Regarding the determination of density of porous and powdered solids

Which one is heavier – a kilogram of lead or a kilogram of cotton? Or are both the same in weight?
Dear readers, the following article is not about the worst possible trick question, it is rather about the evaluation of different materials with regards to their density. In order to determine the density of a solid from its mass, it is required to determine the volume of the solid. The correct way to pose the initial question would therefore be: Which one is heavier – a cube with an edge length of one cm made of lead or a cube with the same edge length made of cotton? Or in short: Which one has the higher density, lead or cotton? Only by introducing the correct term of density, a useful labeling of materials in any field of application requiring information about masses can be carried out. This basically includes any field of applied technology – construction work, food, chemical industry, automotive and aero-space technology, pharma and medicine, cosmetics, geology or paper manufacturing.
The questions posed usually are: How many tons of grain fit into my silo? How is the ratio of a packages weight to its contents weight? How much additional mass is gained by adding an isolating layer? What is the composition of my powder mixture? Has my material changed in a process? Is this raw material or product of sufficient quality? Is my crown made of pure gold?

The answer to those questions requires a reliable way for determining density and thus the careful measurement of the mass and volume of the given sample in order to form the quotient. Masses are determined rather easily and directly by weighing. The actual challenge is the precise analysis of the volume, which varies in complexity depending on the composition, application and constitution of the material. Furthermore, are wide variety of terms for density with high practical relevance exists (see Tab. 1).

Table1 *Terms for density and common synonyms*

Declaration according to DIN 66137-1	Common synonyms	Symbol
Sediment density	Absolute density, true density, helium density, skeletal density	ρ_F
Raw density	Apparent density, envelope density	ρ_R
Pouring density	Tap density, bulk density	ρ_S

The sediment density ρ_F is obtained by dividing the mass m of the sample by the volume of the solid V_F:

$$\rho_F = \frac{m}{V_F}$$

It is mainly dependent on the chemical composition of the material in question. Furthermore, it is dependent on temperature and pressure.

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For porous solids, the raw density or apparent density ρ_R is defined as the quotient of mass and apparent volume of the porous solid. In turn, this volume is composed of the skeletal volume V_F and the pore volume V_P of the sample:

$$\rho_R = \frac{m}{(V_F + V_P)}$$

Raw and sediment density are the same for unporous materials.

For granular and powdered materials, the pouring density can be defined as the quotient between the mass and the volume of a poured fill. This volume is composed of the skeletal volume, the pore volume and the inter-particular void volume V_S:

$$\rho_S = \frac{m}{(V_F + V_P + V_S)}$$

In a poured fill of unporous bodies, no pore volume is available.

Fig. 1 clarifies the discussed terms of density.

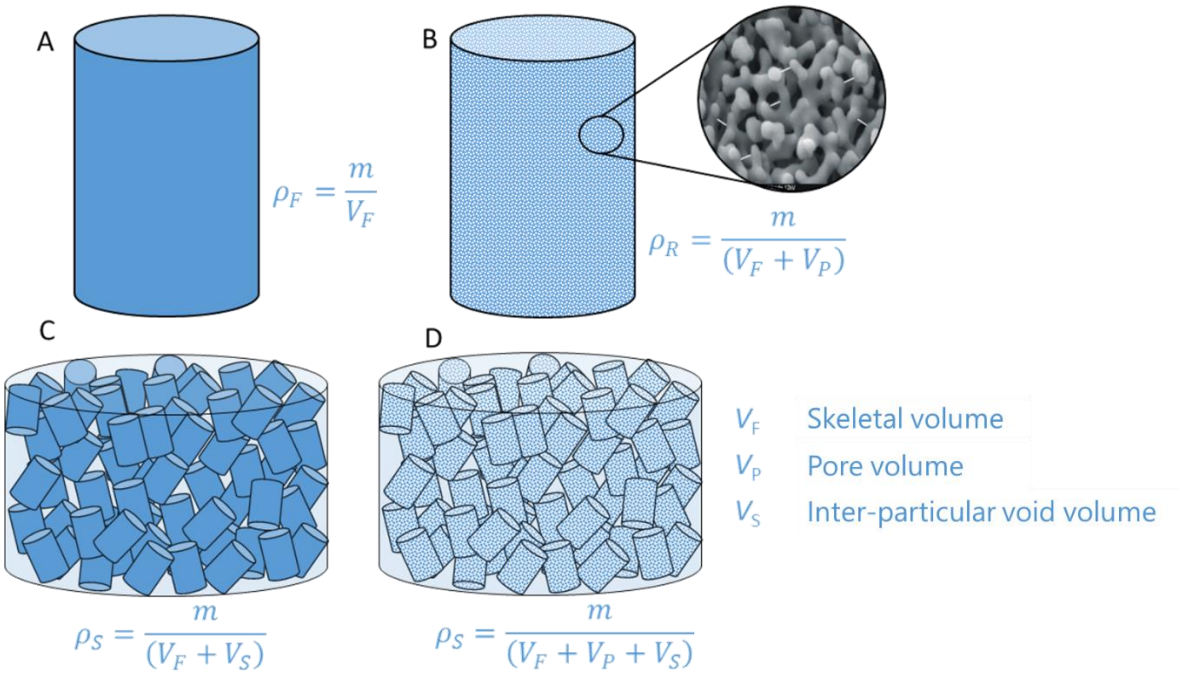

Figure 1 *Elaboration of different terms of density. A: Sediment density of an unporous solid. B: Raw density of a porous solid. C: Pouring density of a bulk of unporous solids. D: Pouring density of a bulk of porous solids.*

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Determination of sediment density

The determination of sediment density is trivial as long as the material in question is an unporous solid with a common geometric form (cube, cylinder, sphere, etc.), which allows the volume determination by simple measuring of its dimensions. However, the sediment volume of irregularly shaped and porous solids cannot be determined by simple measuring of dimensions. Here, the space requirement of the solid can be measured by the displacement of an enveloping fluid in its presence. Volume determination by means of displacement is commonly referred to as ***pycnometry*** (Greek: πυκνός, densely packed).

If a liquid is employed, the volume determination proceeds as follows: A cylinder is filled up to a defined height with a liquid. Afterwards, the sample is administered to the cylinder, causing the level of liquid to rise. By measuring the difference in filling level, the volume of the sample can be easily calculated. If the sample mass is divided by the displaced volume, the sediment density is obtained immediately. One must realize that two highly important prerequisites have to be met in order to obtain a reliable way for density measurements. On the one hand, the sample must be insoluble in the liquid used in the analysis. On the other hand, the liquid must completely envelope the entire surface area of the sample and be able to enter any available pore volume as well.
A slightly different setup can be used by using different gases such as He or N_2 instead of using liquids. This type of analytical setup provides a number of advantages, which are outlined briefly as follows:

- Fast and easy conduct of experiments
- Precise measurement
- Small space requirements for the setup
- Low operating costs
- Sample remains unchanged by analysis
- Fully enveloping (He can penetrate any pore volume)
- Full conformity according to norms (DIN 66137-2)

In preparation to the analysis, the sample can be flushed and/or dried in an inert gas stream or under vacuum. Additionally, the experiment and sample preparation can be fully automated. This allows for the generation of mean values by successive density measurements on the same sample without any operative effort or intervention. Furthermore, there are fully automated gas pycnometers which allow for the simultaneous measurement of multiple samples.
Fig. 2 elaborates on the function of a gas pycnometer by depicting the schematic composition of an instrument.

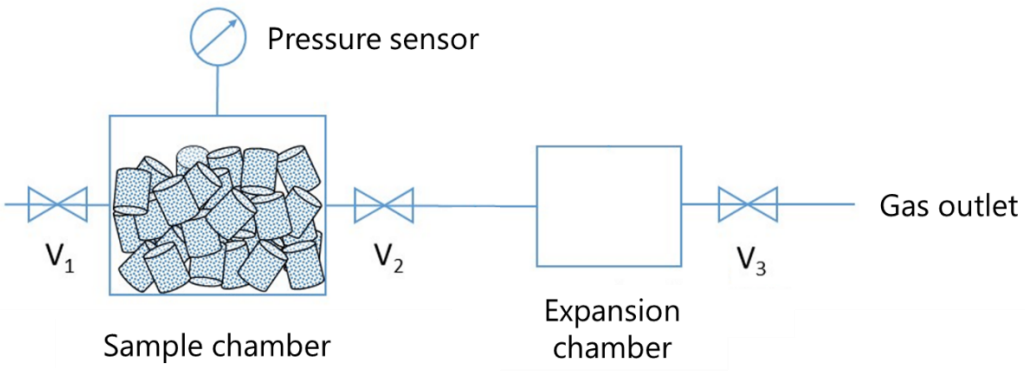

Figure 2 *Schematic construction of a gas pycnometer*

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The sample is in a calibrated sample chamber with a known volume. After opening valve V1, the sample chamber is flooded with an inert gas up to a slight overpressure with regards to ambient conditions. Afterwards, valve V1 is closed. Opening valve V2 allows the inert gas to expand into a reference chamber. As the volume of the reference chamber is known as well, the sediment volume can be determined by calculating the pressure difference before and after the gas expansion by means of the ideal gas law.
The measurement is at its most precise point when the sample chamber is fully loaded with sample. If only small quantities of sample are available, it is advised to use smaller sample carriers and reduce the sample chamber volume by masking. It is also possible to optimize experimental conditions by adding filler materials with a known volume (such as steel spheres).
The density calculation by means of the ideal gas equation requires a constant and stable temperature in all components of the pycnometers. Therefore, the instrument needs to be constructed from materials with a high thermal conductivity and it needs to be placed in an environment with stable conditions.

Sample preparation

A predefined sample preparation is essential for the scientifically reliable determination of sediment density – especially so for porous solids. Physisorbed contamination such as residual humidity or solvents will falsify sample mass, while volatile contaminations might enter the gas stream of the instrument and yield false pressure results during volume determination. In order to dry samples and remove contaminations, sample preparation prior to density measurements needs to be thorough and should be carried out in a (vacuum-)drying cabinet before the sample is transferred into the sample chamber. Modern gas pycnometers allow for a sample preparation inside the sample chamber as well. Here the sample can be dried in the inert gas stream or under vacuum after a pump is installed on the instrument. A sufficiently prepared sample exhibits constant values during a multi-run density determination.

Examples for applications

Gas pycnometers can be found in different branches and fields, e.g., quality control in goods receipt and shipping or in production control of running processes. If a sample is highly inhomogeneous, sediment density results in a mean density over all components. This is especially prevalent in geological samples. As such, the density is a good indicator for the composition of the sample and is also capable to determine the composition of alloys. The most prominent example documented is a pycnometry carried out 2,000 years ago. It was conducted by Archimedes in the service of king Hieron II. of Syracuse. Archimedes was charged to find out if the kings crown was made out of pure gold and he found out that the raw material gold had been stretched by adding cheaper silver by applying a rudimentary liquid pycnometry.
Even the degree of dispersion of a sample has an influence on the sediment density. A nano-dispersed material usually exhibits a lower sediment density than a bulk solid of the same material, which is due to higher interatomic distances on the surface of a material than on the inside of a bulk. The finer a given material is, the higher the expected discrepancy in density.
What happens if a sample contains closed pores (vacuoles)? These are hollow areas inside a solid bulk cut off from any exchange with the outside and thus inaccessible for liquids or gases. Their presence leads to a lower sediment density than the actual constituting material. By measuring density on a broken or milled sample, the amount of closed pores throughout a material can be determined as well. This can usually be correlated by particle size analysis of differently granulated samples in order to obtain information about the spatial distribution of closed pores throughout the material.
Furthermore, gas pycnometry can evaluate the open- and closed-pore content of foams. This allows for a simple yet effective characterization of different insulating-, filling- and packaging materials.

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Figure 3 *Fully automated gas pycnometers of the 3P densi instrument series for determination of sediment density as well as open and closed pore contents of foams*

Determination of raw density

The determination of raw density requires the analysis of the apparent volume of a sample. In a porous material, this apparent volume is composed of both the skeletal volume and the pore volume. Part B in Fig. 1 depicts the schematic representation of a porous solid. Its outer shell, which distinguishes it from the surroundings has the form of a cylinder. This allows the calculation of the apparent volume by simple calculation of the geometric body. The more porous a sold is, the lower the raw density becomes, while in an unporous solid the raw density is maximized and equal to its sediment density. The quotient of raw density and sediment density is a therefore a measure for the porosity ε:

$$\varepsilon = \frac{\rho_R}{\rho_F} = \frac{V_P}{(V_P + V_F)}$$

Different means exist for determining the apparent volume of an irregularly shaped solid by means of displacement.
One possibility is to close the pores of the solid or completely fill them prior to a pycnometry measurement with a sealing agent such as a wax or coating. However, this method increases operative effort for sample preparation and is very challenging for finely ground or powdered samples.
A much more comfortable alternative relies on the displacement of a non-wetting liquid such as mercury, which due to its high contact angle refuses to enter pores on its own. Density measurements with this principle can be carried out on mercury porosimeters. The method is especially effective on finely ground or powdered solids. Only after exerting an external force such as pressure the mercury starts to intrude into the pore system of the material. By measuring the maximum intruded amount of mercury to total pore volume of the sample can be determined. The raw density and porosity of the sample can be calculated together with the sediment density.

In other cases, the apparent volume of a sample can be determined by displacement of a pourable powder or granules. The apparent volume of a bread dumpling may actually be measured with a cylinder and flour or refined sugar. The fine powder (flour) or granulate (sugar) envelopes the outer form of the dumpling, which does not soak up the enveloping material. This would happen if one would be using water or other liquids or a gas. It stands to note that a raw density determined in such a way is highly dependent on the pore width of the sample and the particle size of the displaced powder or granulate.

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Determination of bulk density

To determine the bulk density, the volume and mass of a fill need to be measured. Usually, a measuring cylinder and an analytical scale are sufficient. Depending on the constitution of the sample some other factors need to be considered.
In a coarse fill (for example pebbles, candies or kitchen garbage) it stands to note, that the arrangement of the grains of the bulk is not influenced by the geometry of the measuring cylinder, since it is imperative to retain a likeness to the real fill conditions. The diameter of the cylinder has to be adjusted towards the particle size and the samples volume in order to take a representative sample.
In a fine fill (such as sieved sand, fly ash or starch), the geometry of the measuring cylinder is of no significance and one only needs to adjust towards the amount of sample. The most prevalent influence on the analysis is exerted by sample humidity and compression. Humid powders tend to be more densely packed and have a higher pouring density than a dry sample, which makes a pre-defined sample preparation necessary. Compression describes all outside influence with an effect on the powder fill such as pressure, gravity and mechanical shock. To establish a homogenous compacting of the initially loose fill, the samples vessel needs to be tapped against a surface much like filling a coffee can. To standardize this process and eliminate subjective influences, a defined number of taps and drop height needs to be implemented.

Figure 4 *Simple, reproducible and high practical relevance: The BeDensi series of instruments is suitable for measuring both bulk and raw density. A one-, two- or three-station model is available with a variety of measuring cylinders and adjustable number of taps for analyzing a broad spectrum of samples.*

Conclusion

In this article, we have introduced a number of density terms with high practical relevance. The multitude of challenges with regards to density determination can hardly be covered in one article and this document does not aim for completeness. We have mainly focused on a number of instructive examples from common experiences, which is supposed to cast a spotlight on the diversity in the field of determining density.
Even after 30 years, we are still surprised by the challenges faced by customers using our instruments, which can only be addressed by close collaboration, long-term experience and flexibility in problem solving. We hope to be helpful in aiding you in your application!

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