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Calibration of gas (helium) pycnometer
Information and remarks on calibration balls selection

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A gas (helium) pycnometer operating on gas displacement principle expands gas from the previously pressurized sample chamber to one of the reference chambers that is usually kept at atmospheric pressure before the gas expansion takes place. Reversely, expansion method from the reference chamber to the sample chamber can be also employed. In order to determine the true volume (density) of the solid state sample, the volume of the reference chamber must be known. To obtain the best results for small and large size samples, usually more then one reference chambers are used and the dead-volume of sample chamber is appropriately reduced. Typically, metal balls of well-know volumes are used for calibration of the reference chamber(s). Although some manufacturers supply only few balls for calibration purposes, it is very useful to have quite a few of them to verify the pycnometer performance at selected conditions and for periodical checking. The theoretical presentation of the theory and calibration procedure is commonly available, e.g. from user manuals but the more technological information about the balls themselves and their availability is not. The purpose of the note is to provide users with such additional information.

Since precision solid balls from some metals can be manufactured with high accuracy and inexpensively, they are predominantly used for the pycnometers calibration. Generally, precision balls are made to a specific grade, which determines its geometrical tolerances. The grade numbers range from to 3 to 3000, and the lower the number, the more perfect shape of the ball is and it is closer to its nominal diameter. Practically, smaller size balls can be made closer to the geometrical shape, while larger size balls may not be easily available in low grades. Since for calibration of typical pycnometers balls of diameter of 2" (50.8 mm) and smaller balls are used, and they are easily available in grade 50 and lower, higher grades should rather not be considered.

Material selection and easy availability of specific sizes with low grade at reasonable cost are some of the practical considerations. Generally, stainless-steel balls offer good corrosion resistance but are rather made to higher grade then balls from some other materials often used for ball bearings. The Bearing-Quality Aircraft-Grade E52100 Alloy Steel, often-called chrome steel, is commonly used for producing precision balls due to the material hardness and wear resistance, and it has a reflective finish. Balls below 1.5 " (38.1 mm) are easily available in grade 25 or 24, while up to 3 " in grade 50 from common hardware catalogs at low cost. These balls are commonly used for pycnometers calibration for many practical reasons but they can rust easily if exposed to corrosive agents or water. Another similar material but harder and used in higher temperatures applications, is Bearing-Quality High-Temperature M50 Steel. Grade 10 balls from 1" (25.4mm) down to 1/8" (3.175mm) are easily available but at higher prices. There is no shortage of more exotic materials, like Fracture-Resistant Silicone-Nitride Ceramic, non-porous, where the balls of 9/16" (14.2875mm) and below are easily available in grade 5. Such a grade is highly suitable to use in micropycnometers and especially in the µThermoPyc™ as the material has very high temperature rating.

There are several tolerances associated with the grade definition. For simplicity, the sphericity and the basic diameter tolerance are mentioned. Sphericity, or deviation from the spherical form, or diameter tolerance per ball sphericity, refers to the deviation from ideal (geometrical) form and it is the permissible difference between the largest and the smallest diameter measurable on the same ball. The basic diameter tolerance or nominal ball diameter tolerance is the maximum allowable ± difference between any ball mean diameter and the nominal (basic) diameter which was ordered. For illustration, the table below presents only few fractional and metric grades and the two tolerances but usually others, like maximum surface roughness and lot diameter variations (same as the sphericity tolerances) are usually presented.

	Fractional (Inch) sizes		Metric sizes	
Grade	Sphericity [in]	Basic Diameter Tolerance [in]	Sphericity [mm]	Basic Diameter Tolerance [mm]
5	0.000005	±0.00005	0.00013	±0.0013
10	0.000010	±0.00005	0.00025	±0.0013
25	0.000025	±0.0001	0.0006	±0.0025
50	0.000050	±0.0002	0.0012	±0.0051

Calculating errors of volumes from the sphericity deviations, especially for the lower grade numbers, the values are quite small. Since the basic diameter tolerance is larger, it yields larger volume errors when calculating balls volumes. The practical question is how well the ball diameter (volume) has to be determined to be suitable for calibrating a gas (helium) pycnometer. To provide an answer, first it has to determined of how accurate a gas pycnometer actually is.

It is often the case of creative marketing to state accuracy from the standard deviation of several repetitions or until the declared error is fulfilled in three consecutive repetitions. Such results look great on paper but it is rather error of repeatability, not the actual error of the volume measurements. Measuring the ball of well-known volume as a sample can provide a better measure of the discrepancy between the measured result and the known ball volume. If the accuracy is stated, let say 0.03%, it usually refers to the largest sample chamber volume (not the sample volume) for a given reference chamber used. Let say, if the sample chamber has total volume of 150 cc, then the ±0.03% error yields ±0.045 cc (±45 µL) volume error. For smaller reference chamber, and let say sample volume of 20 cc, the ±0.03% error yields ±0.006 cc (±6 µL) volume error. Such accuracy is obtained rather in optimal conditions for the pycnometer.

There are highly sophisticated systems to measure a ball size and shape with high accuracy, from optical comparators to absolute interferometers, but it is also too expensive to carry out such measurements for a single ball. Having the idea of a pycnometer actual accuracy, it is also not that necessary. Easily available precision micrometers measure length with permissible error of ±0.00005" (±0.00127mm). The table below lists some available ball sizes in inches and mm, their calculated volumes, and error volumes based on the accuracy of the micrometer measurements.

Nominal Ball Diameter	Nominal Ball Diameter **[mm]**	Calculated Volume **[cm^3]**	Max. volume error based on accuracy of measurements (±0.00127 mm) **[cm^3]**
2"	**50.800**	**68.641**	**±0.00515**
1 5/8"	**41.275**	**36.818**	**±0.00340**
1 1/4"	**31.750**	**16.758**	**±0.00201**
1"	**25.400**	**8.5802**	**±0.00129**
11/16"	**17.4625**	**2.7882**	**±0.00061**
1/2"	**12.700**	**1.0725**	**±0.00032**
11/32"	**8.731**	**0.34852**	**±0.00017**

6 mm	**6.000**	**0.1131**	**±0.00007**
4 mm	**4.000**	**0.03351**	**±0.00003**
3 mm	**3.000**	**0.01413**	**±0.00002**
2 mm	**2.000**	**0.004188**	**±0.000008**
1.5 mm	**1.500**	**0.001767**	**±0.000004**
1 mm	**1.000**	**0.0005236**	**±0.000002**

The table clearly demonstrates that the error of volume calculations based on the diameter measurements using precision micrometers is many times below the overall error of volume determinations of a gas pycnometer. From the previous table it is easy to conclude that balls of grade 10 and below are more then suitable for any pycnometer calibration and they do need require any further re-certification, unless it is needed for bureaucratic purposes.

If a ball is maintained at appropriate environmental conditions, there is no rust, dents or pits developed on the surface over time, then it should not require any "yearly" calibration as there is no rational justification for it. Recalibration of a selected reference chamber from time to time, especially when change of experimental conditions takes place (different temperature, gas type, pressurization pressure, etc.), will yield greater error each time then the ball volume uncertainty. Moreover, if a vendor offers a ball for several hundreds dollars with a certificate about the ball size and shape measured by a recognized institution, it is more likely that a large quantity of balls was purchased from a lot and a representative ball was measured, and the same certificate is used for each of the balls. There is not an easy way of finding out which ball has actually been calibrated and which has not been, as any permanent marking/engraving can damage the ball.

Calibration of a pycnometer refers to the calibration of the selected reference chamber. The procedure of carrying out several repetitions of measurements without the calibration ball and several repetitions with the calibration ball yields the reference chamber volume. It is always a good idea to reuse later the same ball as a sample to find out what volume error is actually obtained. The discrepancy between the calculated ball volume used for calibration and the measured volume of the same ball after the calibration should be used as a measure the actual error for a similar volumes of measured objects then the standard deviation of repeatability. Good repeatability can be obtained when the gas pressure is set just above the used pressurization pressure and very close values of pressurization pressure can be achieved in several repetitions. However, that does not guarantee good results as a leakage between the sample chamber and the reference chamber or a problem with transducer linearity signal can generate substantial error, despite of fine repeatability. A newly obtained calibration results should be consulted with previous outcomes of recorded periodic calibrations to see if the new one is acceptable.

Usually the sample is placed in a sample container and the different hardware used and the different size of sample can influence the error value. Once the sample volume is obtained, a precision ball of comparable volume, and perhaps some smaller and larger ones can be measured as samples to generate the calibration curve to determine what the actual accuracy of the sample volume determination is. For that purpose, the HumiPyc gas pycnometers are provided with the most comprehensive calibration kit that comprises of several different ball sizes, from large to small, and a micro-kit to determine the detection limit at a given set of experimental conditions.