p\ resolution}{\sqrt{12}}$	B	Rectangular	50
Calibration and drift of the pressor transducer	$u_{p\ sensor_{cal\ \&\ drift}}$	A	Normal	*n*-1
Calibration and drift of the oscillator in pressure	$u_{p\ oscillator_{cal\ \&\ drift}}$	B	Rectangular	50
εp	$\frac{\varepsilon p}{\sqrt{12}}$	B	Rectangular	50
Sample properties				
α_{fluid}	$u_{\alpha_{fluid}}$	B	Rectangular	50
γ_{fluid}	$u_{\gamma_{fluid}}$	B	Rectangular	50
$\varepsilon\eta$	$\frac{\varepsilon\eta}{\sqrt{12}}$	B	Rectangular	50
ε_{fluid}	$\frac{\varepsilon_{fluid}}{\sqrt{12}}$	B	Rectangular	50
Other sources				
$\tau, V, M_0, A, B, \alpha_{oscillator}, \gamma_{oscillator}, \varepsilon\tau, \varepsilon V, \varepsilon k$	-	B	Rectangular	50
Density relative combined standard uncertainty	u_ρ			
Density relative expanded uncertainty	$u_\rho \cdot k = U$			
Coverage factor (95 %)	k			
Effective degrees of freedom	ν_{eff}			

8 Calibration of the instrument

Since the density given by the instrument is based on an empirical equation (1), it is bound to have an error. A calibration is a set of operations that establishes the relationship between the density of the reference liquid and the corresponding density reading of the instrument. A calibration does not alter the instrument constants *A* and *B*.

To ensure the most accurate measurement, this error needs to be corrected, and to correct it, the instrument needs to be calibrated over the whole density and temperature range. This yields a so-called calibration curve, which can then be used to implement the correction for the density reading at a specific density. Calibration of an oscillation-type density meter should be performed 1-2 times per year to achieve accurate measurements [5].

It is quite typical that these instruments are used in measurements that require quality control, and therefore, accredited calibration of these instrument is often required. In this case, an accredited service provider should be contacted.

8.1 Calibration of the indication using reference liquids

To define calibration curve over the whole density range of the instrument, one must use reference liquids with at least three different densities; close to low end, middle of and close to the high end of the density range. In ideal situation, the calibrations are performed with several densities, corresponding with the densities measured during normal usage. The reference liquids should also have the viscosities close to the viscosities of the sample that are normally being measured with the instrument.

The reference liquids that are used for calibrations should be certified reference materials (CRMs). CRMs are materials (liquids) that are characterized by metrologically valid procedure for one or more specified properties. The CRMs are accompanied by certificate which states the values of the specified properties (e.g. density, viscosity), the associated uncertainties and a statement of the metrological traceability.

Several different types of reference materials (RMs) and CRMs are available, and care needs to be taken that the RMs or CRMs that are being used are suited for the purpose. For example, if the instrument is being calibrated at 60 °C, then the RMs/CRMs need to have values given at 60 °C, or an equation is given which can be used to extrapolate the reference density up to 60 °C.

8.2 Basic principle of the calibration

In essence a basic calibration follows the same set of rules as good practice for measurements in Chapter 5. An example of a very simplified calibration procedure can look something like:

1. Water check -> Needs to pass. If not, see chapter 4.2 and 4.3;
2. Choose the correct CRM for the density in question;
3. Make sure the right cleaning agent is available;

4. CRM preparation according to the needs;
5. CRM injection to the measuring cell;
6. Temperature stabilization;
7. Measurement the density;
8. Write down the ambient pressure and temperature;
9. Inject at least 1,5 mL of new CRM;
10. Repeat point 5 forward. Eventually change to new filled syringe if needed, until there is enough data to meet the needs;
11. Cleaning of instrument with cleaning agent 1;
12. Cleaning instrument with cleaning agent 2;
13. Drying instrument;
14. Check instrument, if failed, repeat points 9 to 12.

The density values for the CRMs are reported in specific temperature and pressure. This reference value needs to be then corrected to the temperature, t_x and pressure, p_x of the measurement. The measurement error, ε_{MS}, of the instrument is then calculated by [8]

$$\varepsilon_{MS} = I - \rho_{\mathrm{CRM}}(t_x, p_x) \tag{7}$$

If a larger range of densities and temperatures need to be covered, then the process needs to be repeated over the whole density and temperature range.

More detailed procedure of calibration and the uncertainty of the calibration is out of the scope of this good practice guide and can be found elsewhere [1], [8].

8.3 Calibration of the measurement cell temperature

Obtaining a full calibration curve over both density and temperature ranges is time consuming and, in many cases, impractical. However, it is also possible to calibrate the oscillation-type density meter over the whole density range, however, only at one temperature, for example 20 °C and then calibrate the temperature of the measuring cell for the whole temperature range in use.

To calibrate the measuring cell temperature, remove the injection adapter of the instrument and carefully insert the flexible Pt100 temperature probe until the tip of the probe reaches the bend of the U-tube. Always place the reference sensor near the internal sensor, which is usually at the bend of the U-tube for highly precise density meters. To view the U-tube, use the camera view, if available. [1]

Wait at least 15 min until the temperature is stable. The standard deviation of the reference thermometer should be 0,0001 – 0,0002 °C.

It is also important to note that this procedure can cause damage to the measuring cell. Always make sure if the oscillation should be switched off manually for your device. This is

the case especially with older devices. If you are unsure, contact the manufacturer, or do not perform this calibration.

9 References

[1] EURAMET, "Guidline on liquid density measurement using oscillation-type density meters," EURAMET Technical guide, unpublished.

[2] EURAMET, "Guideline on liquid density measurement using hydrostatic weighing," EURAMET technical guide, unpublished.

[3] EURAMET, "Guideline on production and use of liquid density (certified) reference materials" EURAMET Technical guide, unpublished.

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[5] Anton Paar GmbH, Good Density Measurement, Anton Paar GmbH.

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[8] SIM, "SIM Guidelines on the calibration of oscillation-type density meters," SIM MWG7/cg-02/v.00, 2016.