



SIM Guidelines on the calibration of oscillation-type density meters



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SIM Guidelines on the calibration of oscillation-type density meters

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PURPOSE

This publication has been discussed within the SIM Metrology Working Group of Mass and Related Quantities (SIM MWG7) with the goal of improving the harmonisation of methods for the calibration of oscillation-type density meters within SIM countries.

This document provides guidance to national accreditation bodies to set up minimum requirements for the calibration of oscillation-type density meters and gives advice to calibration laboratories to establish practical procedures.

This document contains detailed examples of the estimation of the uncertainty of measurements.

OFFICIAL LANGUAGE

The English version of this document is considered as the primary reference, however the Spanish version could be used as a reference as close as possible to the English version.

FURTHER INFORMATION

For further information about this publication, contact the member of the SIM MWG7 of the National Metrology Institute of your country.

See <http://www.science.oas.org/SIM/default.htm> <http://www.sim-metrologia.org.br/>

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1 PURPOSE OF THE GUIDE

Establish specific criteria that must be met by the procedures that serve as a technical basis for the realization of the calibration services of oscillation-type density meters, as well as the generalization in the estimate of the uncertainty of measurement and evaluation of traceability among them.

Achieving consistency and uniformity in the presentation of budgets of uncertainty in the measurements in these calibration services, as well as to establish the requirements for the assessment of the calibration services of oscillation-type density meters.

2 SCOPE OF THE GUIDE

This guide applies to the calibration of oscillation-type density meters manufactured with an indication interval up to 3000 kg m^{-3} . The expanded uncertainty of calibration ($k= 2$) can be up to 0.02 kg m^{-3} , depending on the characteristics of the instrument under calibration and to a value of temperature of $20 \text{ }^\circ\text{C}$. The scope of calibration can vary depending on the availability of reference materials.

This technical guide sets out the minimum requirements for calibration of oscillation-type density meters by the method of comparison against measurement standards, so as to ensure uniformity in the estimation of uncertainty of calibration and evaluation of the traceability of the measurement standards in the calibration laboratories.

It is the responsibility of the laboratory of calibration and the client to agree prior to calibration, about the range of density or values of density in which the measuring instrument will be calibrated in accordance to the use of the oscillation-type density meter, as well as the cost of the calibration.

The goal of these Guidelines is to provide general recommendations for the establishment of the calibration procedures and not to present one or more uniform procedures whose use is compulsory.

3 DEFINITIONS

For the purpose of this Guide, the following definitions apply:

3.1 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.

Notes:

- *Various types of adjustment for a measurement system are: setting of zero, adjust the offset and adjust of the amplitude of scale.*
- *Should not be confused the adjustment of a measurement system with its own calibration.*
- *After your adjustment, usually a measurement system must be calibrated again.*

3.2 Calibration

Operation under specified conditions which establishes, as a first stage, a relationship between the values and their associated uncertainties of measurement derived from the patterns of measurement, and the relevant indications with their associated uncertainties and, in a second stage, uses this information to establish a relationship that would enable it to obtain a result of measured from an indication.

3.3 Calibration (of an oscillation-type density meter)

Set of operations that establish the relationship between the reference patterns in density and the corresponding indications of density of the instrument.

3.4 Points of resonance

Points of resonance are those frequencies of oscillation in which the natural frequency of the density sensor is affected by the oscillations of the "counter of mass" committing the rest of the instruments.

3.5 Pre-adjustment

Adjustment performed at laboratory conditions prior to installation

3.6 Calibration in Laboratory

Calibration applied to the entire range of work of the instrument, carried out at laboratory conditions prior to installation.

3.7 Calibration in-situ

Calibration of the instrument under the actual work conditions in its operating environment.

3.8 Reference Material (MR)

Material or substance for which the value of one or several of its properties is sufficiently homogeneous and well established to be used in the calibration of an instrument, the evaluation of a method of measurement or for the allocation of values to materials.

3.9 Certified Reference Material (CRM)

Reference material, accompanied by a certificate, for which the value of one (or several) of its properties has been certified by means of a procedure that establishes its traceability to an accurate realisation of the unit in which the property values are expressed and in which each certified value is accompanied by an uncertainty with a stated level of confidence.

3.10 Certificate of a reference material

It is the document that accompanies a certified reference material, where it is declared one or several values of the property and its uncertainties and confirms that were carried out the necessary procedures to ensure its validity and its traceability

3.11 Metrological Traceability

Property of a result of measure by which the result can be linked to a reference by an uninterrupted and documented chain of calibrations, each of which contributes to the uncertainty of measurement.

3.12 Certification of a reference material

Procedure that lays down the value(s) of one or more properties of a material or substance, by a process that ensures the traceability to an exact realization of the units in which are expressed the values of the properties, and that leads to the emission of a certificate.

3.13 Verification

Provision of objective evidence that an element satisfies the specified requirements.

Notes:

- *When necessary, it is advisable to take into account the uncertainty of measurement.*
- *Should not be confused with the calibration verification. Not all verification is a validation.*

4 ACCURACY CLASS OF OSCILLATION-TYPE DENSITY METERS

According to the international standard ISO 15212 (Oscillation-type density meters) [2, 3], there are two types of oscillation-type density meters which can be identified with clarity:

- Laboratory instruments
- Process instruments for homogeneous liquids

Within the category of instruments of process for homogeneous materials, there are the following:

- Density meters, laboratory instrument
- Density meters, process instruments for homogeneous liquids

Because the users of the oscillation-type density meters, often used them on the basis of the accuracy class and their tolerances (declared by the manufacturers or set out in standards), it is desirable that the instruments are calibrated and to verify that their display errors are less than the maximum permissible error, according to the resolution and the factor of the instrument (see table 4-1 and 4-2).

The conformity assessment in measurement instruments consisted in a confirmation through the calibration of the following expression [11]:

$$|E \pm U(E)| \leq mpe \quad (4.1)$$

Where the error of indication of the instrument E together with its associated uncertainty $U(E)$ must have a value less than or equal to the maximum permissible error mpe corresponding to its factor and resolution, as shown in Figure 4.1 .

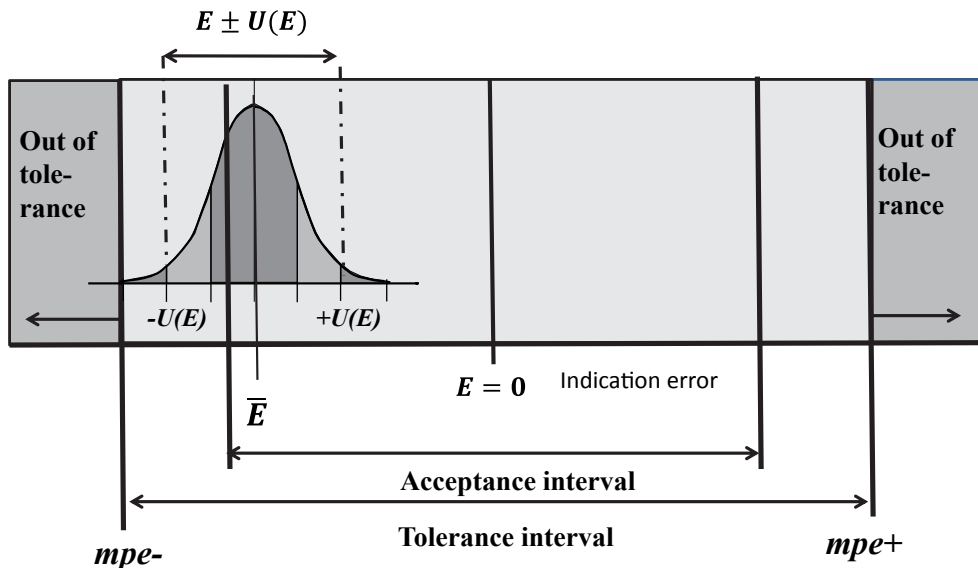


Figure 4.1 Criteria to evaluate calibration of the instrument

4.1 Accuracy of oscillation-type density meters of laboratory

According to the standard ISO 15212-1 [2], the maximum permissible errors of the oscillation-type density meters of laboratory are listed in Table 4 – 1.

Table 4-1 Maximum permissible errors for the oscillation-type density meters, laboratory instruments according to ISO 15212-1:1998

Maximum permissible error (<i>mpe</i>) kg m^{-3}	Resolution kg m^{-3}	Factor
1.0	0.1	1/10
0.5	0.1	1/5
0.20	0.01	1/20
0.10	0.01	1/10
0.05	0.01	1/5

There are oscillation-type density meters for special applications (e.g. scientific research) that could have a density resolution on the screen of 0.001 kg m^{-3} , but only when the maximum permissible error of the instrument does not exceed 0.1 kg m^{-3} , and only if the least significant digits are marked without ambiguity.

4.2 Accuracy of oscillation-type density meters, process instruments for homogeneous liquids

According to the ISO 15212-2 [3], the maximum permissible errors of oscillation-type density meters of process are listed in Table 4 2.

Table 4-2 Maximum permissible errors for oscillation-type density meters, process instruments for homogeneous liquids according to ISO 15212-2:2002.

Maximum permissible error (<i>mpe</i>) kg m ⁻³	Resolution kg m ⁻³	Factor
1.0	0.1	1/10
0.5	0.1	1/5
0.20	0.01	1/20
0.10	0.01	1/10

5 GENERAL ASPECTS OF THE CALIBRATION

5.1 Previous requirements to the calibration

The calibration laboratory must be provided with the CRMs in density¹ necessary to carry out the calibration with the accuracy required, as well as have procedures for the management, control and storage of the CRMs or (the measurement liquids as the case may be) with the intention to maintain the value of the density of the CRMs without alterations.

The value of density of the fluids, and the indication of the oscillation-type density meter depend on the value of the temperature and pressure, for this reason the metrologist must check that the temperature readings and/or pressure of the instrument (whether these are deployed directly on the same instrument or in separate instruments), do not have significant changes in relation to the uncertainty required for calibration.

The variation in the value of density of the fluid ($\Delta\rho$), due to an increase or decrease of temperature (Δt), is a function of the thermal expansion coefficient of the specific fluid (α). On the other hand, the variation in density due to a change in pressure (Δp), depends on the compressibility coefficient of the specific fluid (β).

¹For the purpose of this Guide, the Certified Reference Materials in density, hereinafter they will be referred to only as CRMs for plural or CRM for singular.

Manufacturers recommend to users of the oscillation-type density meters make the user adjustment regularly to the instruments prior to its use, because of them the calibration must be performed after you have applied this type of adjustment to the instrument.

The density meters should be adjusted according to the manufacturer's instructions. The adjustment is performed to identify and set the operation constants of the instrument. Usually, manufacturers recommend that the instruments get adjusted with air and pure water (distilled water as a minimum) or with other liquid whose density is known with the required accuracy. The adjustment must be carried out to the measuring temperature intended [2].

Due to the operation of oscillation-type density meters depends on the constants in itself, it is necessary that in those instruments whose constants are available for reading or change by the user (or by the metrologist), these constants must be registered by the metrologist during calibration. When it applies, the calibration of the oscillation-type density meter will be in the mode of operation of the density meter that the user typically used; this mode must be registered during calibration (e.g. the correction mode of viscosity, among others).

In oscillation-type density meters of laboratory, the impurities or dirt of the cell can cause indication errors, because of this, it is very important that the laboratory has appropriate procedures for cleaning and the revision of accurate placement of all the parts of the instrument, e.g. the nozzles.

In instruments to which it is possible to adjust the temperature of the liquid for their measurement, if the user does not request a different temperature value, calibration should be performed at 20 °C.

5.2 Nominal values for calibration

The calibration generally consists in the comparison of the indication of the instrument against the certified value of density of a reference material, or the density value with demonstrable traceability to SI units, with an uncertainty appropriate according to the required uncertainty of the calibration, depending on the class of the accuracy of the instrument to calibrate.

In oscillation-type density meters of laboratory, the calibration must include evidence in the greater amount of nominal values possible, looking for cover the following three nominal values: the density of water, a density value below the density of water and a density value above the density of water. Whenever possible, you must choose values of density that are the nearest possible to the measuring range of interest of the user, both above and below the value or density range of interest of the user with the intention to cover the needs of the user.

In oscillation-type density meters of process for homogeneous liquids and installed in line, the calibration is performed on the values of density of the liquids where it usually performs at the temperature and pressure of work; this can be only one density value (when the density meter works only with one liquid).

5.3 Required uncertainty in the calibration

With the exception of the instruments factor 1/5 with resolution of 0.01 kg m⁻³, and unless the user explicitly asks for a different calibration uncertainty to the calibration laboratory, the expanded uncertainty (k= 2) associated with the indications errors resulting from the calibration of the oscillation-type density meter shall not exceed one third of the *mpe* of the class of accuracy for the measuring instrument.

$$U_{req}(E) \leq \frac{1}{3} mpe \quad (5.1)$$

For Instruments with factor 1/5 and resolution of 0.01 kg m⁻³ the maximum uncertainty of the calibration is

$$U_{req}(E) \leq \frac{1}{2} mpe \quad (5.2)$$

The maximum required uncertainties in the calibration of the oscillation-type density meters are listed in table 5-1 [11]:

Table 5-1 Maximum required uncertainty in calibration of the oscillation-type density meters depending on the *mpe*, both for laboratory instruments as well as process.

Maximum allowed error (<i>mpe</i>) kg m ⁻³	Resolution kg m ⁻³	Factor	Max. Req. Uncertainty in calibration, U_{req} , k=2 kg m ⁻³
1.0	0.1	1/10	0.33
0.5	0.1	1/5	0.17
0.20	0.01	1/20	0.067
0.10	0.01	1/10	0.033
0.05	0.01	1/5	0.025

5.4 General procedure for calibration

The oscillation-type density meters of laboratory can be calibrated in both the facilities of the user and at the facilities of the supplier of the calibration service, for its part the oscillation-type density meters of process, can be calibrated in the field, installed in the line, or in the laboratory with special facilities that simulate conditions of operation in terms of flow, temperature, pressure, and if the case viscosity, etc.

For field calibration of the oscillation-type density meters of process, in general these are calibrated installed in their normal working conditions, by measuring the working fluid, at the corresponding temperature and pressure.

The calibration procedure of laboratory density meters includes the comparison of the indications of the density meter against the density values of reference (values of the CRMs, or measured by a density meter of superior features). The calibration is usually performed at 20 °C and at atmospheric pressure, with the exception that the user agreed one or several different temperatures.

The calibration of the oscillation-type density meter is performed at atmospheric pressure. In the event that the value of the atmospheric pressure during calibration is different from the value of pressure which was certified to the CRM, then a correction must be applied due to the pressure difference and the compressibility of the fluid.

In the measurement procedure, it should be indicated the type of measuring instruments and equipment that are suitable for use in the calibration service, as the CRMs, thermometer, barometer and hygro-thermometer (if necessary), as well as the equipment and accessories to be used for the handling of the liquids.

As part of the calibration procedure for the oscillation-type density meters, the calibration laboratories must define the steps to be taken to determine the time and number of measurements required to obtain stable results; in oscillation-type density meters of laboratory, prior to the final measurements, repetitions must be performed to evaluate the behaviour of the stability of the instrument, see Appendix D.

The calibration procedure should include the cleaning process of the measuring cell, considering the manufacturer's instructions and the characteristics of the fluid introduced into the cell.

The calibration procedure must include the minimum number of repetitions (measurements) that will be carried out in the calibration, which will depend on the conditions of the instrument under calibration and even of the fluid under

measurement. It is recommended to perform at least five repetitions for oscillation-type density meters of laboratory and at least three repetitions for oscillation-type density meters of process.

The metrologist must take into account that a greater number of measurements increase the reliability of the calibration; however it also increases the cost of the same, therefore an appropriate balance must be found between the accuracy and the cost of the service.

Note: *There is a large variety of instruments on the market that operate on the principle of frequency, among which, some that can have a special form of connection in systems of transference of product, which means that the laboratory should adapt the taking of readings depending on the characteristics of the meter.*

The calibration procedure of the laboratory should include the following elements:

- Choice of the CRMs to use depending on the range of interest of the user.
- Appropriate choice of the type and material of the syringes as well as necessary accessories (such as precipitate vessels) so that they do not react chemically with the CRM(s).
- Record the equipment data to calibrate, brand, model serial number, calibration temperature, flow, the working pressure and the atmospheric pressure of calibration.
- If the accuracy of the density meter requires, the assessment of temperature and pressure readings of the instrument, against calibrated instruments and own certificates of the calibration laboratory.
- Register the constants of the instrument (when applicable).
- For equipment that has internal temperature control, it is appropriate to set the temperature at which calibration will be performed, which will be indicated by the user. In the event that the density meter to calibrate does not count with a temperature controller, the calibration will be performed recording the temperature that the instrument indicates.
- Avoid the formation of bubbles in the measuring cell.
- Inspect the conditions of the instrument.
- Cleaning of the instrument according to the manufacturer's instructions.
- Use properly the comparison method to determine the deviation between the instrument and the CRMs.
- Assessment of the corrections and their associated uncertainties.

5.5 Equipment, measuring instruments and facilities

The calibration laboratory must be provided with the necessary CRMs (both in quantity and accuracy) for the calibration

The certificates from the CRMs and the rest of the instruments must be current at the time of the calibration. The laboratory must ensure that the management of the CRMs does not put at risk their traceability.

Depending on the required uncertainty for calibration (see section 6.3), the laboratory must have appropriate measuring instruments to record the values of environmental conditions (temperature, pressure and relative humidity when needed depending on the uncertainty required for the density of air), these instruments must be calibrated

For field calibration of the density meters of process, the laboratory must have instruments for measuring density previously characterized and calibrated, as well as appropriate methods to obtain the value of the density of the working fluid traceable to the International System and with the required accuracy in the calibration.

Note: *It is the responsibility of the calibration laboratory to demonstrate that the contributions of the uncertainty due to measurement instruments are consistent with the uncertainties required. This demonstration can be done using the table of budgets of uncertainty.*

6 CALCULATION OF THE INDICATION ERROR

6.1 Measurement Method

The method of measurement used in the calibration of the oscillation-type density meters of laboratory is by direct comparison against certified reference materials. This method determines the error of indication of the measuring instrument under test.

The comparison method, consists in, for each value of density to calibrate, to repeatedly introduce a CRM in the cell of the oscillation type density meter in order to register the density values indicated by the instrument, subsequently to calculate the average of the readings in density and to get the deviation between the indication of the density meter and the reference value of density by applying the appropriate corrections.

For field calibration of the oscillation-type density meters of process, samples are taken of the working fluid (when flowing through the density meter) and simultaneously readings of density and line of work pressure are recorded. Subsequently, the indications of fluid density are compared in a calibrated instrument and characterized in density, to calculate the error of indication of the instrument.

6.2 Measurement Model

To obtain the correction of the indication for the density meter, the average of the recorded readings during calibration is calculated, and the correction is calculated from the instrument according to the following mathematical model

$$E = I - \rho_{ref} \quad (6.1)$$

Where,

- E is the indication error of the oscillation-type density meter, kg m^{-3}
 I is the best estimate of the instrument reading, kg m^{-3}
 ρ_{ref} is the reference value of density at temperature t_x and pressure p_x of measurement, kg m^{-3}

The unit of measure is the kilogram per cubic meter kg m^{-3} , however the multiples or fractions of the unit can be used e.g. gram per cubic centimetre, g cm^{-3} .

6.3 Density of reference

The value of the density of reference may come from the certified value of the CRM, or from the measurement with an instrument of superior² metrological characteristics. Whatever the origin of the density value for reference, it must be able to achieve the required accuracy.

The reference value in density must be calculated at temperature t_x and pressure p_x of measurement.

The density value of the CRMs is usually referred to temperature and t_{Ref} and pressure p_{Ref} , so it is necessary to calculate the value of density at temperature t_x and pressure p_x of measurement. The density at measurement conditions is calculated with the following expression,

$$\rho_x = \rho_{Cert} f_t^{-1} f_p^{-1} - \varepsilon_{est} \quad (6.2)$$

Where,

ρ_x	is the value in density at a temperature t_x and pressure p_x , kg m^{-3}
ρ_{Cert}	is the reference density value at the reference conditions, at temperature T and pressure P , units in kg m^{-3}
f_t	is the correction factor of density due to a change in temperature Δt , dimensionless
f_p	is the correction factor of density due to a change of pressure Δp , dimensionless
ε_{est}	is an error in density due to the (lack of) stability of the density value of reference

6.3.1 Calculation of the correction factor for density due to a change in temperature

The correction factor, to correct the density value of reference due to a change in temperature ($\Delta t = t_x - t_{Ref}$), is calculated with the following expression,

$$f_t = 1 + \alpha_{vol}(t_x - t_{Ref}) \quad (6.3)$$

Where,

² The laboratory must have a formalized procedure in its quality system for the measurement of the density of liquids by using oscillation-type density meters or other instrument, capable of achieving the required accuracy (measurement uncertainty).

f_t	is the correction factor of temperature, dimensionless
α_{vol}	is the coefficient of volume expansion of the fluid, °C ⁻¹
t_x	is the temperature x , at which it is desired to know the density of the fluid, °C
t_{Ref}	is the reference temperature of the density of the fluid, °C

Note: The volumetric expansion coefficient of the fluid α_{vol} can be expressed in different ways: in other units (e.g., in kg m⁻³ °C⁻¹) or as a function of the temperature, (e.g., as a polynomial $\alpha_{vol}(t) = a_0 + a_1t + \dots + a_nt^n$). In these cases, the mathematical model of the factor f_t might be different to the one proposed.

6.3.2 Calculation of the correction factor of density due to a change in the value of pressure

The correction factor to correct the density of reference due to a change in pressure ($\Delta p = p_x - p_{Ref}$), is calculated with the following expression,

$$f_p = 1 - \beta(p_x - p_{Ref}) \quad (6.4)$$

Where,

f_p	is the correction factor by pressure, dimensionless
β	is the coefficient of isothermal compressibility of the fluid, Pa ⁻¹
p_x	pressure x , at which it is desired to know the density of the fluid, Pa
p_{Ref}	reference pressure to the known density of the fluid, Pa

Note: The coefficient of isothermal compressibility of the fluid β can be expressed in different ways: in other units (e.g., in kg m⁻³ Pa⁻¹) or as a function of pressure, (e.g., as a polynomial $\beta(p) = b_0 + b_1p + \dots + b_np^n$). In these cases, the mathematical model of the factor f_p might be different to the one proposed.

6.4 The best estimate of the instrument indication

The best estimate of the instrument indication is obtained from the following equation:

$$I = \bar{I} - \varepsilon_{res} - \varepsilon_{reprod} - \varepsilon_{visc} \quad (6.5)$$

Where,

\bar{I}	is the average of the instrument indications, kg m ⁻³
ε_{res}	Is the error due to the finite resolution of the instrument, kg m ⁻³
ε_{reprod}	Is the error due to the reproducibility of the instrument, kg m ⁻³
ε_{visc}	Is the error due to the viscosity of the liquid, kg m ⁻³

6.4.1 Average of the instrument indications

The average of the instrument indications is calculated as follows,

$$\bar{I} = \frac{1}{n} \sum_{i=1}^n I_i \quad (6.6)$$

Where,

I_i is the indication i -th of the instrument, kg m^{-3}

n is the total number of measurements.

It is important to point out that these indications should be independent. Therefore, it is necessary for the fluid sample to be different (that is renewed before registering each measurement).

6.4.2 Error due to the finite resolution of the instrument

The error due to the finite resolution of the instrument has zero average value, but not for their contribution of uncertainty, $E(\varepsilon_{res}) = 0$, $\sigma(\varepsilon_{res})$.

6.4.3 Error due to the reproducibility of the instrument

The error due to the reproducibility of the instrument has zero average value, but not for their contribution of uncertainty, $E(\varepsilon_{rep}) = 0$, $\sigma(\varepsilon_{rep})$.

6.4.4 Error due to the viscosity of the fluid

In oscillation-type instruments, the sample fluid has an effect of damping of vibration. This damping is a function of the viscosity of the fluid. The viscosity of the fluid also has the effect of moving the nodes of oscillation, these two effects combined produce an error k in kg m^{-3} of the order of $k \approx 0.05\sqrt{\eta}$, where η is the viscosity in mPa s .

The error due to the viscosity of the fluid, can be estimated with zero mean, but the uncertainty associated to this error will be according to the value of the viscosity of the liquid $E(\varepsilon_{visc}) = 0$, $\sigma(\varepsilon_{visc})$

Some high-accuracy instruments have the possibility of correcting the viscosity of the fluid under measurement, and therefore the contribution to the uncertainty is considered negligible.

7 UNCERTAINTY ASSOCIATED WITH THE ERROR OF INDICATION

For the estimation of the error uncertainty of indication, it is necessary to use a model of measurement as complete as possible. In this depends that the estimate of uncertainty is the more realistic to reality as possible. For the estimation of uncertainty of the measurand (error of indication), it is necessary to estimate the uncertainty values of all entry magnitudes of the measurement model, as well as calculate the corresponding sensitivity coefficients, to finally combine their contributions in the calculation of the combined standard uncertainty associated with the error of indication of the instrument under calibration. The uncertainty associated to the indication error is usually informed as an expanded uncertainty with a confidence level of approximately 95 %.

7.1 Uncertainty due to the density value of reference

The contribution of the standard uncertainty of certified density $u(\rho_{Cert})$, is obtained as the ratio for the expanded uncertainty $U(\rho_{Cert})$, divided between the coverage factor associated with the level of confidence k ,

$$u(\rho_{Cert}) = \frac{U(\rho_{Cert})}{k} \quad (7.1)$$

7.2 Uncertainty due to the error of stability of the density value of reference

The standard uncertainty due to the stability of the density value can be estimated considering a maximum value of variation (D) and consider this maximum value as a medium range of uniform probability,

$$u(\varepsilon_{est}) = \frac{D}{\sqrt{3}} \quad (7.2)$$

7.3 Uncertainty due to the correction factor for a change in temperature of the density value of reference

The uncertainty of the correction factor for temperature is calculated as follows (taking into account the sensitivity coefficients for the variables of influence):

$$u(f_t) = \sqrt{\left(\frac{\partial f_t}{\partial t_x} u(t_x)\right)^2 + \left(\frac{\partial f_t}{\partial \alpha_{vol}} u(\alpha_{vol})\right)^2} \quad (7.3)$$

Where,

$\frac{\partial f_t}{\partial t_x} = \alpha_{vol}$ is the sensitivity coefficient due to the temperature, °C⁻¹

$\frac{\partial f_t}{\partial \alpha_{vol}} = t_x - t_{Ref}$ is the sensitivity coefficient due to the expansion coefficient, °C

$u(t_x)$ is the standard uncertainty due to the measurement of the temperature, °C
 $u(\alpha_{vol})$ is the standard uncertainty due to the coefficient of volumetric expansion of the fluid, °C⁻¹

The uncertainty of the temperature must include at least the contributions due to the calibration and resolution of the measurement instrument of temperature as well as the stability of the temperature value of the reference.

7.4 Uncertainty due to the correction factor for a change in the fluid pressure of reference

The uncertainty of the correction factor by pressure is calculated in the following way (taking into account the sensitivity coefficients for the variables of influence).

$$u_{f_p} = \sqrt{\left(\frac{\partial f_p}{\partial p_x} u(p_x)\right)^2 + \left(\frac{\partial f_p}{\partial \beta} u(\beta)\right)^2} \quad (7.4)$$

Where,

$\frac{\partial f_p}{\partial p_x} = -\beta$ is the sensitivity coefficient due to the pressure, Pa⁻¹
 $\frac{\partial f_p}{\partial \beta} = p_{Ref} - p_x$ is the sensitivity coefficient due to the coefficient of compressibility, Pa
 $u(p_x)$ is the standard uncertainty due to pressure measurement of the fluid of reference, Pa
 $u(\beta)$ is the standard uncertainty due to the compressibility coefficient of the fluid of reference, Pa⁻¹

The uncertainty of the pressure should include at least the contributions due to the calibration and resolution of the instrument for the measurement of pressure, and the stability of the value of pressure

7.5 Uncertainty due to resolution error of the density meter

The uncertainty due to resolution error of the density meter (d) is calculated as follows,

$$u(\varepsilon_{res}) = \frac{d}{\sqrt{12}} \quad (7.5)$$

7.6 Uncertainty due to repeatability error of the indications of the density meter

The uncertainty due to repeatability error of the indications is calculated as the standard deviation of the average of indications,

$$u(I) = \frac{s(I)}{\sqrt{n}}; \quad u(I) = \frac{1}{\sqrt{n}} \sqrt{\frac{\sum(I_i - \bar{I})^2}{n-1}} \quad (7.6)$$

7.7 Uncertainty due to reproducibility error of the density meter measurements

This contribution is due to the dispersion of the density meter indications caused by a variation in one or more factors such as some own by the density meter, metrologist, the method, the density standard, temperature, pressure, the thermometer, among others.

One way to assess this source of uncertainty would be conducting an analysis of variance (ANOVA³), however it is desirable that the metrologist evaluates the complexity of the test(s) to perform depending on the uncertainty required.

$$u(\varepsilon_{reprod}) = \sqrt{S^2} \quad (7.7)$$

7.8 Uncertainty due to viscosity of the fluid under measurement

This contribution is due to the indication error because of the viscosity of the fluid under measurement.

$$u(\varepsilon_{visc}) = \frac{0.05\sqrt{\eta}}{\sqrt{3}} \quad (7.8)$$

7.9 Uncertainty due to error of indication

The uncertainty due to the error of indication is calculated from the model of full measurement,

$$E = \bar{I} - \varepsilon_{res} - \varepsilon_{reprod} - \varepsilon_{visc} - \rho_{Cert} f_t^{-1} f_p^{-1} - \varepsilon_{est} \quad (7.9)$$

The combined standard uncertainty associated with the error of indication of the instrument is calculated in the following formula,

³ ANOVA – Analysis of variance.

$$u(E) = \sqrt{\left(\frac{\partial E}{\partial \bar{I}} u(\bar{I})\right)^2 + \left(\frac{\partial E}{\partial \varepsilon_{res}} u(\varepsilon_{res})\right)^2 + \left(\frac{\partial E}{\partial \varepsilon_{reprod}} u(\varepsilon_{reprod})\right)^2 + \left(\frac{\partial E}{\partial \varepsilon_{visc}} u(\varepsilon_{visc})\right)^2 + \left(\frac{\partial E}{\partial \rho_{Cert}} u(\rho_{Cert})\right)^2 + \left(\frac{\partial E}{\partial f_t} u(f_t)\right)^2 + \left(\frac{\partial E}{\partial f_p} u(f_p)\right)^2 + \left(\frac{\partial E}{\partial \varepsilon_{est}} u(\varepsilon_{est})\right)^2} \quad (7.10)$$

Where,

$$\frac{\partial E}{\partial \bar{I}} = 1$$

is the sensitivity coefficient due to the average of indications, dimensionless

$$\frac{\partial E}{\partial \varepsilon_{res}} = -1$$

is the sensitivity coefficient due to the error resolution of the instrument, dimensionless

$$\frac{\partial E}{\partial \varepsilon_{reprod}} = -1$$

is the sensitivity coefficient due to the error of reproducibility of the instrument, dimensionless

$$\frac{\partial E}{\partial \varepsilon_{visc}} = -1$$

is the sensitivity coefficient due to the error of fluid viscosity, dimensionless

$$\frac{\partial E}{\partial \rho_{Cert}} = f_t^{-1} f_p^{-1}$$

is the sensitivity coefficient due to the certified density value, dimensionless

$$\frac{\partial E}{\partial f_t} = \rho_{Cert} f_t^{-2} f_p^{-1}$$

is the sensitivity coefficient due to the correction factor due to the temperature, kg m^{-3}

$$\frac{\partial E}{\partial f_p} = \rho_{Cert} f_t^{-1} f_p^{-2}$$

is the sensitivity coefficient due to the correction factor due to the pressure, kg m^{-3}

$$\frac{\partial E}{\partial \varepsilon_{est}} = -1$$

is the sensitivity coefficient due to the stability error of the value of reference in density, dimensionless

The expanded uncertainty associated to the indication error is calculated by using (7.11), where the value of k is usually taken as equal to 2, for a confidence level of approximately equal to 95 % (based on the theorem of central limit).

$$U(E) = k \cdot u(E) \quad (7.11)$$

Note: For more information on the coverage factor k , please refer to Annex C.

7.10 Table of the uncertainty budget

With the intention of keeping the information organized, it is advisable to fill the table of uncertainty budget for each nominal value of density under calibration, such as the one presented below,

Table 7-1 Table of uncertainty budget

	Source	Value ⁴	Variability ⁵	Distribution ⁶	Standard Uncertainty	Degrees of Freedom	Sensitivity Coefficient	Contribution
1	Indication				$u(\bar{I})$		$\frac{\partial E}{\partial \bar{I}}$	$\frac{\partial E}{\partial \bar{I}} u(\bar{I})$
2	Resolution				$u(\varepsilon_{res})$		$\frac{\partial E}{\partial \varepsilon_{res}}$	$\frac{\partial E}{\partial \varepsilon_{res}} u(\varepsilon_{res})$
3	Reproducibility				$u(\varepsilon_{reprod})$		$\frac{\partial E}{\partial \varepsilon_{reprod}}$	$\frac{\partial E}{\partial \varepsilon_{reprod}} u(\varepsilon_{reprod})$
4	viscosity				$u(\varepsilon_{visc})$		$\frac{\partial E}{\partial \varepsilon_{visc}}$	$\frac{\partial E}{\partial \varepsilon_{visc}} u(\varepsilon_{visc})$
5	Certified Density				$u(\rho_{cert})$		$\frac{\partial E}{\partial \rho_{cert}}$	$\frac{\partial E}{\partial \rho_{cert}} u(\rho_{cert})$
6	Temperature correction factor				$u(f_t)$		$\frac{\partial E}{\partial f_t}$	$\frac{\partial E}{\partial f_t} u(f_t)$
7	Pressure correction factor				$u(f_p)$		$\frac{\partial E}{\partial f_p}$	$\frac{\partial E}{\partial f_p} u(f_p)$
8	Error of stability of the density value				$u(\varepsilon_{est})$		$\frac{\partial E}{\partial \varepsilon_{est}}$	$\frac{\partial E}{\partial \varepsilon_{est}} u(\varepsilon_{est})$
							Combined standard uncertainty	$u(E)$
							Effective degrees of freedom	
							Coverage Factor	
	Indication Error ⁷						Expanded Uncertainty, $U = k \times u(E)$	$U(E)$

⁴ The best estimate of the magnitude of entry must be registered

⁵ The variability value of where the metrologist can obtain the value of the standard uncertainty associated with the magnitude of entry must be registered

⁶ The type of distribution associated with the original source of uncertainty must be registered.

⁷ The best estimate of indication error found during calibration must be registered.

8 DENSITY VALUES OBTAINED IN THE USE OF THE INSTRUMENT

The user of an instrument should be aware of the fact that in the normal use of an instrument that has been calibrated, in some cases, if not all, the conditions are different from those that were submitted during the calibration, in the following aspects:

- The indications obtained in the normal use of the instrument for the measurement of liquids are not the same as those that were obtained during calibration,
- The measurement process can be different from the calibration procedure, e.g. surely only one indication, there are no several indications to obtain the average value,
- The measuring conditions/operation may be different (temperature, barometric pressure, etc.) to the calibration,
- With instruments which are not adjusted on a regular basis, the adjustment can be changed by aging or wear. This effect typically depends on the time that has elapsed since the last calibration, and should be considered in relation to a certain time period, e.g. one year or the normal interval between calibrations.

Note: *With the intention to clearly differentiate the indications of the instrument obtained in use of the instrument (after to its calibration), it will be used a symbol R , instead of the symbol I that was used for those indications obtained during the calibration of itself.*

8.1 Handling of the oscillation-type density meter, and the uncertainty associated with itself.

Usually the calibration of an oscillation-type density meter includes the determination of the error and uncertainty in discrete values of density, to determine the error of indication (to correct) is necessary to find the appropriate error of indication for the sample in measurement.

8.1.1 Interpolation

It is important to note that since the density is not directly proportional to the frequency (or to the oscillation period), the interpolation can be used only when the interval limited by two indication errors (found in calibration) includes the indication of the product x (test liquid), and the two nominal values calibrated are close enough to the indication of the product x , then the linearity for that short interval of the scale can be assumed.

The determination of the indication error of the instrument for the density value of a product x , is calculated by interpolating the indication errors found in calibration, using the next inferior and the next superior (indications of density above and below the value of indication of density that needs to be corrected). The formula of the interpolation is as follows,

$$E_x = E_{Ref2} + (R_x - I_{Ref2}) \cdot \left[\frac{E_{Ref2} - E_{Ref1}}{I_{Ref2} - I_{Ref1}} \right] \quad (8.1)$$

Where:

E_x	is the error of indication for the density of the material x
E_{Ref1}	is the error of indication for the density of reference 1
E_{Ref2}	is the error of indication for the density of reference 2
R_x	is the indication of the instrument in use for the liquid x
I_{Ref1}	is the indication of the instrument for the reference material 1
I_{Ref2}	is the indication of the instrument for the reference material 2

Note: It is possible that the indications of the instrument (in use and/or calibration) are in units of density or frequency, with identical results.

The uncertainty of the previous functional relationship can be estimated by assuming a functional relationship between the uncertainties associated with the errors:

$$u(E_x) = u(E_{Ref2}) + (R_x - I_{Ref2}) \cdot \left[\frac{u(E_{Ref2}) - u(E_{Ref1})}{I_{Ref2} - I_{Ref1}} \right] \quad (8.2)$$

where,

$u(E_x)$	is the standard uncertainty associated with the error for the indication in use of the liquid x
$u(E_{Ref1})$	is the standard uncertainty obtained by calibration for the density of reference 1
$u(E_{Ref2})$	is the standard uncertainty obtained by calibration for the density of reference 2

Note: equation (9.2) is a rough estimate for the uncertainty calculation that considers the two reference values (density) completely correlated.

8.1.2 Approximation

The approximation should be performed by calculations or algorithms based on the method of “minimizing χ^2 ”:

$$\chi^2 = \sum p_j v_j^2 = \sum p_j (f(I_j) - E_j)^2 = \text{minimum} \quad (8.3)$$

With:

p_j = Weighting factor (basically proportional to $1/u_j^2$)

v_j = residual

f = approximation function containing n_{par} parameters

In conjunction with the coefficients of the approximation function, the sum of the squares of the deviations should be determined according to (8.3), which is designated by the term $\min\chi^2$. It serves to verify the validity of the approximation.

If the following condition is met:

$$|\min\chi^2 - \nu| \leq \beta\sqrt{(2\nu)} \quad (8.4)$$

with

$\nu = n - n_{par}$ = degrees of freedom, and

β = factor chosen between 1, 2 (most applied value), or 3,

It is justified to assume that the form of the model function E is mathematically consistent with the data in which is based on the approximation.

8.1.2.1 Approximation by polynomials

Approximation by polynomials of the general function

$$E(R) = f(R) = a_0 + a_1R + a_2R^2 + \dots + a_{n_a}R^{n_a} \quad (8.5)$$

The suffix/exponent n_a of the coefficient should be chosen such that $n_{par} = n_a + 1 \leq n/2$.

The calculation is done in a better way through matrix calculation.

- X** a matrix whose n rows are $(1, I_j, I_j^2, \dots, I_j^{n_a})$
- a** A column vector whose components are the coefficients a_0, a_1, \dots, a_{n_a} of the polynomial approximation
- e** is a column vector whose n components are E_j
- U(e)** is the uncertainty matrix of E_j .

$\mathbf{U}(\mathbf{e})$ is either a diagonal matrix whose elements are $u_{jj} = u^2(E_j)$, or has been derived as a complete matrix of variance/covariance.

The weighting matrix \mathbf{P} is

$$\mathbf{P} = \mathbf{U}(\mathbf{e})^{-1} \quad (8.6)$$

and the coefficients a_0, a_1, \dots, a_{n_a} , are found to solve the normal equation

$$\mathbf{X}^T \mathbf{P} \mathbf{X} \mathbf{a} - \mathbf{X}^T \mathbf{P} \mathbf{e} = 0 \quad (8.7)$$

with the solution

$$\mathbf{a} = (\mathbf{X}^T \mathbf{P} \mathbf{X})^{-1} \mathbf{X}^T \mathbf{P} \mathbf{e} \quad (8.8)$$

The n deviations $v_j = f(I_j) - E_j$ are included in the vector

$$\mathbf{v} = \mathbf{X} \mathbf{a} - \mathbf{e} \quad (8.9)$$

And the $\min \chi^2$ is obtained by

$$\min \chi^2 = \mathbf{v}^T \mathbf{P} \mathbf{v} \quad (8.10)$$

If the condition is met from equation (8.4), the variances and covariances for the coefficients a_i are obtained from the matrix

$$\mathbf{U}(\mathbf{a}) = (\mathbf{X}^T \mathbf{P} \mathbf{X})^{-1} \quad (8.11)$$

If the condition of (8.4) is not met, one of the following procedures can be applied:

- a: repeat the approximation with a greater number of coefficients n_a while $n_a + 1 \leq n/2$;
- b: Repeat the approximation after increasing all values u_j e.g. multiplication with an appropriate factor $c > 1$. ($\min \chi^2$ is proportional to $1/c^2$),

The results of the approximation \mathbf{a} and $\mathbf{U}(\mathbf{a})$ can be used to determine the approximate errors and uncertainties assigned for the n calibration points I_j .

The errors E_{apprj} are included in the vector

$$\mathbf{e}_{apprj} = \mathbf{X} \mathbf{a} \quad (8.12)$$

With the uncertainties calculated by

$$u^2(E_{apprj}) = \text{diag}(\mathbf{X} \mathbf{U}(\mathbf{a}) \mathbf{X}^T) \quad (8.13)$$

These uncertainties also serve to determine the error, and the uncertainty assigned for any other indication – calling a reading R in order to differentiate the indications I_j – within the scope of calibrated weighting.

with

\mathbf{r} is a column vector whose elements are $(1, R, R^2, R^3, \dots, R^{na})^T$,

\mathbf{r}' is a column vector whose elements are the derived $(1, 2R, 3R^2, \dots, n_a R^{na-1})^T$

The error is

$$E_{appr}(R) = \mathbf{r}^T \mathbf{a} \quad (8.14)$$

And the uncertainty is obtained by

$$(E_{appr}) = (\mathbf{r}'^T \mathbf{a})^T \mathbf{U}(\mathbf{R})(\mathbf{r}'^T \mathbf{a}) + \mathbf{r}^T \mathbf{U}(\mathbf{a}) \mathbf{r} \quad (8.15)$$

Since the three matrices of the first term on the right side are dimensional, it is simplified as follows

$$(\mathbf{r}'^T \mathbf{a})^T \mathbf{U}(\mathbf{R})(\mathbf{r}'^T \mathbf{a}) = (a_1 + 2a_2R + 3a_3R^2 + \dots + n_a a_{na} R^{na-1})^2 u^2(R) \quad (8.16)$$

$$\text{con } u^2(R) = u^2(\varepsilon_{res(R)}) + u^2(\varepsilon_{rep(R)}).$$

8.2 Calculation of the density value with the calibrated density meter

The value of the density of a liquid measured with a calibrated density meter would be obtained through the following expression,

$$\rho_{x(t,p)} = R_x - E_x - \varepsilon_{res(R)} - \varepsilon_{rep(R)} \quad (8.17)$$

$\rho_{x(t,p)}$ is the value of liquid density x measured to the temperature and pressure of measurement.

$\varepsilon_{res(R)}$ is the error due to the finite resolution of the instrument, associated with the reading of the instrument in use

$\varepsilon_{rep(R)}$ Is the error due to the repeatability of the instrument, associated with the reading of the instrument in use

The uncertainty associated to this density value obtained with the calibrated density meter is obtained from the following expression,

$$u(\rho_{x(t,p)}) = \sqrt{u^2(E_x) + u^2(\varepsilon_{res(R)}) + u^2(\varepsilon_{rep(R)}) + u^2(\varepsilon_{est(Cal)})} \quad (8.18)$$

Where,

- $u(\rho_{x(t,p)})$ is the standard uncertainty associated with the density value for the temperature and pressure of measurement, kg m^{-3}
- $u^2(E_x)$ is the standard uncertainty of the indication error found in the calibration of the instrument, kg m^{-3}
- $u^2(\varepsilon_{res(R)})$ is the standard uncertainty associated with the error resolution of the instrument, kg m^{-3}
- $u^2(\varepsilon_{rep(R)})$ is the standard uncertainty associated with the error of repeatability of the instrument, kg m^{-3}
- $u^2(\varepsilon_{est(Cal)})$ is the standard uncertainty associated to the stability error of the instrument previous to its calibration, kg m^{-3}

The expanded uncertainty of the value of density to the temperature and pressure of measurement is obtained by multiplying the standard uncertainty by the coverage factor, usually $k=2$

$$U(\rho_{x(t,p)}) = k \cdot u(\rho_{x(t,p)}) \quad (8.19)$$

If the fluid density value needs to be known at specific reference conditions e.g. by $T = 20 \text{ }^\circ\text{C}$ y $P = 101\,325 \text{ Pa}$, the appropriate correction factors should be applied,

$$\rho_{x(T,P)} = \rho_{x(t,p)} f_t f_p \quad (8.20)$$

With the following associated uncertainties,

$$u(\rho_{x(T,P)}) = \sqrt{[f_t f_p u(\rho_{x(t,p)})]^2 + [\rho_{x(t,p)} f_p u(f_t)]^2 + [\rho_{x(t,p)} f_t u(f_p)]^2} \quad (8.21)$$

$$U(\rho_{x(T,P)}) = k \cdot u(\rho_{x(T,P)}) \quad (8.22)$$

Sometimes, when the required uncertainty in the measurement permits it, the user of the measuring instrument can use a value of global uncertainty that includes all sources of uncertainty of the measurement, even that due to the contribution due to not apply the correction to the error of indication (use the instrument for its class of accuracy, taking directly the indication without correction, the uncertainty will be greater than applying the corresponding corrections),

$$\rho_{x(t,p)} = R_x \pm U_{global}(\rho_{x(t,p)}) \quad (8.23)$$

With expanded uncertainty associated to the density value,

$$U_{global}(\rho_{x(t,p)}) = 2 \cdot \sqrt{(E_{x,Max})^2 + u^2(E_x) + u^2(\varepsilon_{res(R)}) + u^2(\varepsilon_{rep(R)}) + u^2(\varepsilon_{est(Cal)})} \quad (8.24)$$

where,

$U_{global}(\rho_{x(t,p)})$ is the global expanded uncertainty of the density measurement associated with the direct indication of the instrument (applied if the indication of the instrument is not corrected), kg m^{-3}

$E_{x,Max}$ is an error of indication estimated as maximum in the range of work for the instrument, kg m^{-3}

9 CONTENT OF THE CALIBRATION CERTIFICATE

This section contains advice on the information that can be useful to provide in a calibration certificate. It is intended to be consistent with the requirements of the ISO/IEC 17025, which have priority.

9.1 General Information

- Identification of the calibration laboratory,
- Identification of the certificate (calibration number, issue date, number of pages),
- Signature(s) of authorized person(s),
- Customer Identification,
- Identification of the calibrated instrument,
- Information of the instrument (manufacturer, model, resolution, installation location).

9.2 Information about the calibration procedure

- Calibration date
- Issue date
- Place of calibration and installation location of the instrument, in the event that these are different.
- Environmental and/or use conditions that can affect the results of the calibration.
- Information about the instrument: the constants of operation of the instrument, if these are available for the metrologist, the adjustment performed, any abnormality of the functioning, the adjustment of the software, the installation if this is relevant for calibration, mode of operation, etc.).
- When applicable, a description of the conditions of measurement, in the

event that these are not obvious in the certificate, e.g. stabilization time observed in the indications.

- Reference to calibration method, e.g. comparison method against CRM.
- Agreements with the client e.g. about the scope of the agreed calibration, metrological specifications for which has been declared conformity.
- Information on the traceability of the measurement results.

9.3 Measurement results

- The indications and/or errors for the density values of applied test or related errors to the indications - as discrete values and/or by an equation as a result of an approximation, the temperature and pressure at which the results are declared,
- The determined standard deviation(s), identified as related to a single indication or the average of several indications
- The expanded uncertainty of measurement for the results declared.
- Indication of coverage factor k , with the comment about the probability of coverage.
- For customers with less knowledge (about the topic), as applied, the following advices could be useful about:
 - the definition of indication error,
 - how to correct the readings in use by subtracting the corresponding errors.

Note: *The results of the calibration are reported in SI units [18]; by common agreement and at the request of the client, the results could be presented, in additional way, in different units to SI, by applying the conversion of the results to the units of interest.*

9.4 Additional information

Additional information can be added to the certificate without being part of itself, additional information about the expected uncertainty of measurement in use, including the conditions under which it is applicable.

Where the errors are considered to obtain the corrected density value, the following equation can be used:

$$\rho_{(t,p)} = R - E \pm U(\rho) \quad (9.1)$$

Accompanied by the equation to calculate the value of E for the value of the indication R .

Where the errors are included in the "global uncertainty", the following expression can be used:

$$\rho_{(t,p)} = R \pm U_{global}(\rho) \quad (9.2)$$

It should be added the statement that the expanded uncertainty associated with the resulting values of the formula have a confidence level of at least 95 %.

Optional:

Where applicable a conformity statement can be made with any existing specification (see section 5.1), e.g. tolerance of process, *Tol*, or a maximum allowable error, *emp*, expressed as a range of validity.

This statement could take the form,

$$\rho_{(t,p)} = R \pm Tol \quad (9.3)$$

or,

$$\rho_{(t,p)} = R \pm emp \quad (9.4)$$

And this could be given in addition to the results of measurement, or as separate statement, with reference to the declared measurement results to be retained in the calibration laboratory.

The declaration may be accompanied by a comment indicating that all measurement results in addition to the corresponding expanded uncertainties are within the specification limits.

10 GENERAL RECOMMENDATIONS FOR THE CALIBRATION OF OSCILLATION-TYPE DENSITY METERS

The successful calibration of the oscillation-type density meters depends to a great extent on following the best handling practices and proper use of the instrument under test as well as the standards or reference materials, because of this, it is very important to consider the following recommendations.

10.1 About reference materials

For the calibration of the oscillation-type density meters of laboratory, described in chapter 5, you must employ certified reference materials in density.

In accordance with the ISO Guide [8] the following requirements must be met:

1. The density values of the declared CRMs in the corresponding certificates must be accompanied by an uncertainty to a level of confidence and with documented traceability.
2. Include material description
3. Indicate their purpose of use [9]
4. Indicate the instructions of its correct use
5. The calibration date
6. The period of validity and,
7. Any other relevant information (e.g. the coefficient of thermal expansion and isothermal compressibility of the material).

For its part, the producers of the CRMs in density must comply with the established general requirements in the ISO Guide 34 [10] to prove their competence, having submitted the CRMs to the tests of homogeneity, stability and characterisation in accordance with the ISO Guide 35 [11].

The calibration laboratory must take special care to protect the CRM against any type of pollution, by storing it in dry places and maintaining the temperature within the limits suggested by the manufacturer in order to avoid changing its properties, in the care for the CRMs is important to consider that once the product is used for a calibration this cannot be reused, therefore the CRM that is obtained at the output of the density meter will be stored as process waste.

The label on the bowl containing the CRM must have the minimum data that make reference to the validity, use and properties of the material [7].

In case of using more than one CRM during the calibration services, it is necessary to have a cleaning process that allows maintaining the density meter cell clean

between samples; this prevents the contamination of the fluid sample or CRM and ensures a good measurement.

10.2 Oscillation-type density meter under test

It is very important that both the instrument and all its parts are properly installed, and that the instrument does not present any operational problems.

Due to the fact that it is very difficult that instrument indications obtained by the user, are the same as those obtained during the calibration, it is important that the calibration of the instrument includes density values above and below the range of interest of the user, as well as the closest ones to that range, reducing the uncertainty of the estimated error of indication to apply in the normal use of the instrument.

10.3 Equipment

The laboratories that offer calibration services of oscillation type density meters and manage CRM must have equipment to measure environmental conditions recording the temperature of the air, the atmospheric pressure and the relative humidity. The equipment must have certificates or valid calibration reports.

The equipment must have certificates or valid calibration reports issued by a NMI or by accredited laboratories.

The equipment to determine the pressure and temperature of the ambient air (barometer, hygrometer, and thermometer) must have a scale division and measurement capability suitable for measuring the variation in each magnitude of influence.

When the oscillation-type density meter have temperature and/or pressure sensor, the calibration laboratory must have the instruments of pressure and temperature whose manufacture allows them to perform the corresponding measurement, e.g. probe sensor for density meter of vibrant tube type "U".

Laboratories that offer calibration services of density meters and are located at the sea level have the alternative to omit the correction by pressure to determine the value in density, only if it is demonstrated by a numerical evaluation in its measurement procedure.

For calibration of oscillation-type density meters of process, it is possible that the reference density is determined with an oscillation-type density meter of greater accuracy, this instrument must be calibrated and under strict metrological control

10.4 Accessories

The laboratory should be provided with all the necessary accessories for the handling, transport, and conservation of the CRM in density. For the calibration services of oscillation type density meters the laboratory should have at least, the following points:

- Safety equipment, clothing of laboratory (e.g., gloves, sunglasses, among others) and what is required in the facilities where the calibration is performed.
- Material or certified reference materials.
- Syringes and necessary accessories for the connection to the computer (be careful of the type of material in the syringes and accessories so that they do not react with the CRM).
- Solvent for cleaning of the measuring cell such as acetone, alcohol, pure water, etc.
- Cleaning materials, e.g. paper, solvents, among others.
- Containers with appropriate cover for the sampling of liquids, in the calibrations which is necessary to perform the measurement of liquid with another oscillation-type density meter of greater accuracy.

Note: *It is important to check for compatibility between solvents and materials of the density meter.*

11 METROLOGICAL CONFIRMATION OF OSCILLATION-TYPE DENSITY METER

The user should have a documented procedure to perform the metrological confirmation of oscillation-type density meters.

The metrological confirmation must be designed and implemented to ensure that the measurement characteristics of the measuring equipment meet the metrological requirements of the measurement process. The metrological confirmation is composed of the calibration of the measuring equipment and the verification of the measuring equipment [18].

The re-calibration of the measuring equipment is not necessary if the computer is already in a state of valid calibration. The processes of metrological confirmation should include methods to verify that the uncertainties of measurement and the errors of the measuring equipment are within the limits specified in the metrological requirements, see chap. 5

The evaluation of the metrological requirements of the oscillation-type density meter include the comparison of the metrological characteristics inherent in the design of construction of the instrument, such as: the scope of measurement, the resolution, the temperature and design pressure of the instrument, the recommended installation of the instrument (if relevant) and, the results of the calibration such as: the indication errors and associated uncertainties, the repeatability and/or reproducibility of the indications between other; against the required characteristics of the installation, the working conditions of the density meter, the uncertainty required by the user, and/or tolerances or maximum permissible errors that must comply with the instrument.

The metrological confirmation by instrument must be documented.

11.1 Intervals of metrological confirmation

The intervals of metrological confirmation should be checked and adjusted when necessary to ensure ongoing compliance with the metrological requirements of the oscillation-type density meter.

12 MEASUREMENTS TRACEABILITY

The traceability is the property of the measurements that enables to relate the outcome of measure with a reference value, so it is essential for building confidence in the measurements.

The traceability of a measurement is related to the spread of the unit for this measurement. The expression of the value of a magnitude includes a reference to a unit of measure, which has been chosen by agreement, and therefore, the measures of the same magnitude must be referring to the same unit. Even though the definition of traceability imposes no constraints on the nature of the determined references, it is desirable to attain universal uniformity through the use of the units of the International System of Units, SI, which have already been agreed within the framework of the Meter Convention.

12.1 Elements of traceability in the calibration

An example to develop a scheme of traceability of calibration of oscillation type density meters is provided in Annex A.

It is important to note that in order for the results to have traceability to base units of the SI, there must be compliance with the requirements of the active ISO 17025.

In the specific case of the water density, it is possible to obtain traceability through a certificate, for the case where this is a certified reference material, in which the provider meets all the requirements of the ISO Guide 30 and ISO Guide 31 [5, 7], or by demonstrating the conditions of purity, handling and storing corresponding to maintain the condition of pure water in order to use the formula of Tanaka [16], e.g. by measuring the resistivity of the water, according to a quality system that meets the requirements of the ISO-17025.

For the case in which we use an oscillation-type density meter as a standard for calibration of another instrument of less accuracy, the standard instrument must be under valid calibration (and certification). The method of measurement with the standard instrument that is used (direct measurement or by comparison), should be documented in the quality system of the calibration laboratory, and be able to obtain values of uncertainties in accordance to the required uncertainty for calibration of the instrument under calibration.

13 GOOD PRACTICES FOR MEASURING

With the intention to perform measurements of density in a reliable way, below are some recommendations,

- Maintaining environmental conditions within the appropriate values for work.
- Establish measures to control the entry of dust at the area intended for the calibration.
- Anytime that some type of maintenance is performed to the density meter and significantly affects its value in density, it must be adjusted and calibrated afterwards.
- The laboratory personnel and/or the user must ensure that all the parts of the instrument are correctly installed prior to its use.
- During the cleaning of the measuring cell of the density meter, any type of waste must be removed from the CRM (or any other substance) so as not to contaminate the liquids, affecting the value of density of the samples.
- All indications of the instrument should be taken only when the instrument has reached stability. The laboratory must have a criterion for determining the time of stabilization of the indications, and only when these are stable, take the appropriate indications.
- The laboratory should include in their procedures relevant activities to be performed during the calibration in situ.
- Ensure the cleaning of the material; syringes and hoses, with appropriate use of the solvent recommended by the manufacturer.
- Maintenance and proper storage of the CRMs in density to avoid contamination or degradation. (See the handling recommendations and use in their certificate)

Note: *For no reason the syringe must be disconnected from the nozzle of the measuring cell after injection of the CRM and during the taking of the reading of the density meter. You should avoid submerging the outlet hose from the density meter in the liquid waste, this due to the fact that calibration is performed in conditions of atmospheric pressure.*

14 REFERENCES

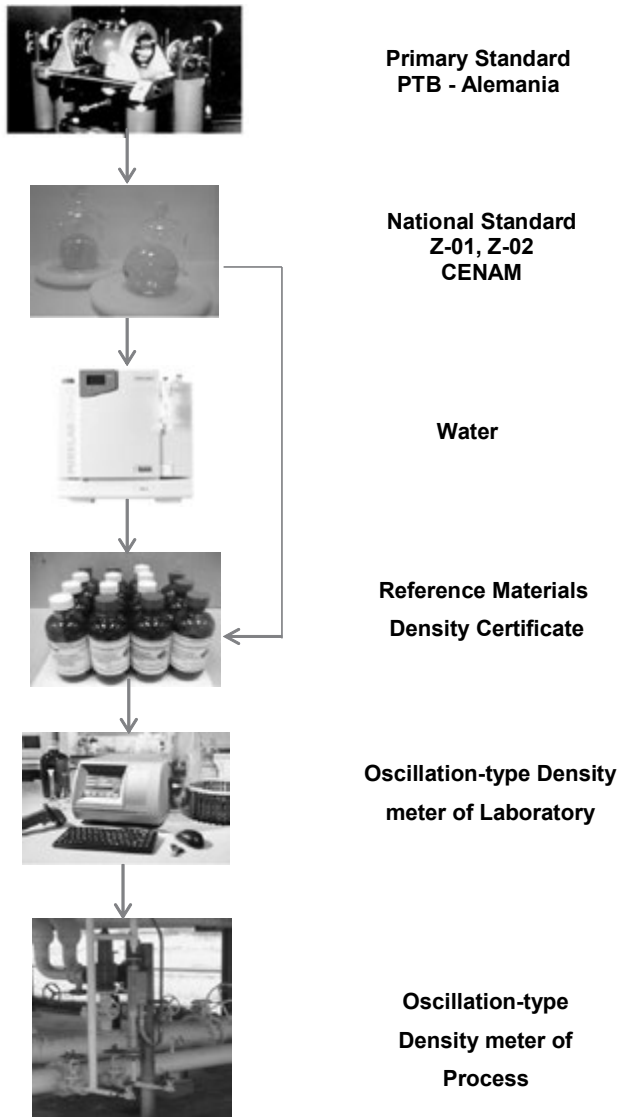
- [1] “ISO/IEC – Guide to the expression of Uncertainty in Measurements, segunda edición 1995.
- [2] ISO 15212-1:1998 (E), Oscillation-type density meters. Part 1: Laboratory instruments.
- [3] ISO 15212-2:2002 (E), Oscillation-type density meters. Part 2: Process instruments for homogeneous liquids.
- [4] ISO/IEC 17025 2005, General requirements for the competence of testing and calibration laboratories
- [5] ISO Guide 30:2015, Reference materials – Selected terms and definitions
- [6] JCGM 200:2008, International vocabulary of metrology — Basic and general concepts and associated terms (VIM)
- [7] ISO/D Guide 31, Reference materials – Contents of certificates, labels and accompanying documentation
- [8] Le Système international d’unités, SI, 8e édition 2006. Bureau international des poids et mesures, Organisation intergouvernementale de la Convention du Mètre
- [9] Instruction Manual DMA 58, Anton Paar GmbH, Graz, Austria.
- [10] JCGM 100:2008, GUM 1995 with minor corrections, Evaluation of measurement data – Guide to the expression of uncertainty in measurement
- [11] Luis O Becerra, Luis M Peña, Arturo A Daued – Incertidumbre requerida en la evaluación de la conformidad de instrumentos para la medición de densidad, Octubre 2012, Simposio de Metrología 2012.
- [12] OIML R111-1:2004 Weights of classes E₁, E₂, F₁, F₂, M₁, M₁₋₂, M₂, M₂₋₃, and M₃, Part 1: Metrological and technical requirements.
- [13] ISO/IEC Guide 99:2007, International vocabulary of metrology – Basic and general concepts and associated terms (14).
- [14] ISO IEC GUIA 99, Traducción del VIM 3a Ed. Vocabulario Internacional de Metrología – Conceptos fundamentales y generales, y términos asociados (VIM).
- [15] Picard A, Davis R S, Gläser M and Fujii K, “Revised formula for density of moist air”, Metrología, 2008, 45, 149–155.
- [16] M. Tanaka, G. Girard, R. Davis, A. Peuto and N. Bignell, Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports, Metrología, Vol. 38, 2001, 301-309.
- [17] Ricardo Medina, Comportamiento y caracterización de densímetros digitales de tipo oscilatorio, en proceso.
- [18] ISO 10012:2003 Measurement management systems -- Requirements for measurement processes and measuring equipment.
- [19] The International Association for the Properties of Water and Steam – Release on the IAPWS Formulation 1995 for the Thermodynamic

- Properties of Ordinary Water Substance for General and Scientific Use -
Fredericia, Denmark, September 1996.
- [20] ISO 3696:1987 Water for analytical use – Specification and test methods.
- [21] SIM Guidelines on the calibration of non-automatic weighing instruments,
SIM MWG7/cg/-01/v.00

ANNEX A. TRACEABILITY

Below is a generalized example to develop the traceability outline for calibration of oscillation-type density meters:

TRACEABILITY OUTLINE FOR CALIBRATION OSCILLATION TYPE DENSITY METERS



ANNEX B. SUGGESTIONS FOR THE ESTIMATION OF THE DENSITY OF AIR AND WATER

The air and water are two fluids commonly used to adjust the oscillation-type density meters. The density of air can be determined using the formula CIPM-2007 [15], from measurements of temperature, pressure and humidity of the location, which offers the best accuracy. If values of less accuracy are required, this is, with greater uncertainty, there are two approaches to the CIPM formula-2007 [15].

For the density of water, the CIPM recommends the use of the formula developed by M. Tanaka et al. [16]. The value of the density of water can be used for quality assurance in the measurements, and this value depends on the purity of the water, which is related to its resistivity/conductivity.

Note: In Annex B, the symbol T is used to indicate the temperature in kelvins, and the symbol t , is used to indicate the temperature in Celsius degrees.

B.1 Equation for the calculation of the density of air

The equation of greater accuracy to determine the density of air with the best uncertainty (as far as the contribution of the formula refers), is recommended by the CIPM [15]⁸. The uncertainty of the density of air, will depend on the characteristics of the instruments for measuring environmental conditions, the calibration of these, and the stability of the environmental conditions.

However for some calibrations, depending on the uncertainty required, it is possible to use a simplified version, which has associated uncertainty (to the formula) greater than the formula of the CIPM 2007.

B.1.1 Simplified version of the equation CIPM-2007, exponential version

$$\rho_a = \frac{0.348\ 48p - 0.009h_r \exp(0.061t)}{273.15 + t} \quad (\text{B.1})$$

with

ρ_a	air density in kg m^{-3}
p	barometric pressure in hPa
h_r	relative humidity of air in %
t	air temperatura in $^{\circ}\text{C}$

⁸ The intervals of pressure, temperature and humidity recommended for the implementation of the equation CIPM-2007 are:

600 hPa $\leq p \leq$ 1100 hPa

15 $^{\circ}\text{C} \leq t \leq$ 27 $^{\circ}\text{C}$

0 $\leq h_r \leq$ 1

The equation gives results with $u_{\rho_{a,form}}/\rho_a \leq 2.4 \times 10^{-4}$ under the following environmental conditions (uncertainties of measurement of p , h_r and t not included):

$$\begin{aligned} 600 \text{ hPa} &\leq p \leq 1100 \text{ hPa} \\ 20 \% &\leq h_r \leq 80 \% \\ 15 \text{ }^\circ\text{C} &\leq t \leq 27 \text{ }^\circ\text{C} \end{aligned} \quad (\text{B.2})$$

B.1.2 Simplified version of the equation CIPM-2007, normal version

$$\rho_a = \frac{0.348\ 444p - h_r(0.002\ 52t - 0.020\ 582)}{273.15 + t} \quad (\text{B.3})$$

With the same symbols for B.1.

The equation gives results with $\Delta\rho_{a,form} \leq 0.001\ 41 \text{ kg/m}^3$ under the following environmental conditions (not including the uncertainties of measurement of p , h_r y t):

$$\begin{aligned} 600 \text{ hPa} &\leq p \leq 1100 \text{ hPa} \\ 20 \% &\leq h_r \leq 80 \% \\ 15 \text{ }^\circ\text{C} &\leq t \leq 27 \text{ }^\circ\text{C} \end{aligned}$$

$\Delta\rho_{a,form}$ is the difference between values obtained from this equation and the corresponding values of the equation CIPM. Therefore, the relative variance of the equation is given by:

$$\hat{w}^2(\rho_{a,form}) = (2.2 \times 10^{-5})^2 + \frac{\left(\frac{0.00141 \text{ kg m}^{-3}}{1.2 \text{ kg m}^{-3}}\right)^2}{3} = 4.61 \times 10^{-7} \quad (\text{B.4})$$

And the relative standard uncertainty of the equation is,

$$\hat{w}(\rho_{a,form}) = 6.79 \times 10^{-4} \quad (\text{B.5})$$

B.2 Equation for the density of water

The equation of M. Tanaka et al [16] offers values of the density of the water, ρ_w free of dissolved air, depending on its temperature t , and valid in the range 0 °C to 40 °C to a reference pressure of 101 325 Pa. The uncertainty of the formula of M. Tanaka has a relative uncertainty of 4.5×10^{-7} , which is combined with the other contributions (e.g. temperature and pressure, among others).

As not all water samples has the same isotopic content, and in order to reach the highest accuracy in the calculation of the water density, the Tanaka equation has the possibility to calculate the water density for the specific isotopic content of the water available.

Since the water is slightly compressible and can contain dissolved air, the equation provides corrections because of these two effects.

When it is required to know the density of pure water, outside the ranges of temperature and pressure which covers the equation of M. Tanaka [16], it can be used the formula known as IAPWS-95 [19].

For some applications, depending on the required uncertainty, it can be used another approach, whose calculation is simpler but with a greater uncertainty.

B.2.1 Alternative equation for the water density, polynomial of fourth degree

The following simplified expression can be used in the range of 1 °C to 40 °C, and at the atmospheric pressure of 101.325 kPa,

$$\rho_w(\text{kg m}^{-3}) = a_0 + a_1t + a_2t^2 + a_3t^3 + a_4t^4 \quad (\text{B.6})$$

where,

ρ_w is the density of the water at the working temperature (kg m^{-3})

$$a_0 = 999.84 \text{ kg m}^{-3}$$

$$a_1 = 6.6054 \times 10^{-2} \text{ }^\circ\text{C}^{-1} \text{ kg m}^{-3}$$

$$a_2 = -8.7291 \times 10^{-3} \text{ }^\circ\text{C}^{-2} \text{ kg m}^{-3}$$

$$a_3 = 7.5787 \times 10^{-5} \text{ }^\circ\text{C}^{-3} \text{ kg m}^{-3}$$

$$a_4 = -4.5058 \times 10^{-7} \text{ }^\circ\text{C}^{-4} \text{ kg m}^{-3}$$

Formula B. 6 provides results with $\Delta\rho_{w,form} \leq 0.005 \text{ kg/m}^3$ in the range of 1 °C to 40 °C. $\Delta\rho_{w,form}$ is the difference between values obtained from this equation and the corresponding values in the equation of M. Tanaka, therefore, the relative variance of the equation is given by

$$\hat{w}^2(\rho_{w,form}) = (4.51 \times 10^{-7})^2 + \frac{\left(\frac{0.005 \text{ kg m}^{-3}}{998.2 \text{ kg m}^{-3}}\right)^2}{3} = 8.905 \times 10^{-12} \quad (\text{B.7})$$

and the relative standard uncertainty is,

$$\hat{w}(\rho_{w,form}) = 3 \times 10^{-6} \quad (\text{B.8})$$

The uncertainty of the density of water is obtained from the combination of this contribution (due to the formula used), with the contributions due to the temperature and pressure of the water and, if this is the case, the contribution due to the correction by dissolved gases in the water.

For the range of temperature between 15 °C to 25 °C, the density differences are $\Delta\rho_{w,form} \leq 0.0005 \text{ kg m}^{-3}$, therefore the relative uncertainty associated to this equation for this range of temperature is,

$$\hat{w}(\rho_{w,form}) = 5.4 \times 10^{-7} \quad (\text{B.9})$$

The corrections due to the pressure and temperature, as well as the correction due to dissolved gases in the water are described in the article by M. Tanaka [16].

ANNEX C. COVERAGE FACTOR k FOR THE EXPANDED UNCERTAINTY OF MEASUREMENT

Note: in this Appendix the general symbol y is used for the result of the measurement, not as a particular quantity, as an indication, an error, a value of the mass of a heavy object, etc.

C.1 Objective

The coverage factor k must be chosen for all the cases that the expanded uncertainty of measurement have a coverage probability of approximately 95 %.

C.2 Basic conditions for the implementation of

A factor of $k = 2$ applies when the following conditions are met:

- A) A normal distribution can be assigned to the resulting estimate y also $u(y)$ is sufficiently reliable.
- B) It can be assumed a normal distribution when several components of uncertainty (e.g. $N \geq 3$), each one derived from distributions of "common behaviours" (normal, rectangular or similar), contribute to $u(y)$ in comparable quantities.

Note: this implies that none of the contributions with different distribution to the normal is a dominant value as defined in C.3.2.

The **sufficient reliability** depends on the effective degrees of freedom. This criterion is met if no contribution Type A of $u(y)$ is based on fewer than 10 observations.

C.3 Determining k for other cases

In any of the following cases the expanded uncertainty is:

$$U(y) = ku(y) \tag{C.1}$$

C.3.1 Distribution assumed as normal

Where the distribution of the estimated for the output variable y can be assumed as a normal distribution, but $u(y)$ is not reliable enough - see chapter C. 2 - then the effective degrees of freedom ν_{eff} have to be determined using the formula of Welch-Satterthwaite, and the value of $k > 2$ is obtained from the corresponding table.

$$v_{eff} = \frac{u^4(y)}{\sum_{i=1}^N \frac{u^4(x_i)}{v_i}} \quad (C.2)$$

Where

v_{eff} are the effective degree of freedom associated to $u(y)$
 $u(y)$ is the combined standard uncertainty associated to measurand Y
 $u(x_i)$ is the standard uncertainty associated to the input quantity i
 v_i are the degree of freedom associated to the uncertainty of the input quantity i

From the corresponding table, take $k_p = t_p(v_{eff})$ and calculate $U_p(y) = k_p u(y)$, to obtain the desired level of confidence..

Note: The selection of the $t_p(v)$ is based on the degrees of freedom and fraction p from the t -distribution table.

C.3.2 Non-normal distribution

It may be obvious in a given situation that $u(y)$ contains a component of type B uncertainty of $u_1(y)$ that has a contribution with non-normal distribution, e.g. rectangular or triangular, which is considerably higher than the rest of the components. In this case, $u(y)$ is divided in the part (possibly dominant) u_1 and in $u_R =$ square root of $\sum u_j^2$ with $j \geq 2$, the combined standard uncertainty includes the remaining contributions, see [1]. If $u_R \leq 0.3u_1$, then u_1 is considered as "dominant" and the distribution of y is considered basically identical to that of the dominant contribution.

The coverage factor is chosen according to the shape of the distribution of the dominant component:

For the trapezoidal distribution with < 0.95 :

($\beta =$ side parameter, rate of lower side to larger side of the trapezoid)

$$k = \{1 - \sqrt{[0.05(1 - \beta^2)]}\} / \sqrt{[(1 + \beta^2)/6]} \quad (C.3)$$

- for a rectangular distribution ($\beta = 1$): $k = 1.65$
- for a triangular distribution ($\beta = 0$): $k = 1.90$
- for a type distribution U: $k = 1.41$

The dominant component may in turn be composed of two dominant components $u_1(y)$, $u_2(y)$, e.g. two rectangles forming a trapezoid, in which case u_R will be determined from the remaining u_j with $j \geq 3$.

ANNEX D. EXAMPLES

The examples presented in this Annex shows some of the different ways of how to apply properly the rules contained in this guide. It is not intended to indicate preference of a procedure against another whose example is not submitted.

D1 Calibration of oscillation-type density meter of laboratory by comparison against CRMs in density

The calibration was performed at the place of use of the density meter, a laboratory with controlled conditions of temperature and relative humidity.

D1.1 Characteristics of the instrument under test

Instrument	Oscillation-type density meter
Resolution	0.000 001 g cm ⁻³
Measuring range of density	0 g cm ⁻³ to 3 g cm ⁻³
Measurement interval of temperature	0 °C to 91 °C
Sensor type	Type "U"
Control of temperature	Integrated thermostat of solid state (Peltier)
Adjustment of viscosity	Yes, automatic setting of viscosity
Scale adjustment of the equipment	Performed prior to start calibration, with air and water according to the procedure recommended by the manufacturer.
Resolution of the thermometer (integrated)	$d_t = 0.001$ °C
Factor (ISO 15212, Table 5-1)	1/5
mpe (Table 5-1)	0.000 05 g cm ⁻³
U_{req} (Table 6-1)	0.000 025 g cm ⁻³

D1.2 Measurement Standards

D1.2.1 Characteristics of the CRM certificates in density, used in calibration

For the calibration were used four certified reference materials in density in the range of 0.768 to 1.113 g cm⁻³.

CRM	Density, ρ_{cert} g cm ⁻³	Expanded Uncertainty, $U(\rho), k=2$ g cm ⁻³	Temperature of ref. t_{ref} , °C	Pressure of ref. p_{ref} , Pa	Coeff. of volumetric expansion, α °C ⁻¹	Coeff. of Isothermal compressibility, β , Pa ⁻¹	Viscosity @ 20 °C η mPa·s
CRM 1 Pentadecane	0.768 551	0.000 020	20	81 000	8.5E-10	-0.000 911	2.86
CRM 2 Polyalphaolefin	0.794 497	0.000 020	20	81 000	7.89E-10	-0.001 053	7.72
CRM 3 Water	0.998 208	0.000 020	20	81 000	4.59E-10	-0.000 206	1.03
CRM 4 Ethylene Glycol	1.113 119	0.000 020	20	81 000	3.64E-10	-0.000 562	1.61

D1.2.2 Equipment for the measurement of temperature and pressure of the samples

For the calibration was used a probe-type thermometer and a barometer to check the value of temperature and pressure of the sample

Thermometer	
Sensor	PT100
Scope of measurement	-260 °C – 962 °C
Thermometer resolution(external)	$d_{term} = 0.001 \text{ °C}$
Unc. Of calibration	$u(t_{term}) = 0.005 \text{ °C}, k=2$
Barometer	
Scope of measurement	0.1 MPa – 276 MPa
Barometer resolution	$d_p = 10 \text{ Pa}$
Unc. of calibration	$u(p_{barom}) = 28 \text{ Pa}, k=2$

D1.3 Measurements

Prior to measurements with the reference materials, the adjustment has to be performed as recommended by the manufacturer (with air and water).

D1.3.1 Maximum difference in temperature

To evaluate the maximum difference in temperature between the indication of the instrument under test and a calibrated external thermometer and certified with a probe-type sensor, the type U sensor was filled with water and the vibration was disabled in order to introduce the probe-type temperature and compare the temperature readings

Note: If you introduce the temperature sensor with the type U sensor in vibratory mode, there is a high risk of damaging both sensors.

Indication of the instrument under test I_{t-inst} , °C	Indication of the standard thermometer I_{t-p} , °C	Absolute difference of temperature $ \Delta t $, °C
10.000	10.001	0.001
15.000	15.001	0.001
20.000	20.000	0.000
25.000	25.000	0.000
30.000	29.999	0.001
35.000	34.997	0.003
40.000	39.997	0.003
45.000	44.997	0.003
	$\Delta t_{max} =$	0.003

D1.3.2 Indications of the instrument under test for the CRMs

Prior to the measurement of the reference materials, the density meter is set to the value of calibration temperature (20 °C), and the instrument measurements are performed with the CRM under measurement. The indications are taken until it is verified that the instrument sensor is completely filled with the CRM to measure, do not have bubbles on the inside and has reached stability of temperature.

10 measurements were made for each CRM, discarding the first 4. The repetitions of the indications are taken by introducing new fluid to the sensor of the density meter.

D1.3.2.1 CRM 1. Pentadecane

	Indication, $l, \text{g cm}^{-3}$	Temperature, $t_x, ^\circ\text{C}$	Pressure, p_x, Pa
1	0.768 589	20.000	$p_i = 80\,960$
2	0.768 589	20.000	$p_f = 81\,005$
3	0.768 589	20.000	
4	0.768 587	20.000	
5	0.768 588	20.000	
6	0.768 590	20.000	
Average	0.768 589	20.000	80 982.5
Standard Deviation	0.000 001	0.000	

D1.3.2.2 CRM 2. Polyalphaolefin

	Indication, $l, \text{g cm}^{-3}$	Temperature, $t_x, ^\circ\text{C}$	Pressure, p_x, Pa
1	0.794 503	20.000	$p_i = 81\,005$
2	0.794 496	20.000	$p_f = 80\,965$
3	0.794 500	20.000	
4	0.794 501	20.000	
5	0.794 503	20.000	
6	0.794 501	20.000	
Average	0.794 501	20.000	80 985.0
Standard Deviation	0.000 003	0.000	

D1.3.2.3 CRM 3 Water

	Indication, $l, \text{g cm}^{-3}$	Temperature, $t_x, ^\circ\text{C}$	Pressure, p_x, Pa
1	0.998 191	20.000	$p_i = 81\ 035$
2	0.998 196	20.000	$p_f = 81\ 002$
3	0.998 172	20.000	
4	0.998 173	20.000	
5	0.998 193	20.000	
6	0.998 194	20.000	
Average	0.998 187	20.000	81 018.5
Standard Deviation	0.000 011	0.000	

D1.3.2.4 CRM 4 Ethylene Glycol

	Indication, $l, \text{g cm}^{-3}$	Temperature, $t_x, ^\circ\text{C}$	Pressure, p_x, Pa
1	1.113 030	19.999	$p_i = 80\ 960$
2	1.113 030	19.999	$p_f = 80\ 990$
3	1.113 024	19.999	
4	1.113 028	19.999	
5	1.113 027	19.999	
6	1.113 028	19.999	
Average	1.113 028	19.999	80 975
Standard Deviation	0.000 002	0.000	

D1.4 Calculations of the indication error and associated uncertainty**D1.4.1 CRM 1, Pentadecane**

Source	Value	Variability	Distribution	Standard Unc. u(xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Indication $I, \text{g cm}^{-3}$	0.768 589	5.467E-06	normal, k=1	5.47E-06	5	-1.00E+00	-5.47E-06
Resolution $\varepsilon_{res}, \text{g cm}^{-3}$	0	1.000E-06	rectangular	2.89E-07	200	-1.00E+00	-2.89E-07
Reproducibility $\varepsilon_{reprod}, \text{g cm}^{-3}$	0	0.000E+00	normal, k=1	0.00E+00	50	-1.00E+00	0.00E+00
Viscosity $\varepsilon_{visc}, \text{g cm}^{-3}$	0	0.000E+00	rectangular	0.00E+00	50	-1.00E+00	0.00E+00
Density $\rho_{cert}, \text{g cm}^{-3}$	0.768 551	2.000E-05	normal, k=2	1.00E-05	200	-1.00E+00	-1.00E-05
Correction Factor for Temperature f_t	1.000 000 000	2.424E-06	normal, k=1	2.42E-06	200	7.69E-01	1.86E-06
Correction Factor for Pressure f_p	1.000 000 015	2.739E-08	normal, k=1	2.74E-08	200	7.69E-01	2.10E-08
Density Stability $\varepsilon_{est}, \text{g cm}^{-3}$	0	---	---	---	---	---	---
Standard Unc.	---	---	---	---	---	---	0.000 012
Degrees of freedom	---	---	---	---	---	---	78
$k(95.45\%)$	---	---	---	---	---	---	2.01
Indication error $E, \text{g cm}^{-3}$	0.000 038	---	---	---	---	---	0.000 024

D1.4.1.1 Temperature correction factor

Source	Value	Variability	Distribution	Standard Unc. u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Thermal Expansion Coefficient $\alpha, ^\circ\text{C}^{-1}$	-9.11E-04	1.37E-04	rectangular	3.94E-05	50	0.00E+00	0.00E+00
Measuring Temperature $t_x, ^\circ\text{C}$	20	0.002 66	normal, k=1	2.66E-03	200	-9.11E-04	-2.42E-06
Reference Temperature $t_{ref}, ^\circ\text{C}$	20	---	---	---	---	---	---
Temperature Correction Factor f_t	1.000 000 000	---	normal, k=1	2.424 1E-06	200	---	---

D1.4.1.2 Pressure correction factor

Source	Value	Variability	Distribution	Standard Unc. u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Compressibility Coefficient β, Pa^{-1}	8.50E-10	1.28E-10	rectangular	3.68E-11	50	1.75E+01	6.44E-10
Pressure Measurement p_x, Pa	80 982.5	32.22	normal, k=1	3.22E+01	200	-8.50E-10	-2.74E-08
Reference Pressure p_{ref}, Pa	81 000	---	---	---	---	---	---
Pressure Correction Factor f_p	1.000 000 015	---	normal, k=1	2.738 8E-08	200	---	---

D1.4.2 CRM 2, Polyalphaolefin

Source	Value	Variability	Distribution	Standard Unc. u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Indication $I, \text{g cm}^{-3}$	0.794 501	5.467E-06	normal, k=1	5.47E-06	5	-1.00E+00	-5.47E-06
Resolution $\varepsilon_{res}, \text{g cm}^{-3}$	0	2.887E-07	rectangular	2.89E-07	200	-1.00E+00	-2.89E-07
Reproducibility $\varepsilon_{reprod}, \text{g cm}^{-3}$	0	0.000E+00	normal, k=1	0.00E+00	50	-1.00E+00	0.00E+00
Viscosity $\varepsilon_{visc}, \text{g cm}^{-3}$	0	0.000E+00	rectangular	0.00E+00	50	-1.00E+00	0.00E+00
Density $\rho_{cert}, \text{g cm}^{-3}$	0.794 497	2.000E-05	normal, k=2	1.00E-05	200	-1.00E+00	-1.00E-05
Correction Factor for Temperature f_t	1.000 000 000	2.803E-06	normal, k=1	2.80E-06	200	7.94E-01	2.23E-06
Correction Factor for Pressure f_p	1.000 000 012	2.542E-08	normal, k=1	2.54E-08	200	7.94E-01	2.02E-08
Density Stability $\varepsilon_{est}, \text{g cm}^{-3}$	0	---	---	---	---	---	---
Standard Unc.	---	---	---	---	---	---	0.000 012
Degrees of freedom	---	---	---	---	---	---	80
k(95.45%)	---	---	---	---	---	---	2.01
Indication error $E, \text{g cm}^{-3}$	0.000 004	---	---	---	---	---	0.000 024

D1.4.2.1 Temperature correction factor

Source	Value	Variability	Distribution	Standard Unc. u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Thermal Expansion Coefficient $\alpha, \text{ }^\circ\text{C}^{-1}$	-0.001 053 12	1.58E-04	rectangular	4.56E-05	50	0	0
Measuring Temperature $t_x, \text{ }^\circ\text{C}$	20	0.002 66	normal, k=1	2.66E-03	200	0.001 053 12	-2.80283E-06
Reference Temperature $t_{ref}, \text{ }^\circ\text{C}$	20	---	---	---	---	---	---
Temperature Correction Factor f_t	1.000 000 000	---	normal, k=1	2.802 83E-06	200	---	---

D1.4.2.2 Pressure correction factor

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Compressibility Coefficient $\beta, \text{ Pa}^{-1}$	7.89E-10	1.18E-10	rectangular	3.42E-11	50	15	5.12E-10
Pressure Measurement $p_x, \text{ Pa}$	80 985	3.22E+01	normal, k=1	3.22E+01	200	-7.89E-10	-2.54E-08
Reference Pressure $p_{ref}, \text{ Pa}$	81 000	---	---	---	---	---	---
Pressure Correction Factor f_p	1.000 000 012	---	normal, k=1	2.542 11E-08	200	---	---

D1.4.3 CRM 3, Water

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Indication $I, \text{g cm}^{-3}$	0.998 187	5.467 E-06	normal, k=1	5.47E-06	5	-1.00E+00	-5.47E-06
Resolution $\varepsilon_{res}, \text{g cm}^{-3}$	0	2.887 E-07	rectangular	2.89E-07	200	-1.00E+00	-2.89E-07
Reproducibility $\varepsilon_{reprod}, \text{g cm}^{-3}$	0	0.000 E+00	normal, k=1	0.00E+00	50	-1.00E+00	0.00E+00
Viscosity $\varepsilon_{visc}, \text{g cm}^{-3}$	0	0.000 E+00	rectangular	0.00E+00	50	-1.00E+00	0.00E+00
Density $\rho_{cert}, \text{g cm}^{-3}$	0.998 208	2.000 E-05	normal, k=2	1.00E-05	200	-1.00E+00	-1.00E-05
Correction Factor of Temperature f_t	1.000 000 000	5.492 E-07	normal, k=1	5.49E-07	200	9.98E-01	5.48E-07
Correction Factor of Pressure f_p	0.999 999 992	1.479 E-08	normal, k=1	1.48E-08	200	9.98E-01	1.48E-08
Density Stability $\varepsilon_{est}, \text{g cm}^{-3}$	0	---	---	---	---	---	---
Standard Unc.	---	---	---	---	---	---	0.000 012
Degrees of freedom	---	---	---	---	---	---	74
k(95.45%)	---	---	---	---	---	---	2.02
Indication error $E, \text{g cm}^{-3}$	-0.000 022	---	---	---	---	---	0.000 024

D1.4.3.1 Temperature correction factor

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Thermal Expansion Coefficient $\alpha, \text{ }^\circ\text{C}^{-1}$	-0.000 206 37	3.10E-05	rectangular	8.94E-06	50	0	0
Measuring Temperature $t_x, \text{ }^\circ\text{C}$	20	2.66E-03	normal, k=1	2.66E-03	200	-0.000 206 37	-5.492 44E-07
Reference Temperature $t_{ref}, \text{ }^\circ\text{C}$	20	---	---	---	---	---	---
Temperature Correction Factor f_t	1.000 000 000	---	normal, k=1	5.492 44E-07	200	---	---

D1.4.3.2 Pressure correction factor

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Compressibility Coefficient $\beta, \text{ Pa}^{-1}$	4.59E-10	6.89E-11	rectangular	1.99E-11	50	-18.5	-3.68E-10
Pressure Measurement $p_x, \text{ Pa}$	81 018.5	32.21	normal, k=1	32	200	-4.59E-10	-1.48E-08
Reference Pressure $p_{ref}, \text{ Pa}$	81 000	---	---	---	---	---	---
Pressure Correction Factor f_p	0.999 999 992	---	normal, k=1	1.479 03E-08	200	---	---

D1.4.4 CRM 4, Etilenglicol

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Indication $I, \text{g cm}^{-3}$	1.113 028	5.467E-06	normal, k=1	5.47E-06	5	-1.00E+00	-5.47E-06
Resolution $\varepsilon_{res}, \text{g cm}^{-3}$	0	2.887E-07	rectangular	2.89E-07	200	-1.00E+00	-2.89E-07
Reproducibility $\varepsilon_{reprod}, \text{g cm}^{-3}$	0	0.000E+00	normal, k=1	0.00E+00	50	-1.00E+00	0.00E+00
Viscosity $\varepsilon_{visc}, \text{g cm}^{-3}$	0	0.000E+00	rectangular	0.00E+00	50	-1.00E+00	0.00E+00
Density $\rho_{cert}, \text{g cm}^{-3}$	1.113 119	2.000E-05	normal, k=2	1.00E-05	200	-1.00E+00	-1.00E-05
Correction Factor of Temperature f_t	1.000 000 562	1.497E-06	normal, k=1	1.50E-06	200	1.11E+00	1.67E-06
Correction Factor of Pressure f_p	1.000 000 009	1.173E-08	normal, k=1	1.17E-08	200	1.11E+00	1.31E-08
Density Stability $\varepsilon_{est}, \text{g cm}^{-3}$	0	---	---	---	---	---	---
Standard Unc.	---	---	---	---	---	---	0.000 012
Degrees of freedom	---	---	---	---	---	---	77
k(95.45%)	---	---	---	---	---	---	2.01
Indication error $E, \text{g cm}^{-3}$	-0.000 091	---	---	---	---	---	0.000 024

D1.4.4.1 Temperature correction factor

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Thermal Expansion Coefficient $\alpha, \text{ }^\circ\text{C}^{-1}$	-0.0005 623 84	8.44E-05	rectangular	2.44E-05	50	-0.001	-2.435 19E-08
Measuring Temperature $t_x, \text{ }^\circ\text{C}$	19.999	2.66E-03	normal, k=1	2.66E-03	200	-0.000 562 384	-1.496 76E-06
Reference Temperature $t_{ref}, \text{ }^\circ\text{C}$	20	---	---	---	---	---	---
Temperature Correction Factor f_t	1.000 000 562	---	normal, k=1	1.496 96E-06	200	---	---

D1.4.4.2 Pressure correction factor

Source	Value	Variability	Distribution	Standard Unc u (xi)	Degrees of Freedom	Sensitivity Coeff. C(xi)	Contribution u(xi) C(xi)
Compressibility Coefficient $\beta, \text{ Pa}^{-1}$	3.64E-10	5.46E-11	rectangular	1.58E-11	50	25	3.94E-10
Pressure Measurement $p_x, \text{ Pa}$	80 975	32.21	normal, k=1	32	200	-3.64E-10	-1.17E-08
Reference Pressure $p_{ref}, \text{ Pa}$	81 000	---	---	---	---	---	---
Pressure Correction Factor f_p	1.000 000 009	---	normal, k=1	1.173 2E-08	200	---	---

D1.5 Calibration results

The calibration results are presented in the following table:

Material	Indication I g cm^{-3}	Error E g cm^{-3}	Standard Unc $u(E)$, $k=1$ g cm^{-3}	Expanded Uncertainty $U(E)$, $\approx 95\%$ g cm^{-3}	Required Unc. U_{req} , $k=2$. g cm^{-3}
CRM 1 Pentadecane	0.768 589	0.000 038	0.000 012	0.000 024	0.000 025
CRM 2 Polyalphaolefin	0.794 501	0.000 004	0.000 012	0.000 024	0.000 025
CRM 3 Water	0.998 187	-0.000 022	0.000 012	0.000 024	0.000 025
CRM 4 Etilenglicol	1.113 028	-0.000 091	0.000 012	0.000 024	0.000 025

Note: The calibration uncertainty is less than the maximum uncertainty required according to the class of the accuracy of the instrument under calibration.

D1.5.1 Approximation by polynomials

With the intention of obtaining a error function of the density of the calibrated instrument depending on the indication of the form

$$E = a_0 + a_1 I + a_2 I^2$$

Design Matrix:

X			
1	0.768 589	0.590 729 051	
1	0.794 501	0.631 231 839	
1	0.998 187	0.996 377 287	
1	1.113 028	1.238 831 329	

Weighting Matrix

P			
6.9444E+09	0	0	0
0	6.9444E+09	0	0
0	0	6.9444E+09	0
0	0	0	6.9444E+09

Vector of indication errors

e
3.80E-05
4.00E-06
-2.20E-05
-9.10E-05

Matrix of variance – covariance

$$\mathbf{U}(\mathbf{a})$$

2.34048E-07	-5.11526E-07	2.72898E-07
-5.11526E-07	1.11994E-06	-5.98435E-07
2.72898E-07	-5.98435E-07	3.20273E-07

with (8.8) are obtained the coefficients of the polynomial of adjustment

a

$$a_0 = -0.000\ 495$$

$$a_1 = 0.001\ 364$$

$$a_2 = -0.000\ 897$$

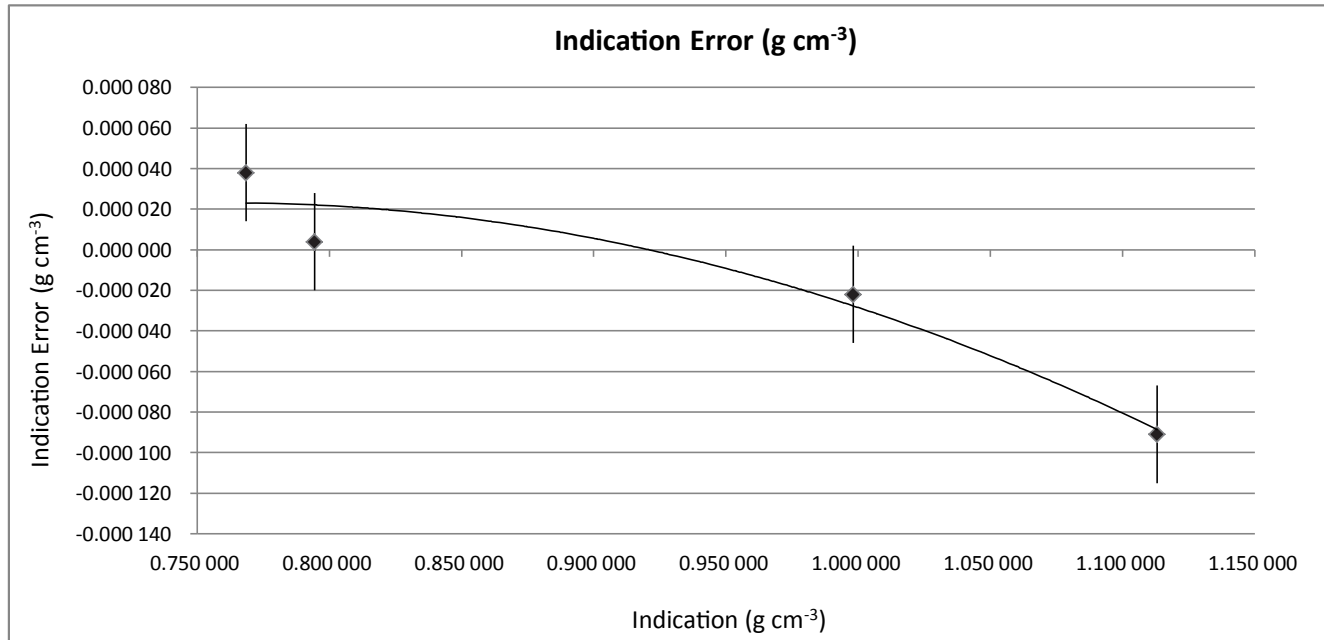


Fig. D1-1 Indication errors of the oscillation-type density meter under test

D1.6 Density measurement of a liquid with the calibrated instrument

With the calibrated density meter, the density of a liquid (Diesel) was measured. Indications of the instrument are presented in the following table

	Indication, $l, \text{g cm}^{-3}$	Temperature, $t_x, ^\circ\text{C}$	Pressure, p_x, Pa
1	0.811 030	20.000	$p_i = 97\ 652$
2	0.811 045	20.000	$p_f = 97\ 601$
3	0.811 038	20.000	
4	0.811 041	20.000	
5	0.811 040	20.000	
6	0.811 051	20.000	
Average	0.811 041	20.000	97 626.5
Standard Deviation	0.000 007	0.000	

The vector of the instrument indications in use is

r
 1.000 000
 0.811 041
 0.657 788

The approximate indication error of the measuring instrument $E_{appr}(R)$, and its corresponding uncertainty $u^2(E_{appr})$, are obtained from (8.12) and (8.15) respectively, $E_{appr}(R) = 2.1 \times 10^{-5} \text{ g cm}^{-3} \pm 8 \times 10^{-6} \text{ g cm}^{-3}$

The density of the fluid under measurement and its uncertainty (at the measurement temperature and pressure) are obtained from (8.17) and (8.18).

	Indication, I , g cm^{-3}	Error E g cm^{-3}	Standard Unc. $u(E)$, $k=1$ g cm^{-3}	Density ρ g cm^{-3}	$u(\rho)$ g cm^{-3}	$U(\rho)$, $\approx 95.45\%$ g cm^{-3}	Temp. t_x $^{\circ}\text{C}$	$u(t)$, $k=1$ $^{\circ}\text{C}$	Pressure p_x Pa	$u(p)$, $k=1$ Pa
Diesel	0.811 041	0.000 021	0.000 008	0.811 020	0.000 016	0.000 032	20. 000	0. 002	97 626.5	29.0

Note: For the calculation of the expanded uncertainty, it has been used a coverage factor $k = 2$, to obtain a level of confidence of 95 %, assuming a normal probability distribution based on the Central Limit Theorem. To have a better approximation of the wished confidence level, the coverage factor value could be obtained according to effective degrees of freedom (see Annex C).

D2 Calibration of the oscillation-type density meter of process

In this example of calibration, the density meter was calibrated while installed in its place and conditions of operation.

D2.1 Characteristics of the instrument under test

Instrument	Oscillation-type density meter
Resolution	0.000 1 g cm ⁻³
Interval of density measurement	0 g cm ⁻³ to 3 g cm ⁻³
Interval of temperature measurement	0 °C to 91 °C
Sensor type	Vibrant Element
Temperature control	No
Viscosity adjustment	No
Adjustment of equipment scale	Prior to installation with the constants of the manufacturer
Constants of the Instrument	$K_0 = -1.190\ 760 \times 10^{-03}$ $K_1 = -2.931\ 290 \times 10^{-01}$ $K_2 = 1.268\ 730 \times 10^{-03}$ $K_{18} = 1.686\ 000 \times 10^{-06}$ $K_{19} = 2.910\ 00 \times 10^{-02}$ $K_{20a} = 5.510\ 000 \times 10^{-05}$ $K_{20b} = -1.129\ 000 \times 10^{-06}$ $K_{21a} = 7.543\ 000 \times 10^{-02}$ $K_{21b} = -1.546\ 000 \times 10^{-03}$
Thermometer resolution (integrated)	$d_t = 0.1\ ^\circ\text{C}$
Manometer resolution (integrated)	100 Pa
Factor (ISO 15212, Table 5-1)	1/10
mpe (Table 5-1)	0.001 g cm ⁻³
U_{req} (Table 6-1)	0.000 33 g cm ⁻³

D2.2 Measurement Standards

D2.2.1 Oscillation-type density meter of laboratory

For the calibration was used an oscillation-type density meter of laboratory with which were measured samples taken from the pipeline.

Instrument	Oscillation-type density meter
Resolution	0.000 001 g cm ⁻³
Interval of density measurement	0 g cm ⁻³ to 3 g cm ⁻³
Interval of temperature measurement	0 °C to 91 °C
Sensor type	Type "U"
Temperature control	Thermostat of integrated solid state (Peltier)
Viscosity adjustment	Yes, automatic adjustment of viscosity
Adjustment of equipment scale	Performed prior to start calibration, with air and water according to the recommended procedure by the manufacturer
Resolution of the thermometer (integrated)	$d_t = 0.001$ °C
Factor (ISO 15212, Table 5-1)	1/5
<i>mpe</i> (Table 5-1)	0.000 05 g cm ⁻³
<i>U_{req}</i> (Table 6-1)	0.000 025 g cm ⁻³

D2.2.2 Auxiliary equipment to verify the temperature and pressure of the indications of the integrated meters.

Thermometer	
Sensor	PT100
Measurement scope	-260 °C – 962 °C
Thermometer resolution (external)	$d_{term} = 0.01$ °C
Calibration unc.	$u(t_{term}) = 0.02$ °C, k=2
Barometer	
Measurement scope	0.1 MPa – 276 MPa
Barometer resolution	$d_p = 10$ Pa
Calibration unc.	$u(p_{barom}) = 28$ Pa, k=2

D2.3 Measurements

In the calibration, 6 samples of fluid were taken and simultaneously the indications of the measuring instrument under test were recorded at the operation conditions, $Q = 944\ 230$ L h⁻¹

Sample	Indication l , g cm ⁻³	Temperature t_x , °C	Pressure p_x , Pa
1	0.821 300	24.0	205 935
2	0.821 300	24.2	205 985
3	0.821 200	24.0	
4	0.821 200	24.2	
5	0.821 300	24.1	
6	0.821 200	24.1	
Average	0.821 250	24.10	205 960
Standard Deviation	0.000 055	0.09	35
Range	0.000 1	0.20	50.0

D2.4 Reference Value

The reference value was obtained by measuring the density of the samples collected in the oscillation-type density meter of laboratory calibrated and certificated, using a procedure similar to A1.6.

Material	Identification	Density ρ g cm ⁻³	$U(\rho)$, ≈95 % g cm ⁻³	pressure p_x Pa	Coefficient of isothermal compressibility, β , Pa ⁻¹	Temp. t_x °C	Coefficient of volumetric expansion, α °C ⁻¹	Viscosity @ 20 °C η mPa s
Diesel	Samples	0.820 230	0.000 042	97 627	7.60E-10	33.32	-8.423E-04	2.40

D2.5 Calculations of the indication error and associated uncertainty**D2.5.1 Diesel**

Source	Value	Variability	Distribution	Standard Unc. $u(x_i)$	Degrees of Freedom	Sensitivity Coeff. $C(x_i)$	Contribution $u(x_i) C(x_i)$
Indication $I, \text{g cm}^{-3}$	0.821 250	1.179E-05	normal, k=1	1.18E-05	5	-1.00E+00	-1.18E-05
Resolution $\varepsilon_{res}, \text{g cm}^{-3}$	0	2.887E-05	rectangular	2.89E-05	200	-1.00E+00	-2.89E-05
Reproducibility $\varepsilon_{reprod}, \text{g cm}^{-3}$	0	0.000E+00	normal, k=1	0.00E+00	50	-1.00E+00	0.00E+00
Viscosity $\varepsilon_{visc}, \text{g cm}^{-3}$	0	4.472E-05	rectangular	4.47E-05	50	-1.00E+00	-4.47E-05
Density $\rho_{cert}, \text{g cm}^{-3}$	0.813 762 024	3.141E-05	normal, k=2	1.57E-05	200	-1.00E+00	-1.58E-05
Correction Factor of Temperature f_t	0.996 546 570 0	1.808E-04	normal, k=1	1.81E-04	101	8.19E-01	1.48E-04
Correction Factor of Pressure f_p	0.999 917 682	3.565E-06	normal, k=1	3.56E-06	50	8.17E-01	2.91E-06
Density Stability $\varepsilon_{est}, \text{g cm}^{-3}$	0	---	---	---	---	---	---
Standard Unc.	---	---	---	---	---	---	0.000 16
Degrees of freedom	---	---	---	---	---	---	131
$k(95.45\%)$	---	---	---	---	---	---	2.00
Indication error $E, \text{g cm}^{-3}$	0.004 601	---	---	---	---	---	0.000 32

D2.5.2 Temperature correction factor

Source	Value	Variability	Distribution	Standard Unc. $u(x_i)$	Degrees of Freedom	Sensitivity Coeff. $C(x_i)$	Contribution $u(x_i) C(x_i)$
Thermal Expansion Coefficient $\alpha, ^\circ\text{C}^{-1}$	-0.000 842 3	1.26E-04	rectangular	3.65E-05	50	1.67E-03	6.08E-08
Measuring Temperature $t_x, ^\circ\text{C}$	33.322	1.19E-01	normal, k=1	1.19E-01	200	-8.42E-04	-1.00E-04
Reference Temperature $t_{ref}, ^\circ\text{C}$	33	---	---	---	---	---	---
Temperature Correction Factor f_t	0.999 998 596	---	normal, k=1	0.000 100 268	200	---	----

D2.5.3 Pressure correction factor

Source	Value	Variability	Distribution	Standard Unc. $u(x_i)$	Degrees of Freedom	Sensitivity Coeff. $C(x_i)$	Contribution $u(x_i) C(x_i)$
Compressibility coefficient β, Pa^{-1}	7.60E-10	1.14E-10	rectangular	3.29E-11	50	-1.08E+05	-3.56E-06
Measurement pressure p_x, Pa	205 939.65	43.16	normal, k=1	4.32E+01	200	-7.60E-10	-3.28E-08
Reference pressure p_{ref}, Pa	97 627	---	---	---	---	---	---
Correction factor for pressure f_p	0.999 917 68	---	normal, k=1	3.564 62E-06	50	---	---

D2.6 Calibration results

Fluid	Indication $l, \text{g cm}^{-3}$	Error E g cm^{-3}	Standard Unc. $u(E), k=1$ g cm^{-3}	Expanded Unc. $u(E), k=2$ g cm^{-3}	Measurement Temp. t_x $^{\circ}\text{C}$	Measurement Pressure p_x Pa	Measurement Flow Q L/h
Diesel	0.821 3	0.004 60	0.000 16	0.000 32	24. 1	205 940	944 230

Note: The resulting uncertainty of the calibration was less than the required according to its class of accuracy. The results of calibration correspond to the instrument under the calibration conditions (temperature, pressure, flow of the fluid, constants of the instrument, among others).

