Determination of actual performance of a gas pycnometer versus quoted specifications

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Very often, measurements of a sample volume using a gas pycnometer yield different results from one run to another and the differences are far greater than the claimed specifications. Therefore, a closer look at the possible sources of errors is presented and an unbiased method of proving a pycnometer performance is suggested.

Background

In principle, a pycnometer consists of two chambers that are connected by a common valve. There are at least two additional valves, one for providing gas and another valve for releasing the gas to the ambient atmosphere. The chamber that is used for introduction of the user-defined object is called the cell volume (**Vc**) for the purpose of the discussion. The other chamber is called the reference volume (**Vr**). After placing an object of volume **Vobj** into the Vc, the cell is subsequently pressurized to pressure **Pp**. Assuming that the ambient pressure **Pa** is established in the Vr chamber, the connecting valve is open and after the depressurization the final pressure is **Pd**. Since the total amount of gas in both chambers before and after opening the connecting valve must remain the same, and assuming ideal behavior of the used gas, the mass balance is given by the equation:

$$\frac{Pp*(Vc - Vobj)}{RT} + \frac{Pa*Vr}{RT} = \frac{Pd*(Vc - Vobj + Vr)}{RT} \qquad (1)$$

Assuming further constancy of temperature during the experiment, the sought Vobj volume can be calculated as follows:

$$Vobj = Vc - \frac{Vr(Pd - Pa)}{Pp - Pd} \qquad (2)$$

This is a working equation employed by gas pycnometers. However, to obtain the Vobj, the Vc and Vr must be determined first. Since there are two unknowns, two independent experiments are needed. Typically, one experiment is conducted with empty Vc. Since the Vobj=0 in this case, the above equation allows calculation relationship of Vc vs Vr:

$$Vc = Vr\frac{P_1d - P_1a}{P_1p - P_1d} \qquad (3)$$

In the second experiment, an object of known volume, typically a calibrated sphere (ball) of volume **Vsphere**, is used. The equation (1) for the second experiment becomes:

$$Vsphere = Vc - Vr\frac{P_2d - P_2a}{P_2p - P_2d} \qquad (4)$$

Combining equations (3) and (4) allows calculation of Vr:

$$Vr = \frac{Vsphere}{\frac{P_1d - P_1a}{P_1p - P_1d} - \frac{P_2d - P_2a}{P_2p - P_2d}} \qquad (5)$$

Simple analysis

The denominator of the equation (5) is a difference of two fractions where in each of them there are also pressure differences. Since the pressure values in those fractions are relatively large numbers comparing to the result of their differences, the potential of loss of significant figures can affect the accuracy of the final determination of the volume Vr. To have better understanding of the calculation process of Vr, the theoretical calculations in **Table 1** illustrate the step-by-step process.

It is clear that depending on selection of experimental conditions, the accuracy of the final results vary. In general, there is loss of at least one significant digit. The optimal experimental conditions are when the volumes of Vsphere and Vr are comparable and pressurization pressure is substantially distant from ambient pressure (Case 1). Filling unused volume of Vc when using smaller calibration volume seems to hold number of significant figures relatively well (Case 3). However, one needs to notice that the denominator value (last column) is small and propagation of any error will be more pronounced. Using pressures just above ambient yields loss of up 3 significant figures in most cases. **One conclusion from the simple analysis is that a single specification number (standard deviation), that is obtained in the most favorable conditions will not be representative of a pycnometer performance.**

Another conclusion is that in order to assure large range of accurate volume determination, high quality transducers, and utilizing high-resolution A/D converters (24-bit) with very low noise are necessary to achieve at least 6 significant digits in reading the pressure values. Additionally, since all pressure transducers exhibit non-zero thermal drifts, thermal stabilization and temperature uniformity are required to achieve repeatable results.

Handling of errors

Normally, instead of carrying out of single measurements, two multiple runs, one with empty Vc and one with the sphere inside Vc are conducted. From the first set of data the average ratio of Vc/Vr (eq.3) and its standard deviation $\boldsymbol{\sigma_1}$ can be calculated. Likewise, the second experiment yields average value of (Vc-Vsphere)/Vr (eq.4) and its standard deviation $\boldsymbol{\sigma_2}$. Therefore, the standard deviation of the denominator of the equation 4 can be calculated:

$$\sigma_D = \sqrt{\sigma_1^2 + \sigma_2^2} \qquad (6)$$

Usually the volume of the calibrated sphere is known quite precisely and typically the error in Vsphere determination is rather a second degree correction compared with the actual errors in Vr and Vc volume determination. However, should that error, $\boldsymbol{\sigma_{sphere}}$, be stated, the absolute standard deviation of Vr, $\boldsymbol{\sigma_{Vr}}$, can be calculated as follows:

$$\sigma_{Vr} = Vr\sqrt{(\frac{\sigma_{sphere}}{V_{sphere}})^2 + (\frac{\sigma_D}{D})^2} \qquad (7)$$

where D is the denominator value of eq. 5.

Since the reference volume Vr is used in subsequent experiments for volume and density determination of samples (eq.2), this error necessarily propagates and affects accuracy of the results. **However, the value of σ_{Vr} does not seem to be taken into account in stating results of subsequent determinations of sample volume and density.**

To measure volume occupied by a sample, typically the Vc with empty sample holder is determined first although sometimes the sample holders are "pre-calibrated". In either case, the value of Vc determination is often conveniently omitted. Practically, the standard deviation is calculated only from the multiple runs when the sample is placed in the sample holder. Even so, a very problematic approach is often employed to make the standard deviation to be as small as possible. Namely, while declaring multiple runs, the experiment stops when the requested standard deviation error is met in three consecutive cycles. It surely can yield what user asks for, but there is no guarantee that the measurements are converging to a constant value and that the average of such three runs (and its error) is representative of the average volume of the complete experiment. But the only justification of such approach is that depending on luck, much lesser error is achieved that it otherwise would be if all the runs were completed.

A better way of "proving" pycnometer performance

Since pycnometers are often operated from a keypad and the user gets only the results, it is difficult to independently carry out the error calculations. In addition, the user manuals do not provide very detailed presentation of the errors calculation process. The obtained standard deviation is rather a measure of reproducibility (repeatability, precision) at the selected experiment conditions, but does not necessarily determines the accuracy of determination of the sample volume.

To find out how close the measured volume data are to the exact value, a simple test can be conducted. **Using a calibrated sphere (of volume close to the measured sample volume), the experiment can be repeated in the same way as it was carried out with the sample. The difference between the actual sphere volume and the obtained volume will indicate if the instrument is only repeatable or it is repeatable and accurate.**

The user should be aware that the sample volume determinations could be influenced by instrumental factors as well as by the properties of sample itself. Some instrumental factors are:

1. Size of Vc, Vr, and volume of sample
2. Pressure level to which the Vc is pressurized to,
3. Temperature (distribution) at which measurements are taken
4. Particular design

Experimental determinations of Vc volume vs. pressurization pressures (from just above ambient to maximum available range) show that the Vc values are not the same throughout the pressure range. Therefore, recalibration of Vr is often recommended when substantially changing the pressurization pressure set point. If there is no temperature control, the heat from activating valves and other components may cause local temperature fluctuations and consequently, the repeatability will be harder to achieve.

To avoid multi-parameter analysis, some factors like maintaining the same pressurization pressure and conducting experiments at the same temperature (if the instrument has such capability) can be kept constant. The reference volume can be calibrated using a suitable calibrated sphere. To determine accuracy of a given pycnometer over the range of intended volume measurements at the selected conditions, a straightforward methodology can be employed.

Once the Vr volume is determined, a series of experiments using calibrated spheres of different volumes as "test samples" can be carried out. Comparing differences between the actual sphere volumes and measured volumes would serve two purposes. First, to find out the accuracy of the volume determination. Second, to find out the optimal range of samples volume that can be measured with satisfactory accuracy. Moreover, one could get real understanding of the instrument performance versus the quoted specifications.

Some specifications claim typical accuracy better than 0.01%. From the size of the volume of the test samples, it can be concluded that a gas pycnometer can resolve volumes of the order of micro liters (µL) or less. That brings the subject of determining the detection limits of a given pycnometer, which is also easy to verify using a series of small diameter balls. To reduce the number of the balls, they can be selected in such a way that the volume ratio of two nearest sizes is at least a factor of two. For example, balls of diameter 1, 1.5, 2, 3, and 4 mm, yield volumes of approximately 0.524, 1.77, 4.19, 14.1, and 33.5 µL, respectively.

Adding the tiny balls to either empty sample cell or to the cell containing a large ball of know volume, the volumes of the tiny balls can be determined. **Comparing the ball volumes obtained using the pycnometer with their actual measured volumes; it will yield the smallest volume difference that the pycnometer (at selected experimental conditions) is able to measure reliably.**

Providing the value of the detection limit and the standard deviation data for volume determination at clearly specified conditions would reflect better performance specifications and it would be easily verifiable by the user.

Experiment 1 data (empty Vc)			Experiment 2 data (sphere inside Vc)			Experiment 1 calculations			Experiment 2 calculations			Eq.(5) denominator
P_1p [kPa]	P_1d [kPa]	P_1a [kPa]	P_2p [kPa]	P_2d [kPa]	P_2a [kPa]	P_1d-P_1a [kPa]	P_1p-P_1d [kPa]	$(P_1d-P_1a)/(P_1p-P_1d)$	P_2d-P_2a [kPa]	P_2p-P_2d [kPa]	$(P_2d-P_2a)/(P_2p-P_2d$	$(P_1d-P_1a)/(P_1p-P_1d)-(P_2d-P_2a)/(P_2p-P_2d$
Case1: Vc = 100.00 cc, Vsphere = 66.000cc												
106.325	104.337	101.325	106.325	102.958	101.325	3.012	1.988	1.515	1.633	3.367	0.4848	1.030
151.325	131.446	101.325	151.325	117.652	101.325	30.120	19.880	1.5151	16.327	33.673	0.48485	1.0303
301.325	221.807	101.325	301.325	173.815	101.325	120.482	79.518	1.5151	72.490	149.510	0.48485	1.0303
Case 2: Vc = 100.00, Vsphere = 16.700cc												
106.325	104.337	101.325	106.325	104.160	101.325	3.012	1.988	1.515	2.835	2.165	1.309	0.206
151.325	131.446	101.325	151.325	129.672	101.325	30.120	19.880	1.5151	28.346	21.654	1.3090	0.2061
301.325	221.807	101.325	301.325	227.183	101.325	120.482	79.518	1.5151	125.858	96.142	1.3090	0.2061
Case 3: Vc = 30.00, Vsphere = 16.700cc												
106.325	102.888	101.325	106.325	102.320	101.325	1.563	3.438	0.4545	0.995	4.005	0.248	0.206
151.325	116.950	101.325	151.325	111.277	101.325	15.625	34.375	0.45450	9.9515	40.049	0.24848	0.20606
301.325	163.825	101.325	301.325	145.510	101.325	62.500	137.500	0.45450	44.184	177.816	0.24848	0.20606

Table 1. Loss of significant figures during calibration of Vr volume at different setup conditions. Initial pressurization of Vc is assumed to be 5, 50, and 200 kPa above standard ambient pressure. Reference volume Vr is 66.00cc in all cases. Six significant digits of pressure readings is assumed.
Experiment 1: Runs with empty cell (Vc). Experiment 2: Runs with sphere placed inside the Vc.