GUIDE

OIML G 14

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Density measurement

Mesure de la masse volumique

OIML G 14 Edition 2011 (E)

ORGANISATION INTERNATIONALE
DE MÉTROLOGIE LÉGALE

INTERNATIONAL ORGANIZATION
OF LEGAL METROLOGY

Contents

Foreword

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This publication - reference OIML G 14, edition 2011 (E) - was developed by the BIML in cooperation with external technical experts. It replaces the 1987 edition.

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Preface to the second edition

This edition is a reprint of the first edition with an improved lay-out, some corrections to the text and a new set of pictures included.

We thank *Mr. John Carter* of the New Zealand Measurement and Product Safety Service (MAPSS) for reviewing the text and supplying the pictures.

BIML (September 2011)

Preface to the first edition

This brochure is an adapted translation of a document issued by the prepackage control department of the Dutch metrology service, authors *J.A. Dalm* and *P. Hogervorst*.

Though it is mainly intended as a guide for inspectors and technicians doing prepackage control, the methods and calculations described follow such rigorous lines that the brochure may also be useful for other industrial and laboratory applications.

We thank the Dutch metrology service for its collaboration as well as *Mr. Degavre* of the Belgian metrology service for his assistance in the translation.

BIML (March 1987)

Density measurement

Guidance for inspectors

1 Introduction

When the quantity of product in a pre-package is expressed in terms of volume but verified by weighing, it is also necessary to determine the density of the product.

It seems that, in practice, methods for measuring density are frequently not well understood, so that significant systematic errors may occur.

This brochure provides an (non-exhaustive) overview of the commonly used density measurement methods and their applications.

2 Units of measurement

2.1 Volume

The SI unit for volume is the *cubic metre*, symbol: m^3. In chemical laboratories and in retail transactions the commonly used unit is the *litre*, symbol l or L.

The 12th General Conference of Weights and Measures in 1964 decided to abolish an earlier definition of the litre and to define 1 litre to be exactly 1 dm^3.

Thus:

$$1\ \text{l} = 1\ \text{dm}^3$$

$$1000\ \text{l} = 1\ \text{m}^3$$

$$1\ \text{ml} = 1\ \text{cm}^3$$

The units *decilitre* (dl) and *centilitre* (cl) are by tradition admitted as legal units in a number of countries. However, to avoid possible confusion with the *cubic decimetre* and the *cubic centimetre* respectively, their use in industry and science is not recommended.

The *millilitre* (symbol: ml or mL) is, however, commonly used in laboratories and for declaring the quantity of product on prepackages. It is also used in the calculations in this brochure.

2.2 Density

Density is defined as the ratio of the mass of the product (i.e. as if it was weighed in vacuum) to its volume. The coherent SI unit for density is kg/m^3 and should normally be used for reporting the density values of products. As the measurements of mass in this brochure in grams (g) and the measurements of volume in milliliters (ml), the formulas and calculations exceptionally use the unit g/ml, which should not be confused with the unit for concentration.

$$1 \text{ g/ml} = 1 \text{ g/cm}^3 = 1000 \text{ kg/m}^3$$

In order to avoid mistakes, the units have been repeated for each formula where density values have been introduced.

3 Possible sources of error

By the term error we mean the difference between the measured density value and the "true" density value of the product. This error should not be confused with measurement uncertainty.

In general, errors originate from the following causes:

a) Temperature difference if the density measurement is made at a temperature different from 20 °C and no correction to 20 °C is applied.

b) Use of unsuitable measuring means.

c) Buoyancy effect in the measurement of mass.

d) Inappropriate sampling.

3.1 Temperature

National regulations usually prescribe that the actual content of prepackages declared in units of volume shall be stated for the temperature of 20 °C, except for frozen or deep frozen products for which the content shall be declared for the temperature of sale, i.e. generally −5 °C and −18 °C respectively. Some economies require products, notably dairy products, to be stored and sold at temperatures lower than 20 °C. In this case the declared content will be of the temperature at the time of sale.

The measurement may possibly be done at a different temperature than 20 °C but this requires knowledge of the volume expansion coefficient of the product concerned. In this case the conversion may be done using the following formula:

$$\rho = \rho_t[1 + \gamma(t - 20)] \qquad (1)$$

where:

ρ = density of the product at 20 °C,
ρ_t = density of the product at t °C, and
γ = volume expansion coefficient of the product.

The temperature at the density measurement should anyway not depart too much from 20 °C as the coefficient of volume expansion may not be known with sufficient accuracy.

In general, no correction is applied if the temperature does not deviate from 20 °C by more than ± 0.5 °C. A lower temperature leads to a higher estimate of the density of the product which, if the correction is disregarded, is to the disadvantage of the filler (producer of the pre-package).

3.2 Choice of means and methods of measurement

The means and methods are likely to be unsuitable in the following cases:

a) Method not suitable for the type of product.

   Example: Use of a plunger in products with very high viscosity.

b) Means of measurement technically unsuitable (not sufficiently rigid or having other defects).
   Example: Poorly fitting stopper or lid of a pycnometer leading to bad reproducibility.

c) Use of weighing instruments which are not sufficiently accurate compared to the other means of measurement.

   Example: Use of a 50 ml pycnometer with a weighing instrument having a scale interval of 1 g.

d) Calibration not sufficiently accurate.

   Example: Use of the nominal (marked) value of a 100 ml pycnometer when the actual value is 99.89 ml.

3.3 Buoyancy effect in mass measurement

When the volume of a product is determined by measurement of mass and density it is necessary to take into account the effect of air buoyancy. This effect follows the principle of Archimedes which says that a body immersed in a fluid (gas or liquid) is subjected to a vertical upthrust equal to the weight of the displaced fluid.

According to the law of equilibrium of forces, the indication of a weighing instrument depends on this upthrust and the mass is consequently in most cases slightly higher than the value indicated, which is a function of the volumes or mean densities of both the product and the weights used for the weighing, or for the pre-adjustment of the weighing instrument.

It is not necessary to account for this difference in commercial transactions for which the result indicated by the weighing instrument is considered exact by convention (see OIML D 28:2004 *Conventional value of the result of weighing in air*).

However, it is important to take the buoyancy in air into account when making density measurements with high accuracy.

In practice, the calculations are made using as density for standard weights the value: $\rho_n = 8$ g/ml and as a mean density of air: $\rho_l = 0.001\,2$ g/ml. Using these two values one may deduce the following expression:

$$mass = apparent\ mass \times 0.999\,85 \frac{density\ of\ product}{density\ of\ product - 0.001\,2}\ \mathrm{g/ml} \qquad (2)$$

The calculations in the methods of measurement described in the annexes all take into account the effect of buoyancy.

Note concerning the development of air buoyancy formulas

The weighing instrument, generally an electronic balance, is assumed to have been adjusted at its place of use with standard weights (mass = m_n). If the product weighed (mass = m) has a density (ρ) which is different from that of the standard weight (ρ_n), we have:

$$m \cdot g - \frac{m}{\rho} \cdot \rho_l \cdot g = m_n \cdot g^* - \frac{m_n}{\rho_n} \cdot \rho_l^* \cdot g^*$$

where g and $g^*$are the accelerations due to gravity which act on the product and on the standard weights respectively.

For an electronic balance which is adjusted at the site of use ($g = g^*$), one also assumes that the density of air is the same ($\rho_l = \rho_l^*$).

With the values ρ_l = 0.001 2 g/ml and ρ_n = 8 g/ml one obtains:

$$m = \frac{m_n \cdot 0.999\ 85}{V} + 0.001\ 2\ \text{ g/ml}$$

This latter expression is currently used for measurements with pycnometers.

To calculate very exactly the volume of a product from the result of weghings in air and a known density, one has finally to use the following formula:

$$V = \frac{M \cdot 0.999\ 85}{\rho - 0.001\ 2}\ \text{ml}$$

where the mass indicated by the balance (M) is expressed in grams and ρ in g/ml.

3.4 Other sources of error

3.4.1 Inclusion of air

One has to distinguish between two cases:

a. Inclusion of air in the product itself and thus also in the sample.

   For a certain number of products air is introduced by its own during various phases of production without the possibility to escape; it is thus already present in these products during the sampling.

b. Introduction of air into the sample during the sampling procedure.

   Air introduced during the sampling may in some cases escape rapidly from the product and in other cases may disappear only very slowly. It may thus take hours or days before the product is fully free of air (example: shampoos). There are also cases where air remains continually in the product after its introduction, e.g. in putties.

Non-transparent liquids, where the presence of air is not perceptible make measurements still more uncertain.

Guidance:

- Density measurements shall only be made after having eliminated the air from the sample. Pouring and mixing of liquids should therefore be done smoothly and with great care.
- For certain products air is introduced in the manufacturing process and is considered as an inseparable part of the product.
- If there is evidence that air is introduced after the filling procedure and that phenomenon is only temporary (the air will not remain in the final product), it may be possible to take the samples from the vats or elsewhere before the filling.

3.4.2 Sedimentation or separation of constituents

Products composed of several constituents of differing densities may have a tendency to settle non-homogeneously. The following cases are examples of causes of error in sampling:

a. The sample is taken from a non-homogeneous phase.

The density of the sample is then different from the mean density and it is possible that the density decreases during continued filling of the pre-packages. It is necessary to take this into account during sampling and

- either choose a sample elsewhere in the production line, or
- take a greater number of samples.

b. There is separation of the sample itself.

Solution: Stir slowly or mix parts of the product just before measurement without introducing air.

4 Methods of density measurement and their application

4.1 Methods

Main methods in an industrial environment

Pycnometer	(See 5.1)
Plunger	(See 5.2)
Product container (line marked bottle)	(See 5.3)
Product container (filled to the brim)	(See 5.4)
Hydrometer	(See 5.5)
Electronic (portable) densimeter	(See 5.6)

Main methods in a laboratory environment

Electronic densimeter, laboratory type	(See 5.7)
Mohr's balance	(See 5.8)
Plunger method for putties	(See 5.9)

Figure 1: Density kit for determining the density of solid, liquid, porous and viscous substances

4.2 Applications

Product	Method
a. Liquids without CO_2 or other gas	- plunger - metallic pycnometer - hydrometer - electronic densimeter
b. Products with or without CO_2 in transparent but not deformable container	- line marked bottle
c. Product including CO_2 in non-transparent container	Not easily measurable. If semi-transparent use the line marked bottle if possible. If not possible leave CO_2 to escape, then follow a.

Product	Method
d. Viscous liquids	- metallic pycnometer - electronic densimeter, laboratory type
e. Putties	- plunger method for putties - pycnometer with non-dissolving liquid
f. Aerosol products	- electronic densimeter, laboratory type - special high pressure pycnometer
g. Products in several phases in non-deformable and non-transparent container	- container used as pycnometer and filled with water
h. Products in several phases in deformable container	- transfer the product into an Erlenmeyer bottle used as pycnometer (see g.)

5 Density measurement procedures

5.1 Pycnometer

Description

Pycnometers are measures made of glass or metal having a fixed volume.

The pycnometer is closed by a stopper or lid in which there is a small hole which enables air and excess product to be eliminated so that the quantity contained in the pycnometer is constant after completion of the filling operation.

The capacity of pycnometers varies but is frequently 50 or 100 ml. The latter value, or more, is preferable to obtain the best accuracy.

The use of pycnometers with capacity smaller than 25 ml is not recommended.

> *Important*: The actual volume contained in the pycnometer may, with respect to the highest accuracy, be different from the nominal (marked) capacity.

Fields of application

Glass pycnometers:	- clear liquids without CO2 or other solutes under pressure
- filled with non-dissolving liquids:	- pasty products: putties, glues, products conditioned in deformable tubes
Metal pycnometers:	- viscous and slightly pasty products (products for cleaning, lacquers, etc.)

Figure 2: Pycnometers

Necessary equipment

- Calibrated pycnometer as described above (the method of calibration should be known).
- Weighing instrument with scale intervals of 10 mg (0.01 g) or less for a 100 ml pycnometer and 1 mg (0.001 g) or less for a 25 ml pycnometer.
- Weights of accuracy class M_1.
- Thermometer graduated in 0.1 or 0.2 °C intervals.
- Thermostatic bath.

Preparation and measurements

A. Method without use of non-dissolving ancillary liquid

- Clean the pycnometer with water and alcohol.
- Apply a fine film of vaseline to the upper edge of the pycnometer so as to ensure tightness of the lid.
- Place the pycnometer and its lid on the weighing instrument and record the weighing result (M_0).
- Fill the pycnometer very carefully. Avoid the introduction of air bubbles. Also avoid as far as possible to put the product on the walls close to the location of the lid. The filling level should be such that after adjusting definitely the stopper or the lid (see below) a small quantity of the product can escape through the opening.
- Place the stopper or the lid loosely on the pycnometer and place the whole in a thermostatic bath operating at 20 °C ± 0.2 °C.
- Take out and dry the pycnometer after 20 to 30 minutes, rather quickly, so as to avoid temperature drift.
- The stopper or the lid of the pycnometer is then placed or screwed firmly on and the excess of product wiped off with a suitable tissue paper placed around the stopper or around the hole in the lid.

- The pycnometer is then weighed (M_v), emptied, cleaned, dried and weighed again together with standard weights corresponding to approximately the value of $M_v - M_0$, i.e. to the mass contained in the pycnometer.
- Record the indication I_0 of the weighing instrument. This last operation enables the determination of the correction to be applied to compensate for systematic errors of the weighing instrument.

Note: Additional precautions may be necessary to avoid the introduction of air bubbles during manipulation of non-transparent viscous and pasty products using metal pycnometers.

B. Method using filling with a non-dissolving ancillary liquid.

If the pycnometer is filled with a product from a tube or a pot, one may avoid the introduction of air by first filling the pycnometer with a non-dissolving liquid of known density which does not mix with the product (water is often suitable).

One weighs in this case the empty pycnometer (see A.) and then fills it with a small quantity (for instance 1/3) of the non-dissolving liquid followed by a new weighing.

The product to be measured is then introduced so as to approach the level of the lid of the pycnometer and the whole is weighed for a third time.

The filling of the pycnometer is then completed using the non-dissolving liquid followed by a fourth weighing.

See A. for the remainder of the operation.

__**Calculations**__

Method A

$$\rho = 0.999\,85 \cdot \frac{M_p}{V} + 0.001\,2 \text{ g/ml} \qquad (3)$$

where:

ρ = density of the product at 20 °C
M_p = apparent mass of the product: $M_p = M_v - M_0 + C$
where
$C = M_0$ + additional standard weights $- I_0$
V = volume of the pycnometer at the temperature of measurement

Method B

$$\rho = 0.99985 \cdot \frac{m_2 - M_1}{V - 0.999\,85 \cdot \frac{(m_1 - m_0) - (m_2 - m_3)}{\rho_V - 0.001\,2}} + 0.001\,2 \text{ g/ml} \qquad (4)$$

where:

m_0 = weighing result (apparent mass) of empty pycnometer
m_1 = pycnometer + partial filling with ancillary liquid
m_2 = pycnometer + partial filling with ancillary liquid + product
m_3 = pycnometer + complete filling with ancillary liquid + product
ρ_v = density of the ancillary liquid at the temperature of measurement

Example of calculation using method A:

Empty pycnometer:	M_0 = 733.95 g
Fully filled pycnometer:	M_V = 859.94 g
Empty pycnometer + 130 g of standard weights:	I_0 = 863.97 g
Correction weighing instrument (M_0 + 130 g − I_0):	C = −0.02 g
Actual capacity of the pycnometer:	V = 99.75 ml

$$\rho = 0.999\,85\ \cdot \frac{(859.94 - 733.95 - 0.02)}{99.75} + 0.001\,2 = 1.264\ \mathrm{g/ml} \qquad (5)$$

Calibration of a pycnometer:

The actual volume of the pycnometer is:

$$V = 0.999\,85 \cdot \frac{M_n}{\rho_w - 0.001\,2}\ \mathrm{ml} \qquad (6)$$

where:

V = volume of the pycnometer at the temperature of measurement
M_n = weighing result (apparent mass of the water contained in the pycnometer
ρ_w = density of water (for instance at 20 °C: 0.998 201 g/ml)

The density of air during the weighing is assumed to be 0.001 2 g/ml.

5.2 Plunger (gamma sphere)

Figure 3: Spherical plunger

Description

The plunger is a sphere usually made of chromium plated brass and fixed to a rod the length of which can be adjusted by rotation.

It is available in two sizes: 100 and 10 ml.

The 100 ml model has a rod with line divisions to indicate depth of immersion.

The use of the 10 ml model is not recommended because of the rather high relative error due to surface tension of the liquids to be tested.

The approximate value of the surface tension of these liquids should, however, also be known when using the 100 ml plunger.

Fields of application

Clear and slightly viscous liquids with or without CO_2 or other solutes. Because of the ease of cleaning the spherical plunger is particularly recommended for use with lacquers, paints and similar products of medium viscosity.

Necessary equipment

- Calibrated (and certified) plunger.
- Weighing instrument with scale intervals ≤ 10 mg (0.01 g) and a weighing capacity of 800 g or more for tests with a 100 ml plunger.
- Set of weights of class M1.
- Thermometer with scale intervals of 0.1 or 0.2 °C.
- Beaker of 500 or 600 ml.
- Support for holding the plunger.
- Thermostatic bath.

Preparation and measurements

- The plunger and the beaker are first cleaned. Then fill the beaker with the product until it is possible to completely immerse the sphere to the foreseen depth (for instance: 300 ml). Avoid introduction of air during this operation.
- Place the beaker and the plunger in the thermostatic water bath set to 20 °C ± 0.2 °C for 20 to 30 minutes and then dry them externally as required.
- Then place the beaker on the balance and weigh (M_0) or tare if this is possible.
- Bring the plunger carefully into the liquid until approaching the line mark on the rod (for instance: down to 5 mm from the liquid level).
- Turn the lower part of the rod by maintaining the upper part and bring the line mark so as to be slightly below the level of the liquid.
- Again turn slightly the rod to bring it upwards so as to form a good meniscus. The meniscus should be fully formed so as to enable to know and calculate correctly the influence of surface tension on the density measurement. Read the balance at this moment and record the value (M_v).
- Finally, with a view of eliminating possible systematic errors of the balance, place the beaker with its liquid, but without the plunger, on the balance and add an amount of standard weights corresponding to an approximate value of the difference $M_\mathrm{v} - M_0$ and record the indication I_0.

Calculations

$$\rho = 0.999\ 85 \cdot \frac{M_\mathrm{p}}{V} + \frac{\pi \cdot d}{g \cdot V} \cdot \sigma + 0.001\ 2 \text{ g/ml} \qquad (7)$$

where:

ρ = density of the product at 20 °C in mg/l

M_p = apparent mass of the mass displaced by the plunger: $M_\mathrm{p} = M_\mathrm{v} - M_0 + C$,
where C is a correction for systematic errors of the balance:
$C = M_0$ + additional standard weights − I_0

V = volume of the plunger in ml at the temperature of measurement

g = local acceleration due to gravity (for instance: 9.81 m/s^2)

d = diameter of the plunger rod in mm γ = surface tension of the product in N/m

π = 3.1416

Notes:

1. It is desirable to know as exact as possible the value of the surface tension, otherwise errors of the order of 0.000 7 g/ml may typically be introduced using the 100 ml sphere.
2. The formula uses for the density of air the mean value 0.001 2 g/ml and, for the standard weights, 8.0 g/ml.

Example of calculation using a 100 ml plunger:

Measurement of the density of a paint.

Weighing:	
beaker with paint	M_0 = 534.96 g
with plunger	M_v = 638.58 g
without plunger but with 100 g of standard weights	I_0 = 634.91 g
correction $M_0 + 100 - I_0$	C = 0.05 g
Volume of plunger (from certificate)	V = 100.04 ml
Surface tension	σ = 0.04 N/m
Diameter of the plunger rod	d = 3 mm

$$\rho = 0.9985 \cdot \frac{638.58-534.96+0.05}{100.04} + \frac{3.1416 \cdot 3}{9.81 \cdot 100.04} \cdot 0.04 + 0.001\ 2 = 1.037\ 7\ \text{g/ml} \qquad (8)$$

Calibration of the plunger:

The volume of the plunger is calibrated by immersion in a liquid of known density. The actual volume of the plunger is obtained from:

$$V = \frac{0.999\ 85 \cdot M + \frac{\pi \cdot d \cdot \sigma_c}{g}}{[\rho_c - 0.001\ 2] \cdot [1 + (t-20) \cdot \alpha_v]}\ \text{ml} \qquad (9)$$

where:

- V = volume of the plunger at 20 °C in ml
- M = apparent mass of the liquid displaced by the plunger (weighing result corrected for systematic balance errors) in g
- T = temperature during the measurement in °C
- d = diameter of the plunger rod in mm
- g = acceleration due to gravity in m/s^2
- α_v = cubic expansion coefficient of the material of the plunger in K^{-1}
- σ_c = surface tension coefficient of the liquid used for calibration in N/m
- ρ_c = density of the calibration liquid at the temperature t in g/ml

  (The liquid most frequently used is distilled water, for which: σ_c = 0.072 N/m and ρ_c = 0.998 201 g/ml at 20 °C)

Method for volatile products:

Volatile liquids may evaporate too quickly for using the normal method described. Measurements can in this case still be made by putting the support of the plunger on the balance.

Attention: In this case the positive sign of the surface tension component in the formula must be changed to minus sign.

5.3 Line marked bottle

Description

This method uses the container of the product. The principle is basically the same as that of the pycnometer with the difference that the volume of the container or bottle (up to the line mark) is initially unknown.

The container must:

a. not be deformable;

b. be transparent at the location of the line mark;

c. have a diameter at the location of the line mark (neck) which is small (not more than 35 mm).

The marking of the line and the leveling of the liquids must be done carefully to avoid serious errors.

Figure 4: Marking of Level

Fields of application

- Drinks containing CO2;
- non-homogenous products;
- volatile products.

Necessary equipment

- Non-deformable and transparent bottle filled with the product to be measured.
- Weighing instrument with suitable capacity and having scale intervals of 10 mg for containers up to 500 ml and 100 mg for others.
- Thermostatic bath.
- Black marker, water resistant.

Preparation and measurements

- Select a filled bottle from the production line having, if possible, a high level of liquid and place it in a thermostatic bath at 20 °C ± 0.2 °C for 20 to 30 minutes.
- Place the bottle on a horizontal surface and trace with the marker a thick vertical line crossing the level of the liquid and trace (or scratch) a horizontal line with a ball point pen across the vertical line at the location of the meniscus while observing the bottom line of the meniscus by transparency.
- Then weigh the bottle and record the result (*M*v).
- Empty the bottle and clean it by suitable means, then fill it with distilled water up to a level which is slightly below the horizontal line. Measure the temperature of the water in the bottle (t).
- Then place the bottle on the horizontal surface and fill it up to the correct level of the line mark. Close the bottle and weigh it (*M*w).
- Empty the bottle again and dry it completely before weighing together with its capsule or lid (*M*t).
- If necessary, one can determine and take into account the systematic error of the weighing instrument by making separate measurements using standard weights approaching *M*v, *M*w and *M*t for which the corrections designated as *C*v, *C*w and *Ct* apply, see the calculation example below.

Calculations

The general formula for the line marked bottle is:

$$\rho = \left(\rho_\mathrm{w} - 0.001\,2 \cdot \frac{M_\mathrm{p}}{M_\mathrm{n}} + 0.001\,2\ \mathrm{g/ml}\right) \qquad (10)$$

where:

ρ = density of the product at 20 °C in g/ml

ρ_w = density of water at t °C in g/ml

M_p = apparent mass of the product in g

$$M_\mathrm{p} = (M_\mathrm{v} + C_\mathrm{v}) - (M_\mathrm{t} + C_\mathrm{t})$$

M_n = apparent mass of water in the bottle in g

$$M_\mathrm{n} = (M_\mathrm{w} + C_\mathrm{w}) - (M_\mathrm{t} + C_\mathrm{t})$$

Example for a bottle containing a carbonated drink:

Bottle + product + capsule:	M_v = 1 971.23 g
Bottle + water + capsule:	M_w = 1 927.11 g
Empty bottle + capsule:	M_t = 928.25 g
Indication for 1970 g of standard weights:	1 969.83 g
Correction (1970 g - 1969.83 g):	C_v = +0.17 g
Indication for 1930 g of standard weights:	1 929.84 g
Correction (1930 g - 1929.84 g):	C_w = +0.16 g
Indication for 930 g of standard weights:	929.93 g
Correction (930 g - 929.93 g):	C_t = +0.07 g
Temperature of water:	t = 17.4 °C

Density of water according to table X at 17.4 °C: $\rho_w = 0.998\ 7$ g/ml

$$\rho = 0.98\ 7 - 0.001\ 2 \cdot \frac{(1\ 971.23+0.17)-(928.25+0.07)}{(1\ 927.11+016)-(928.25+0.07)} + 0.01\ 2 = 1.0428\ \text{g/ml} \qquad (11)$$

5.4 Container filled with water to the brim

Description

This method, like that of the line marked bottle, uses the product container as a pycnometer but with a lid made from methylmethecrylate (“Plexiglass” or “Perspex”) in which a small hole defines the level.

The container must:

a. not be deformable,

b. have a flat edge,

c. be so designed that air cannot be entrapped after complete filling.

This method is much less accurate than the preceding ones but still valid for certain applications.

Figure 5: Container used as a pycnometer

Fields of application

Containers completely filled containing water, inhomogeneous products such as soups, drinks containing fruit, paint in several phases, etc.

Important: Water must not modify the molecular structure of the product itself.

Necessary equipment

- Container or non-deformable bottle with flat upper edge of such shape that air cannot be entrapped during filling with water.
- Weighing instrument with scale intervals equal to or less than 10 mg for containers with a capacity smaller than 500 ml and 100 mg (0.1 g) for containers of 500 ml or more.
- Lid made of glass or methylmethecrylate (“Plexiglass” or “Perspex”) with a hole at the center.
- Thermometer with scale intervals of 0.1 or 0.2 °C.
- Thermostatic bath.

Preparation and measurements

- Take a closed container from the production line and put it for 20 to 30 minutes in a thermostatic bath set at 20 °C ± 0.2 °C.
- Open the container and grease the edge with vaseline to affect a seal for the special lid.
- Put the container on the balance as well as the lid (separately) and weigh the whole (M_p). (See figure 6.)

- Add water at 20 °C to the container up to 5 mm from the edge, adjust the lid on the container so that its opening is in the center and place the whole on the balance.
- Add water carefully up to the defined level without introducing air bubbles under the lid. If such are present, tap slightly on the lid and complete the filling. (See figure 7.)
- Record the indication of the new weighing (M_s).
- Empty, clean and dry the container carefully and lightly grease the edge. Weigh the empty container together with the lid (M_t). (See figure 8.)
- Fill the container with distilled water until about 10 mm from the edge and measure the temperature of the water *(t)*.
- Adjust the lid on the container, place the whole on the balance, complete the filling with water and record the indication of the balance (M_w). (See figure 9.)
- Determine, if necessary, the corrections for the weighing instrument using standard weights of approximately the same mass values as the indications M_p, M_s, M_t and M_w; the corresponding corrections are designated C_p, C_s, C_t and C_w.

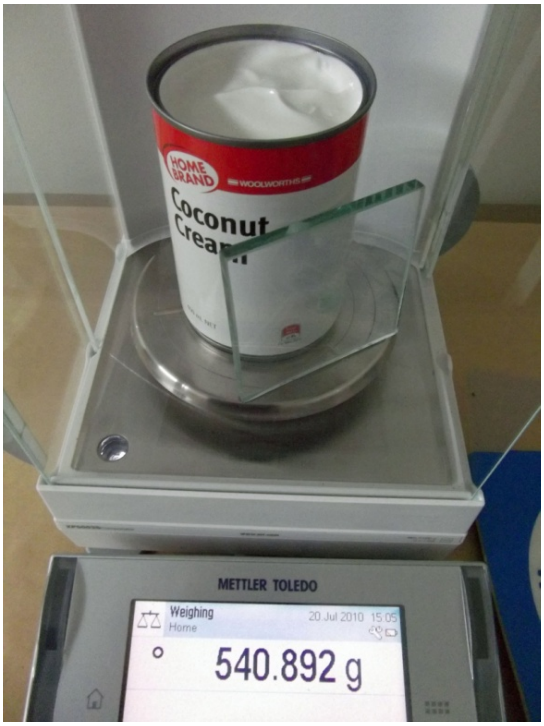

Figure 6: Weighing of container, product and strike

Figure 7: Adjustment of level with water and weighing

Figure 8: Weighing empty container and strike

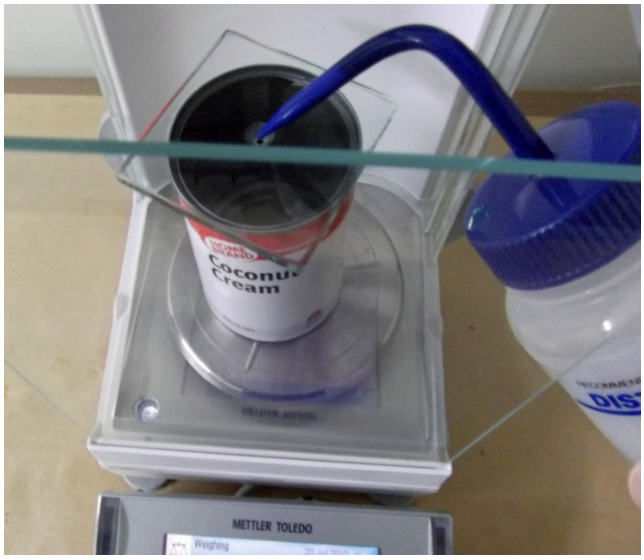

Figure 9: Filling with water and weighing

Calculations

The general formula for the density in this case is:

$$\rho(\rho_{\mathrm{w}} - 0001\ 2) \cdot \frac{M_{\mathrm{p}}^{*} - M_{\mathrm{t}}^{*}}{M_{\mathrm{p}}^{*} - M_{t}^{*} + M_{\mathrm{w}}^{*} - M_{\mathrm{s}}^{*}} + 0.001\ 2\ \mathrm{g/ml} \qquad (12)$$

where:

ρ = density of the product at 20 °C in g/ml
ρ_{w} = density of water at t °C in g/ml
$M_{\mathrm{p}}^{*} = M_{\mathrm{p}} + C_{\mathrm{p}}$
$M_{\mathrm{s}}^{*} = M_{\mathrm{s}} + C_{\mathrm{s}}$
$M_{t}^{*} = M_{t} + C_{t}$
$M_{\mathrm{w}}^{*} = M_{\mathrm{w}} + C_{\mathrm{w}}$

Example: tomato soup in 1 l *container:*

Opened container with product and special lid:	M_{p} = 938.15 g
Container with lid, product and additional water:	M_{s} = 1 005.21 g
Container with lid, entirely filled with water:	M_{w} = 968.89 g
Empty container with lid:	M_{t} = 94.49 g
Indication for 950 g of standard weights:	949.92 g
Correction (950 g − 949.92 g):	C_{p} and C_{w} = 0.08 g
Indication for 1 000 g of standard weights:	995.95 g
Correction (1 000 g − 999.95 g):	C_{s} = 0.05 g

Indication for 95 g of standard weights: 95.01 g

Correction (950 g − 95.01 g): C_t = -0.01 g

M_p^* = 938.15 g + 0.08 g = 938.23 g

M_s^* = 1005.21 g + 0.08 g = 1005.29 g

M_w^* = 968.89 g + 0.05 g = 968.94 g

M_t^* = 94.49 g − 0.01 g = 94.48 g

Temperature of water: t = 17.8 °C

Density of water at t = 17.8 °C according to table X: ρ_w = 0.998 63 g/ml

$$\rho = (0.998\ 63 - 0.001\ 2) \cdot \frac{938.23 - 94.48}{938.23 - 94.48 + 968.94 - 1\ 005.29} + 0.001\ 2 = 1.044\ \text{g/ml} \qquad (13)$$

5.5 Hydrometer

Description

The hydrometer has a cylindrical body made from glass. Its lower part, which is immersed in use, is filled with ballast material and the upper part, which is partially immersed in use, has the form of a narrow graduated tube.

The method of operation is based on the principle of Archimedes, the plunging depth depending on equilibrium between the weight of the hydrometer and the upthrust force determined by the weight of the displaced liquid.

There are various types of hydrometers:

- with or without incorporated thermometer,
- of various accuracies: 0.02 to 0.0001 g/ml,
- with different ranges (depending on accuracy).

The most commonly used type for the measurement of density in the field of prepackage control in Europe (with 'e'-mark) is a hydrometer without incorporated thermometer and with an accuracy of 0.000 5 g/ml.

Because of the narrow range of each hydrometer (0.05 g/ml), nine hydrometers are necessary to cover the range from 0.750 0 to 1.200 0 g/ml.

The correct use, or adjustment, also depends of the type of product to be measured: if the liquid is transparent, the reading can be taken on the line determined by the bottom of the meniscus; if this is not the case it is necessary to take the reading at the top of the meniscus. (See figure 11.)

It is also necessary to take into account the surface tension of the liquid to be measured which must be known with respect to the liquid used for the calibration of the hydrometer.

A weighing instrument is not required.

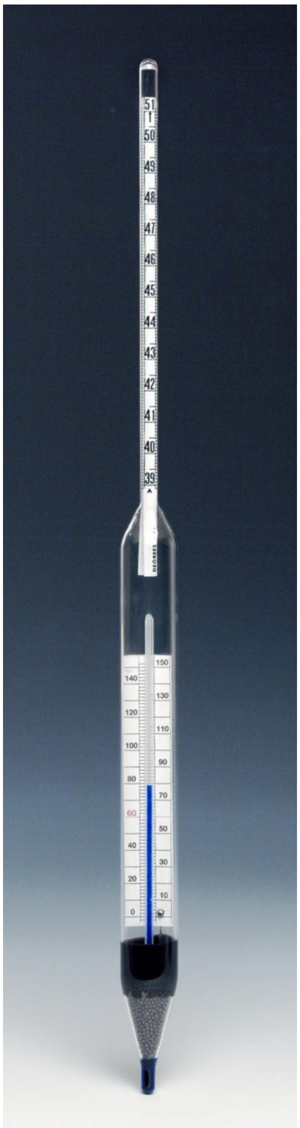

Figure 10: Hydrometer

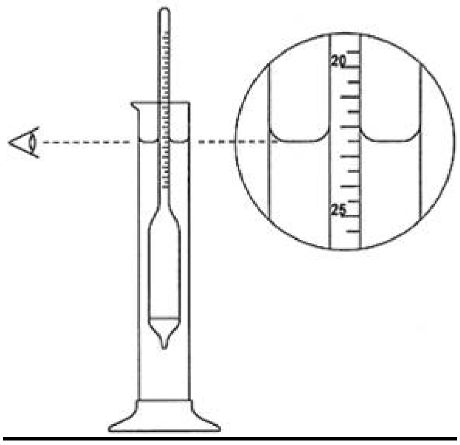

Figure 11: Reading the meniscus for transparent liquids

Fields of application

Non-carbonated liquids, liquid products with low viscosity and in a homogenous phase.

Necessary equipment

- Certified hydrometer, accurate to 0.000 5 g/ml for the products concerned.
- Thermometer with scale intervals of 0.1 or 0.2 °C.
- Cylindrical container of sufficient height and not too narrow.
- Thermostatic bath.

Preparation and measurements

- The glass cylinder and the hydrometer must first be carefully cleaned.
- The glass cylinder is filled with the liquid to be measured without introducing air bubbles. Place the cylinder and the hydrometer in the thermostatic bath to obtain a uniform temperature of 20 °C.
- Lift the hydrometer and drop it very gently so that it floats freely and vertically in the product. The readings are taken using either the bottom line or the top of the meniscus, depending on the type of liquid and the calibration.

Calculations

The density of the product is:

$$\rho = \text{reading} + \text{correction factor g/ml} \tag{14}$$

The correction factor is stated individually on the calibration certificate of each hydrometer.

5.6 Portable electronic density meter

Description

Electronic density meters are commercially available which have scale intervals of 0.001 g/ml in density and 0.1 °C in temperature and which may be suitable for density measurements of pre-packed products.

Their principle is based on the measurement of the natural frequency of a U-shaped glass tube which has a constant volume at a given temperature. This frequency is related to the mass of the tube and thus to the density of the product contained in it. The display indicates density directly in g/ml.

This type of instrument may not include temperature control but can allow temperature to be taken into account by calculation.

The incorporated thermometer can be accurate to 0.5 °C and the density indication to 0.001 g/ml.

It is generally necessary to use the instrument within the following operating ranges:

- the density of the product should be within the range of 0.7 to 1.2 g/ml,
- the operating temperature should be within +10 to + 30 °C.

The instrument may be used in two ways:

- with an incorporated rubber suction bulb,
- with external plastic syringes.

Figure 12: Portable electronic density meter

The first method is not advisable as it may easily introduce air bubbles leading to errors in the measured density values.

The small sample quantity required has a low thermal capacity and its temperature is therefore rapidly adjusted to the ambient temperature as indicated by the instrument.

As the volume expansion coefficient of the products is generally not known, it is preferable to operate at the temperature of 20 °C.

Important: As glass is fragile, it is necessary to avoid pressure in the U-tube as well as heavy and viscous products.

Fields of application

According to the manufacturer's specifications. Generally: non viscous liquids which contain neither air, nor carbon dioxide and for which the density lies in the range of 0.7 to 1.2 g/ml.

Necessary equipment

- Portable electronic density meter which is calibrated (certified) and adjusted before measurements.
- Distilled water for this adjustment.
- Plastic syringes, capacity 2 ml.
- Suction bulb or aquarium pump.
- Thermometer with 0.1 or 0.2 °C scale intervals.
- Installation in accordance with manufacturer's instructions.

Preparation

- Check the calibration of the density meter every time before use, or at least once at the beginning of each day of use.
- Use a syringe for injecting distilled water as specified by the manufacturer, after having eliminated any air bubbles.
- Wait the time specified by the manufacturer. Read the density and the corresponding temperature. If the density differs from that indicated in table 1 by more than 0.001 g/ml the instrument shall be adjusted using the device provided for that purpose.
- Then empty the measurement cell, rinse with alcohol and dry it. The zero indication without product shall be 0.000 or 0.001 or 0.002 g/ml. Otherwise start the calibration operation again.

Measurements

- Fill two or three syringes with the sample product. Eliminate the air by tapping while holding the syringe needle upwards.
- Measure the ambient temperature with a separate thermometer. The ambient temperature shall preferably be between 19.5 and 20.5 °C; however, density measurements can still be made if this is not the case.
- One can distinguish between three situations:

  A. The ambient temperature is between 19.5 and 20.5 °C;

  B. It is lower than 19.5 °C;

  C. It is higher than 20.5 °C.

  Case A: The product can be introduced directly in the density meter using a syringe. Wait until the temperature indicated by the instrument does no longer vary. Then read the density to 0.001 g/ml. Repeat the operation using the second syringe. In case of doubt use the third syringe for confirmation of the result.

  Case B: The same procedures as for A, after having first placed the syringe in a stream of water at, for instance, 25 °C, making the injection and then leaving the temperature to drop to 20 °C as indicated by the thermometer of the instrument.

Case C: The same procedure as B, but by first cooling the sample in a stream of water at, for instance, 15 °C.

- In the three cases the measurement of density is made by direct reading of the instrument and valid for the temperature of 20 °C.
- After each measurement, clean the measuring cell of the density meter with water and alcohol and dry it using the suction ball or the aquarium pump.

5.7 Electronic density meter for laboratory use

Description

These types of density meter which are of higher accuracy than the portable type also use the natural frequency of a tube filled with the product to be measured. They may incorporate temperature regulation or require the use of an external thermostatic bath.

Some types may withstand higher pressures, up to 10 bar, and thus enable density measurements of aerosol products.

Fields of application

These instruments allow measurements on all products, whether liquid or pasty, but which do not contain air bubbles or CO2.

For the correct use of the instruments it is necessary to follow the manufacturer's instructions.

5.8 Hydrostatic balance (Mohr's balance)

(For laboratory use only.)

Description

The operation of this balance is based on the principle of Achimedes.

The balance weighs a plunger hanging on a fine metallic wire.

The plunger is usually a cylinder with a volume from 1 to 10 ml. The difference between the result of weighing in air and the result of weighing in the liquid enables the determination of the density of the liquid.

In the so-called Mohr's balance, the plunger is previously balanced in air so that the amount of weights added to re-establish equilibrium in the liquid furnishes directly density values in g/ml.

Commercial Mohr's balances of this type with direct reading are not usually of high accuracy (at best about 0.001 g/ml) though the principle, when adapted on an analytical balance may, subject to problems with surface tension, enable measurements to 0.000 1 g/ml on thermostatically controlled liquids.

For application and operation follow the manufacturer's instructions.

Figure 13: Mohr's balance

5.9 Plunger method for putties

Description

Principle: The sample of the product is immersed in a liquid of known density. The difference between the weighing in air and in the liquid enables the density to be calculated.

Necessary equipment

- Beaker, capacity 600 ml.
- Distilled water at 20 °C.
- Thin brass or copper strips.
- Nylon or metal wire (for instance fishing line 0.18 mm).
- Balance equipped for hydrostatic weighing, scale interval 1 mg (0.001 g) or smaller.
- Support for the balance so as to allow weighing below its pan.
- Small platform support, adjustable in height, for the beaker.

Preparation and measurements

- Attach the metal strip to the wire and suspend it under the balance. Take the balance reading for the strip in air (M_1).
- Place the beaker half filled with water at 20 °C under the balance so that the metal strip is fully immersed. Take the reading of the balance with the strip in water (M_2).
- Remove the metal strip from the beaker, dry it and cover it carefully with the putty lengthwise. Remove the beaker and weigh the product and the strip in air (M_3).
- Bring the beaker under the balance and weigh the product and the strip fully immersed in water (M_4).
- Correct, if necessary, the readings M_1 -M_4 for systematic errors of the balance.

Calculations

$$\rho = \frac{M_3 - M_1}{(M_3 - M_1) - (M_4 - M_2)} \cdot (\rho_\text{w} - 0.001\,2) + 0.001\,2 \text{ g/ml} \quad (15)$$

where:

ρ = density of the product at the temperature of measurement

ρ_w = density of water at the temperature of measurement (from table)

Note: If the product to be tested dissolves in water, use another reference liquid (methanol or methyl-ethyl-ketone (MEK) for silicon putties).

6 Table: Density of air free water as a function of temperature

(From a paper by H. Wagenbreth and W. Blanke, published in PTB-Mitteilungen, No. 6, 1971, p.412-415)

Values are expressed in kg/m^3. To obtain values in g/ml, divide by 1000.

t (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	999.8396	999.8463	999.8528	999.8591	999.8653	999.8713	999.8771	999.8827	999.8882	999.8934
1	999.8985	999.9035	999.9082	999.9128	999.9172	999.9214	999.9254	999.9293	999.9330	999.9365
2	999.9399	999.9431	999.9461	999.9489	999.9516	999.9541	999.9565	999.9587	999.9607	999.9625
3	999.9642	999.9657	999.9670	999.9682	999.9692	999.9701	999.9708	999.9713	999.9717	999.9717
4	999.9720	999.9718	999.9716	999.9711	999.9705	999.9698	999.9689	999.9678	999.9666	999.9652
5	999.9637	999.9620	999.9602	999.9582	999.9560	999.9537	999.9513	999.9487	999.9459	999.9430
6	999.9399	999.9367	999.9334	999.9299	999.9262	999.9224	999.9184	999.9143	999.9101	999.9057
7	999.9011	999.8964	999.8916	999.8866	999.8815	999.8762	999.8708	999.8652	999.8595	999.8537
8	999.8477	999.8416	999.8353	999.8289	999.8223	999.8157	999.8088	999.8019	999.7947	999.7875
9	999.7801	999.7726	999.7649	999.7571	999.7492	999.7411	999.7329	999.7246	999.7161	999.7075
10	999.6987	999.6898	999.6808	999.6717	999.6624	999.6530	999.6434	999.6337	999.6239	999.6140
11	999.6039	999.5937	999.5834	999.5729	999.5623	999.5516	999.5408	999.5298	999.5187	999.5074
12	999.4961	999.4846	999.4730	999.4612	999.4494	999.4374	999.4253	999.4130	999.4007	999.3882
13	999.3756	999.3628	999.3500	999.3370	999.3239	999.3106	999.2973	999.2838	999.2702	999.2565
14	999.2427	999.2287	999.2146	999.2004	999.1861	999.1717	999.1571	999.1424	999.1276	999.1127
15	999.0977	999.0826	999.0673	999.0519	999.0364	999.0208	999.0051	998.9892	998.9733	998.9572
16	998.9410	998.9247	998.9083	998.8917	998.8751	998.8583	998.8414	998.8244	998.8073	998.7901
17	998.7728	998.7553	998.7378	998.7201	998.7023	998.6845	998.6665	998.6483	998.6301	998.6118
18	998.5934	998.5748	998.5562	998.5374	998.5185	998.4995	998.4804	998.4612	998.4419	998.4225
19	998.4030	998.3833	998.3636	998.3438	998.3238	998.3037	998.2836	998.2633	998.2429	998.2224
20	998.2019	998.1812	998.1604	998.1395	998.1185	998.0973	998.0761	998.0548	998.0334	998.0119
21	997.9902	997.9685	997.9467	997.9247	997.9027	997.8805	997.8583	997.8360	997.8135	997.7910
22	997.7683	997.7456	997.7227	997.6998	997.6767	997.6536	997.6303	997.6070	997.5838	997.5600
23	997.5363	997.5126	997.4887	997.4648	997.4408	997.4166	997.3924	997.3680	997.3436	997.3191
24	997.2944	997.2697	997.2449	997.2200	997.1950	997.1699	997.1446	997.1193	997.0939	997.0685
25	997.0429	997.0172	996.9914	996.9655	996.9396	996.9135	996.8873	996.8611	996.8347	996.8083
26	996.7818	996.7551	996.7284	996.7016	996.6747	996.6477	996.6206	996.5935	996.5661	996.5388
27	996.5113	996.4837	996.4561	996.4284	996.4003	996.3726	996.3446	996.3165	996.2883	996.2600
28	996.2316	996.2032	996.1746	996.1460	996.1172	996.0884	996.0595	996.0305	996.0014	995.9722
29	995.9430	995.9136	995.8842	995.8546	995.8250	995.7953	995.7655	995.7356	995.7056	995.6756
30	995.6465	995.6152	995.5848	995.5544	995.5239	995.4934	995.4627	995.4319	995.4011	995.3701
31	995.3391	995.3080	995.2768	995.2456	995.2142	995.1828	995.1512	995.1196	995.0879	995.0561
32	995.0243	994.9923	994.9603	994.9282	994.8960	994.8637	994.8313	994.7988	994.7663	994.7337
33	994.7010	994.6682	994.6353	994.6024	994.5693	994.5362	994.5030	994.4697	994.4364	994.4029
34	994.3694	994.3358	994.3021	994.2683	994.2345	994.2005	994.1665	994.1324	994.0982	994.0640
35	994.0296	993.9952	993.9607	993.9261	993.8915	993.8567	993.8219	993.7870	993.7521	993.7170
36	993.6819	993.6467	993.6114	993.5760	993.5406	993.5050	993.4694	993.4338	993.3980	993.3622
37	993.3263	993.2903	993.2542	993.2181	993.1818	993.1455	993.1092	993.0727	993.0362	992.9996
38	992.9629	992.9261	992.8893	992.8524	992.8154	992.7784	992.7412	992.7040	992.6668	992.6294
39	992.5920	992.5545	992.5169	992.4792	992.4415	992.4037	992.3658	992.3279	992.2899	992.2518
40	992.3126									