
**Determination of density by
volumetric displacement — Skeleton
density by gas pycnometry**

*Détermination de la masse volumique par déplacement
volumétrique — Masse volumique du squelette mesurée par
pycnométrie à gaz*

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Contents

Page

Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Symbols and abbreviated terms	2
5 Principle of the method	2
6 Apparatus and procedure	3
6.1 Apparatus.....	3
6.2 Sample pre-treatment and determination of sample mass.....	4
6.3 Determination of the solid skeleton volume of the sample.....	5
6.4 Calculation of skeleton density.....	6
6.5 Calibration procedure.....	6
7 Test report	8
Annex A (informative) Interferences	9
Bibliography	11

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 24, *Particle characterization including sieving*, Subcommittee SC 4, *Particle characterization*.

Introduction

The true solid state density of a material is defined as the ratio of the mass to the volume occupied by that mass. Therefore, the contribution to the volume made by pores or internal voids and also interparticle voids (in the case of granulated or highly dispersed samples) shall be subtracted when calculating the true density.

If the material has no porosity, the true density can be measured by displacement of any fluid in which the solid remains inert. The accuracy of the method is limited by the accuracy with which the fluid volume can be determined. Usually, however, the pores, cracks, or crevices of the material will not easily be completely penetrated by a displaced liquid. In these instances, the true density can be measured by using a gas as the displaced fluid if the material does not contain closed pores, which cannot be penetrated by the analysis gas. Therefore, the density experimentally determined by gas pycnometry generally is the so called skeleton density of the material which equals the true solid state density only for samples without closed pores.

Apparatus used to measure solid volumes are often referred to as pyknometers or pycnometers after the Greek “pyknos”, meaning thick or dense. With gas pycnometry, materials of irregular shape can be analysed.

Once the volume of solid skeleton of the sample and the sample mass have been determined, the skeleton density is readily calculated.

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Determination of density by volumetric displacement — Skeleton density by gas pycnometry

1 Scope

This International Standard specifies a method for rapid and efficient determination of the skeleton density of solid material samples of regular or irregular shape, whether powdered or in one piece, by means of a gas displacement pycnometer.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

ISO 9277, *Determination of the specific surface area of solids by gas adsorption — BET method*

ISO 15901-3, *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 3: Analysis of micropores by gas adsorption*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

density

ratio of the mass of a certain amount of a sample to the volume occupied by that mass

3.2

true solid state density

ratio of the sample mass to the volume of the compact solid skeleton of the sample which excludes the volume of open and closed pores or internal voids and also interparticle voids as in the case of granulated or highly dispersed samples

3.3

skeleton density

ratio between sample mass and the volume of the sample including the volume of closed pores (if present) but excluding the volumes of open pores as well as that of void spaces between particles within the bulk sample

3.4

closed pore

pore totally enclosed by its walls and hence not interconnecting with other pores and not accessible to fluids

3.5

open pore

pore not totally enclosed by its walls and open to the surface either directly or by interconnecting with other pores and therefore accessible to fluids

3.6

gauge pressure sensor

because gauge pressure is defined relative to atmospheric conditions, the signal or reading of a gauge pressure sensor is the total pressure minus atmospheric pressure

3.7

absolute pressure sensor

absolute pressure sensor measures the pressure relative to an absolute vacuum that means the reference is full vacuum (zero pressure)

4 Symbols and abbreviated terms

Table 1 — Symbols

Symbol	Name	Unit
ρ_s	skeleton density	g cm^{-3}
m_s	sample mass	g
V_s	skeleton volume of the sample	cm^3
V_{cell}	sample chamber volume	cm^3
V_{ref}	reference chamber volume	cm^3
V_{cal}	volume of the calibrated reference sample	cm^3
p_1	equilibrated gauge pressure prior to expansion ^a	Pa
p_2	equilibrated gauge pressure after expansion ^a	Pa
p_{A1}	equilibrated gauge pressure before expansion (calibration step A) ^a	Pa
p_{A2}	equilibrated gauge pressure after expansion (calibration step A) ^a	Pa
p_{B1}	equilibrated gauge pressure before expansion (2nd calibration step) ^a	Pa
p_{B2}	equilibrated gauge pressure after expansion (2nd calibration step) ^a	Pa
p_a	pycnometer pressure at start of analysis	Pa
p_i^*	pycnometer absolute gas pressure i ($i = 1, 2, A1, A2, B1, \text{ or } B2$)	Pa
p_i	pycnometer excess gas pressure i ($i = 1, 2, A1, A2, B1, \text{ or } B2$)	Pa

^a gauge pressure (excess gas pressure) p_i is defined as the difference between the absolute pressure p_i^* and the pycnometer pressure p_a at start of analysis, i.e. $p_i = p_i^* - p_a$ (see 3.6, 3.7, and 6.3.2.1)

5 Principle of the method

The skeleton density will be determined volumetrically in a gas expansion pycnometer. This technique is based on the displacement of a volume of gas by the solid space. The measurement is performed by expanding gas from one chamber to another (see Figure 1) under isothermal conditions. First, the weight of the dry sample is to be determined and the sample loaded into the sample chamber. The sample chamber then is pressurized to a set value when using the experimental configuration 1 of Figure 1. In a further step, the analysis gas will be expanded into a second chamber, the reference volume. The equilibrated pressures for both steps will be recorded by the instrument. Density is calculated using these values.

For gas pycnometers according to the experimental configuration 2 of Figure 1, the first step consists in pressurizing the reference chamber to a set value followed by the expansion into the sample chamber having a lower initial pressure than the set value. It is important for both experimental pycnometer configurations, that every chamber of the pycnometer is at the same pressure p_a prior to starting the

analysis steps (see [Clause 6](#)) Furthermore, all parts of the pycnometer shall have the same controlled temperature.

The analysis gas of sufficient purity (see [6.1](#)) shall be nonreactive and also non-adsorbing onto the solid sample. It has to behave as ideally as possible. Therefore, helium is used for most applications. Another reason for the preferred use of helium as the analysis gas for gas pycnometry is that it is able to penetrate even the smallest pores or cracks of a material.

NOTE 1 Because of its pronounced ability to permeate thin inner walls of samples with closed cells, helium can cause difficulties if permeable samples are to be analysed. Therefore, as described in Annex [A.6](#), gas pycnometric measurements using helium can be erroneous in the case of organic samples like cellulose and cellular polymers with low density. For density measurements of those samples, the use of alternative inert gases such as nitrogen, argon, or sulfur hexafluoride as well as dry air is recommended.

NOTE 2 If the sample contains no closed pores, then the volume measured by gas pycnometry is the true volume. To test the presence of closed pores, after a first density determination the sample can be powdered revealing any possible closed pores accessible to the test gas. An increased density value of the ground sample material indicates closed pores in the original sample.

6 Apparatus and procedure

6.1 Apparatus

6.1.1 Gas expansion pycnometer, with fixed-volume sample chamber (see [Figure 1](#)).^{[1] [2] [3]}

6.1.2 Calibrated reference sample, (in general calibration spheres made of stainless steel with known traceable volume).

6.1.3 Analysis gas, in general helium (see [Clause 5](#)) with a minimum purity of 99,996 % (by volume).

6.1.4 Analytical balance.

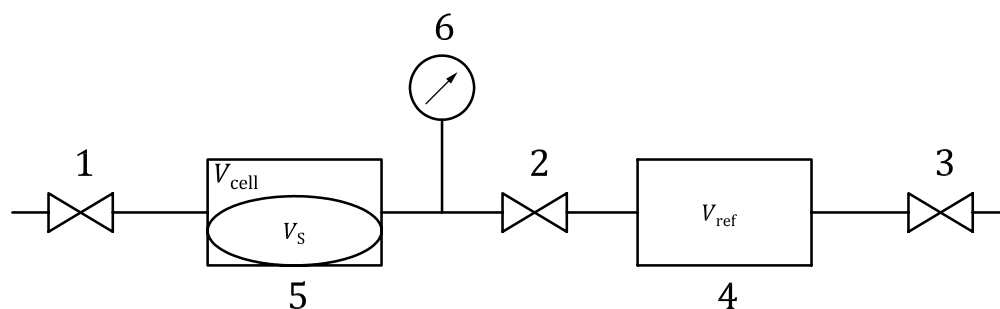
6.1.5 Drying oven, for pre-treatment of samples preferably with the option of purging during heating or heating in a vacuum.

[Figure 1](#) is a schematic diagram of the two principal configurations of automatic gas expansion pycnometers having fixed sample chamber size. Main components of such instruments are two chambers connected by tubes (a sample chamber which can be sealed for inserting the sample or the calibration spheres and a reference chamber), a pressure-measuring sensor, and three valves. The difference between the pycnometer configurations is in the sequence of the sample chamber and the reference chamber.

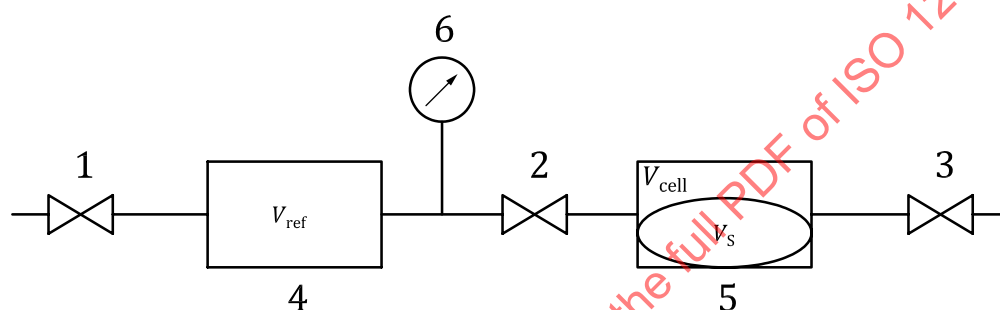
Sample volumes of commercially available gas expansion pycnometers vary from 0,1 cm³ to about 500 cm³. This is accomplished either by having fixed-volume sample chambers of different sizes, or by means of volume-filling inserts placed into a sample chamber. These variations in sample chamber

volume are necessary because the accuracy of the pycnometric measurement is related to the percent of total capacity the sample material occupies in the sample chamber.

Configuration 1



Configuration 2



Key

- | | | | |
|---|---------------------|---|-------------------|
| 1 | valve 1, gas inlet | 4 | reference chamber |
| 2 | valve 2 | 5 | sample chamber |
| 3 | valve 3, gas outlet | 6 | pressure sensor |

NOTE The pressure sensor can be either an absolute pressure sensor or a gauge sensor.

Figure 1 — Two principal experimental gas pycnometer configurations

6.2 Sample pre-treatment and determination of sample mass

Preparing the sample is the first step in obtaining accurate results from the pycnometer. Samples shall be free of moisture in order to obtain true sample mass and to avoid the distorting effect of water vapour on the volume measurement. The following procedures are recommended, however, modifications may be necessary for some materials.

Sampling shall be carried out in accordance with ISO 14488. Removing the atmospheric gases from the sample can be carried out by timed evacuation, timed flow of purge gas, or repetitive pulsing (think multiple rinses) of purge gas. External oven drying of wet samples is recommended.

Heat sensitive materials can be dried by long-time exposure to silica gel, freeze drying, etc. Materials having a low melting point can be dried using the purge process. In this case, do not weigh the sample and cup until after the purge and analysis have been completed.

NOTE Outgassing can be considered complete when the results of duplicate skeleton density analyses are found within the repeatability limits of the pycnometer used.

It is important to consider that each preparation step should be conducted to avoid exposure of the dried sample to atmospheric moisture. This means weighing (see below) as rapidly as possible and installing the sample in the instrument without unnecessary delay.

The sample chamber should be capped except when inserting or removing a sample. The sample chamber shall be free of particles and as dry as possible for accurate analysis results.

For the determination of sample mass m_s , use an analytical balance readable, without estimation, to at least 0,1 % of the sample mass.

- Weigh the empty sample cup (sample holder).
- Place a quantity of sample in the sample cup. Use as large a quantity of sample as possible to fill the cup (see Annex A.1). The cup, however, should be at least two-thirds full.
- Place the sample cup with sample in a drying oven. The amount of time the sample shall be heated depends upon the material and the temperature it will tolerate; this can be established by other tests. Remove the sample cup from the oven and transfer it to a desiccator provided with active desiccant. Allow it to cool until near room temperature. In the steps which follow, minimize air exposure of the sample.
- Weigh the cup and sample and record the weight. Subtract the empty sample cup weight from the sample cup and sample weight to determine the sample weight.
- Insert sample cup with sample into the sample chamber and seal it carefully.

Microporous materials should be prepared according to the recommendations given in ISO 15901-3 and ISO 9277.

Microporous materials such as carbons, zeolites, or metal organic frameworks readily adsorb atmospheric impurities and often have a high affinity for atmospheric moisture. Contaminants can contribute to a significant fraction of the sample mass. The undesirable effects can be that the mass of the sample material is difficult to establish with precision, and a long sequence of analyses is required to obtain stable volume measurements as the impurities are being purged.

The recommended procedure for such materials is to transfer the sample in a previously weighed pycnometer sample cup directly from a vacuum oven to the pycnometer and start the analysis even though the sample is still above room temperature. Allow the analysis to proceed long enough for the sample to cool and thermal equilibrium to be established. Weigh the sample immediately after the analysis. If possible perform this weighing with the sample blanketed by nitrogen or dry air. Use this weight to calculate sample density.

6.3 Determination of the solid skeleton volume of the sample

6.3.1 Pycnometric measurement

Pycnometric analysis should be performed according to the operator's manual. A typical modern automated pycnometer allows performing automated multiple determinations on a single sample. Repeat measurements are usually required to ensure the complete removal of atmospheric gases and the proper thermal equilibration of the sample with analysis gas. Sample skeleton volume should be determined a minimum of five times. The average skeleton volume and the standard deviation are calculated using standard statistical methods.

Initially, all valves are closed with both chambers of the system at the same pressure p_a . When valve 1 opens, the sample chamber (pycnometer configuration 1) or the reference chamber (pycnometer configuration 2) is filled with the analysis gas at an elevated pressure $p_1 > p_a$. This valve closes and the pressure p_1 about the sample (pycnometer configuration 1) or in the reference chamber (pycnometer configuration 2) is measured accurately. Valve 2 opens allowing the analysis gas to expand into the second chamber and the new equilibrium pressure p_2 in both chambers again is measured accurately.

Valve 3 now opens, the gas is vented to atmosphere or to a vacuum, and the cycle repeated until consecutive volume determinations are reproduced within user-prescribed limits.

As described in 6.3.2.2 and 6.3.2.3, the sample skeleton volume will be calculated using the known calibrated volumes V_{cell} and V_{ref} of the sample chamber and the reference chamber respectively as well as the pressure readings p_1 before and p_2 after the gas expansion step. Finally, the skeleton density is then calculated from the sample mass divided by the solid skeleton volume of the sample (see 6.4).

6.3.2 Calculation of the skeleton volume of the sample

6.3.2.1 General remarks

The pressure p_i used in the equations for calculation of the sample volume is excess values above the initial gas pressure p_a in the pycnometer at the start of the measurement. This means that every pressure value used here represents the difference between the absolute pressure and the initial pressure. This shall be noted for pycnometers without the option of zeroing the pressure sensor at the beginning of each analysis or calibration run. After zeroing, the pressure readings directly represent excess gas pressure values.

6.3.2.2 Calculation of V_s from the configuration 1 pycnometer

The volume V_s of solid skeleton of the sample is calculated by Formula 1 when using a pycnometer according to configuration 1 in Figure 1.

$$V_s = V_{\text{cell}} - \frac{p_2}{p_1 - p_2} \cdot V_{\text{ref}} \quad (1)$$

6.3.2.3 Calculation of V_s from the configuration 2 pycnometer

In the case of pycnometer configuration 2, the volume V_s of solid skeleton is calculated by Formula 2.

$$V_s = V_{\text{cell}} - \frac{p_1 - p_2}{p_2} \cdot V_{\text{ref}} \quad (2)$$

6.4 Calculation of skeleton density

Use Formula 3 for the calculation of skeleton density.

$$\rho_s = \frac{m_s}{V_s} \quad (3)$$

6.5 Calibration procedure

6.5.1 General remarks

Calibration is an operation for determination of the exact values of the internal pycnometer volumes V_{cell} of the sample chamber and the volume V_{ref} of the reference chamber. Calibrating the pycnometer is necessary after changing the measurement temperature and after any changes to the sample chamber, tubing, fitting, sample cup/vessel, etc. Calibration should be performed according to the operator's manual. The calibration procedure consists of two independent expansion experiments (calibration steps A and B) because two volumes are to be calibrated. Calibration step A is an expansion experiment with an empty sample chamber including measurement of pressure values p_{A1} and p_{A2} . This gives a relationship between the sample chamber volume V_{cell} and the volume V_{ref} of the reference chamber.

Calibration step B is an expansion experiment with a calibrated reference sample of volume V_{cal} in the sample chamber including measurement of pressure values p_{B1} and p_{B2} .

NOTE The reference sample can be a certified calibration sphere of sufficient size made of high performance material such as stainless steel, titanium, silicon nitride, etc (as obtainable from accredited institutions either as primary or traceable secondary standards). In general, such spheres (or balls) are provided in form of calibration kits as standard equipment for commercial gas pycnometers.

Combining the results of these two calibration steps yields the sample chamber volume and the reference volume. Note that all pressures used are excess values (see 6.3.2.1) above the initial gas pressure p_a in the pycnometer at the start of the calibration procedure.

6.5.2 Calibration of pycnometer configuration 1

Calibration step A (gas expansion experiment with the empty pycnometer, experimental readings are p_{A1} and p_{A2}).

Relationship between sample chamber volume and reference chamber volume:

$$V_{\text{cell}} = \frac{p_{A2}}{p_{A1} - p_{A2}} \cdot V_{\text{ref}} \quad (4)$$

Calibration step B (gas expansion experiment with calibrated reference sample of volume V_{cal} in the sample chamber, experimental readings are p_{B1} and p_{B2})

Relationship between sample chamber volume, reference chamber volume, and the volume of the reference sample:

$$V_{\text{cell}} = V_{\text{cal}} + \frac{p_{B2}}{p_{B1} - p_{B2}} \cdot V_{\text{ref}} \quad (5)$$

Combining Formulae (4) and (5) gives the relationships (6) and (7) for the calculation of the sample chamber volume and the reference chamber volume using the volume of the calibrated reference sample and the pressure readings of calibration steps A and B.

Calculation of the sample chamber volume:

$$V_{\text{cell}} = \frac{p_{A2} \cdot (p_{B1} - p_{B2})}{p_{A2} \cdot p_{B1} - p_{A1} \cdot p_{B2}} \cdot V_{\text{cal}} \quad (6)$$

Calculation of the reference chamber volume:

$$V_{\text{ref}} = \frac{(p_{A1} - p_{A2}) \cdot (p_{B1} - p_{B2})}{p_{A2} \cdot p_{B1} - p_{A1} \cdot p_{B2}} \cdot V_{\text{cal}} \quad (7)$$

6.5.3 Calibration of pycnometer configuration 2

Calibration step A (gas expansion experiment with the empty pycnometer, experimental readings are p_{A1} and p_{A2}).

Relationship between sample chamber volume and reference chamber volume:

$$V_{\text{cell}} = \frac{p_{A1} - p_{A2}}{p_{A2}} \cdot V_{\text{ref}} \quad (8)$$

Calibration step B (gas expansion experiment with calibrated reference sample of volume V_{cal} in the sample chamber, experimental readings are p_{B1} and p_{B2}).

Relationship between sample chamber volume, reference chamber volume, and the volume of the reference sample:

$$V_{\text{cell}} = V_{\text{cal}} + \frac{p_{\text{B1}} - p_{\text{B2}}}{p_{\text{B2}}} \cdot V_{\text{ref}} \quad (9)$$

Combining Formulae (8) and (9) gives the relationships (10) and (11) for the calculation of the sample chamber volume and the reference chamber volume using the volume of the calibrated reference sample and the pressure readings of calibration steps A and B.

Calculation of the sample chamber volume:

$$V_{\text{cell}} = \frac{p_{\text{B2}} \cdot (p_{\text{A1}} - p_{\text{A2}})}{p_{\text{A1}} \cdot p_{\text{B2}} - p_{\text{A2}} \cdot p_{\text{B1}}} \cdot V_{\text{cal}} \quad (10)$$

Calculation of the reference chamber volume:

$$V_{\text{ref}} = \frac{p_{\text{A2}} \cdot p_{\text{B2}}}{p_{\text{A1}} \cdot p_{\text{B2}} - p_{\text{A2}} \cdot p_{\text{B1}}} \cdot V_{\text{cal}} \quad (11)$$

7 Test report

The test report shall include the following details:

- the date of the test;
- a reference to this International Standard (ISO 12154:2014) and any agreed deviations from it;
- details of the sample and the sample preparation;
- the type of pycnometer and its manufacturer, chamber volumes, sample mass, sample volume, temperature;
- the skeleton density of the sample including the uncertainty [combined standard deviation of repeat measurements according to the Guide to the Expression of Uncertainty in Measurement (GUM)].^[4]