OPTIMUM DESIGN OF GAS PYCNOMETERS FOR DETERMINING THE VOLUME OF SOLID PARTICLES

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Abstract: Gas pycnometry is based on Boyle-Mariotte's law. There are three kinds of gas pycnometers reported in literature: "constant-volume", "variable-volume" and "comparative". These instruments are widely used to determine the volume -and thus the density- of granular, porous or soluble compounds (e.g., rocks, soil particles, pigments, ceramic, drugs, seeds). However, many users do not know the optimum use conditions of their gas pycnometer. This work provides a synthesis of recent studies about the optimum design of the gas pycnometers. It seems possible to use commercially available components for constructing gas pycnometers that can determine the volume of solid particles with a relative standard uncertainty smaller than 0.25%. Compared against other gas pycnometers, the constant-volume pycnometer presents several practical advantages.

1. INTRODUCTION

Gas pycnometry [1,2] is based on Boyle-Mariotte's law of volume-pressure relationship. This is an attractive method to determine the volume of solid particles because it does not have some of the problems inherent to other testing methods. For one thing, the volume of substances that react chemically or physicochemically with water can be determined. Further, the problem of air entrapment, which is common in liquid pycnometry (e.g., [3]), does not exist. It has also been claimed that routine sample-volume determinations with gas pycnometers can be performed in less than twenty minutes and automatically.

There are three kinds of gas pycnometers reported in literature: "constant-volume" (e.g., [4]), "variable-volume" (e.g., [5]) and "comparative" (e.g., [6]).

Gas pycnometry has been widely used to determine the volume -and thus the density- of granular, porous and/or soluble compounds such as rock fragments, soil particles, coal, pigments, ceramic, salts, drugs, aerogels, plastic films, teeth, chocolate, seeds, insects and even living birds. Surprisingly, the literature suggests that many users do not know the optimum use conditions of their gas pycnometer [7]. A synthesis of recent studies [7-9] about the optimum design of the gas pycnometers follows.

2. BASICS

2.1. Fundamental hypotheses

Four fundamental hypotheses are made: (1) the gas inside the pycnometer behaves ideally, i.e., its compressibility is negligible and it does not adsorb on solids; (2) the sample and the pycnometer's components are rigid; (3) the pycnometer is gas tight and the expanding gas quickly reaches a static equilibrium, and (4) the gas temperature is uniform and constant, at least when the pressure or the volume measurements are performed.

2.2. Constant-volume pycnometer

A constant-volume gas pycnometer (figure 1) is composed of a sample chamber with a screw cap, a tank and an absolute pressure transducer. The chamber and the tank can be connected pneumatically through a tube with a coupling valve ("Z"). The tank is also connected to the pressure transducer and can be connected to a gas supply through a tube with a main coupling valve ("M").

To determine the volume of a sample, (1) the sample is placed in the chamber, valves are opened and the pycnometer is filled with gas; (2) valve "M" is closed and the absolute pressure transducer is used to measure the initial gas pressure in the pycnometer (P_i); (3) valve "Z" is closed to isolate the sample chamber, valve "M" is opened and some gas is introduced into the tank (or removed from it), valve "M" is closed again and the gas pressure in the tank is measured (P_j), and (4) valve "Z" is opened so that the gas can expand from the tank to the sample chamber (or vice versa) and the final gas pressure is measured (P_f) when the gas expansion is finished.

The equation of the constant-volume pycnometer is deduced by assuming that the decrease of internal volume of valve "Z" is small, i.e.

$$V_s = V_c^\circ + V_t^\circ \tau \qquad (1a)$$

$$\tau = \frac{P_f - P_j}{P_f - P_i} \qquad (1b)$$

Equation (1) shows that the sample-volume estimation (V_s) depends linearly on an experimental coefficient (τ). The origin (V_cº) and slope (V_tº) of this relation are estimates of the sample-chamber and tank volumes, respectively. These coefficients are usually determined by a calibration procedure

The calibration of a gas pycometer is theoretically very simple: it requires at least two tests performed: one with the empty sample-chamber and the other one with a known-volume object put into the sample chamber. Aluminum cylinders or pieces of quartz can be used as known-volume objects [4-6].

2.3. Variable-volume pycnometer

Basically, a variable-volume gas pycnometer is composed of a sample chamber, a piston chamber and a pressure sensor. In the past, mercury was used as the volume and pressure regulating medium [1]. However, the use of mercury has become superfluous [5]. We therefore consider a variable-volume gas pycnometer (figure 2) that is composed of a sample chamber with a screw cap, a two-position piston chamber and an absolute pressure transducer. These three components are pneumatically interconnected. The pycnometer can be also connected to a gas supply through a tube with a coupling valve.

To determine the volume of a sample, (1) the sample is placed in the chamber, the piston is placed at an initial position ("close" or "open"), the valve is opened and the pycnometer is filled with gas; (2) the valve is closed and the absolute pressure transducer is used to measure the initial gas pressure in the pycnometer (P_i), and (3) the piston is moved to another position ("open" or "close") and the final gas pressure is measured (P_f) when the gas expansion (or compression) is finished.

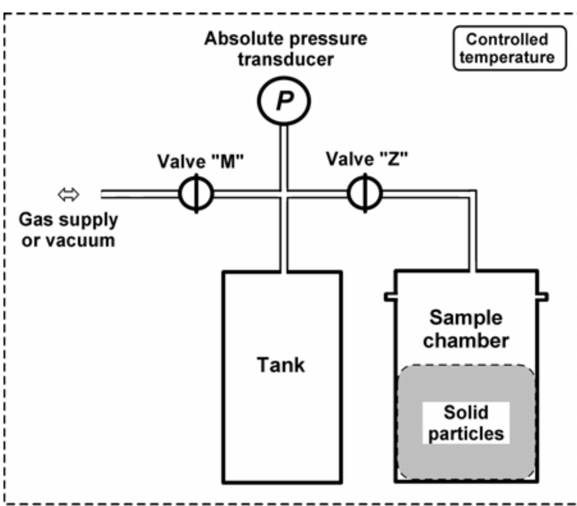

Fig. 1 *Diagram of a constant-volume pycnometer.*

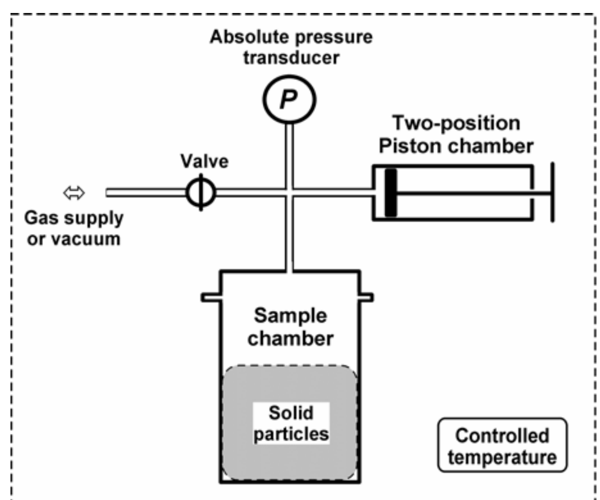

Fig. 2 *Diagram of a variable-volume pycnometer.*

The equation of the variable-volume pycnometer is

$$V_s = V_c^\circ + V_p^\circ \ \tau \qquad (2a)$$

$$\tau = -\left(\frac{P_{min}}{P_{max} - P_{min}}\right) \qquad (2b)$$

where P_{max} = max(P_i,P_f) and P_{min} = min(P_i,P_f). Equation (2) shows that the sample-volume estimation (V_s) depends linearly on an experimental coefficient (τ). The origin (V_cº) and slope (V_pº) of this relation are estimates of the sample-chamber and piston-chamber volumes, respectively. As for the constant-volume pycnometer, these coefficients are usually determined by a calibration procedure.

2.4. Comparative pycnometer

Basically, a comparative gas pycnometer is composed of a sample chamber with a screw cap, a tank, a two-position piston chamber, a volume controller (i.e. a piston chamber whose internal volume is known for any piston position), a differential pressure transducer and a valve. In this study, we consider that the sample chamber is pneumatically connected to the volume controller, and that the tank is connected to the piston chamber. The pressure transducer measures the difference between gas pressures in the sample chamber and in the tank (figure 3). Both the sample chamber and the tank can be connected at the same time to a gas supply through a tube with a coupling valve.

To determine the volume of a sample, we consider the following procedure: (1) the sample is placed in the chamber, the piston chamber and the volume controller are left so that their internal volume is minimum (or maximum), the valve is opened and the pycnometer is filled with gas; (2) the valve is closed so that there is no difference between gas pressures in the sample chamber and in the tank; (3) the piston is pulled (or pushed) to a maximum; (4) the volume controller is then adjusted so that again there is no difference between gas pressures in the sample chamber and in the tank, and (5) the internal volume of the volume controller (V_r) is measured.

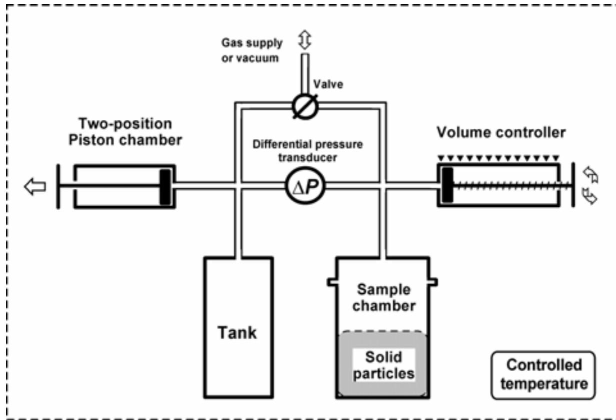

Fig. 3 *Diagram of a comparative pycnometer.*

The equation of the comparative pycnometer is

$$V_s = V_c^\circ - \left(\frac{V_t^\circ}{V_p^\circ}\right) V_r \qquad (3)$$

Equation (3) shows that the sample-volume estimation (V_s) depends linearly on the final volume of the volume controller (V_r). The origin (V_cº) and slope (V_tº/V_pº) of this relation are related with estimates of the sample-chamber, tank and piston-chamber volumes. As for the other gas pycnometers, these coefficients are usually determined by a calibration procedure.

3. OPTIMUM DESIGN

3.1. Optimization method

The "law of propagation of uncertainty" [10] was used to estimate the uncertainty of sample-volume estimation (V_s) by the different kinds of gas pycnometers. This law states that $u^2(V_s) \approx \sum_i (\partial V_s / \partial X_i)^2 \, u^2(X_i)$, where $u(V_s)$ is the combined standard uncertainty of V_s and $u(X_i)$ is the standard uncertainty of the terms contributing to the uncertainty of V_s. Due to reasons discussed in a previous study [7], we discarded the following sources of error on V_s: non-ideal gas behaviour, deformation of pycnometer's components, pycnometer's calibration and gas leakage.

The terms contributing significantly to the uncertainty of sample-volume estimation (V_s) were thought to be: (1) gas pressure measurements, (2) chamber(s) handling and (3) non isothermy during a pycnometric test.

For the purpose of the error analysis, some dimensionless coefficients were introduced [7-9]. The most important one was referred to as the *filling factor*, i.e. $\varphi = V_s / V_c$, where V_c is the sample-chamber volume. The range $0.4 < \varphi < 0.7$ was thought to be realistic for a sample chamber filled with as many solid particles as practical [7].

This way, equations (1), (2) and (3) were used to derive general formulas that predict the relative standard uncertainty of V_s by the different kinds of gas pycnometers [7-9]. Figure 4 shows that these theoretical formulas can reasonably describe some experimental trends reported in literature. The formulas were analyzed and the conditions for which they predict the smallest uncertainty were investigated. This was the basis for proposing an optimum design of each kind of gas pycnometer.

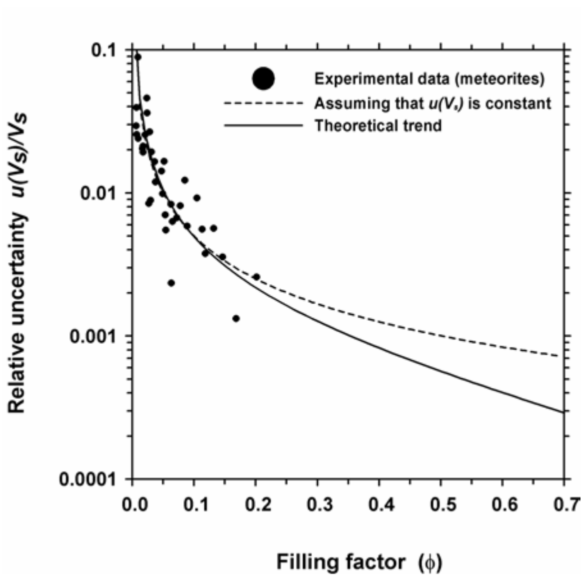

Fig. 4 *The ability of a real gas pycnometer to determine the volume of meteorites. The pycnometer accuracy is greater when the part of the sample chamber occupied by a meteorite (φ) is larger. The dotted curve is based on the empirical hypothesis that u(V_s) is constant [4]. The solid curve is based on a theoretical formula for predicting the pycnometer's accuracy [7].*

3.2. Results and discussion

The proposed optimum design of the different kinds of gas pycnometer is summarized in table 1. It seems possible to use commercially available components for constructing any kind of gas pycnometer that can determine the volume of solid particles ($0.4 < \varphi < 0.7$) with a relative standard uncertainty smaller than ±0.25%.

The constant-volume pycnometer has a widespread use [7]. Below, the variable-volume and comparative pycnometers are compared to this gas pycnometer:

- *Variable-volume pycnometer vs. constant-volume pycnometer* [8]: (1) literature suggests that the variable-volume gas pycnometer is easy to construct and handle; (2) as for the constant-volume gas pycnometer, the uncertainty $u(V_s)$ decreases for the variable-volume pycnometer, as the filling factor φ increases; (3) only two pressure measurements are required to perform a test (instead of three with the constant-volume pycnometer); (4) however, the variable-volume pycnometer requires an accurately calibrated pressure transducer (instead, the only requirement for the constant-volume pycnometer is that the transducer's response varies linearly with pressure); (5) it also requires a piston chamber with a good reproducibility, and (6) a pressure transducer and tubes with an internal volume as small as possible.

- *Comparative pycnometer vs. constant-volume pycnometer* [9]: (1) the comparative gas pycnometer is attractive because it only requires a differential pressure transducer, that does not need to be calibrated; (2) the uncertainty $u(V_s)$ is practically independent of the filling factor φ; (3) another advantage is that there is no need for the temperature of the comparative gas pycnometer to be the same at the beginning and at the end of a test; (4) however, the comparative pycnometer is less easy to construct (all the literature about this kind of instrument refers to the commercial "model 930" of Beckman), and (5) literature suggests that the handling of the comparative pycnometer is tedious in practice.

Table 1. *Optimum design of the different kinds of gas pycnometer for determining the volume of solid particles with a relative standard uncertainty smaller than 0.25%* [a]

	Constant-volume pycnometer	Variable-volume pycnometer	Comparative pycnometer
Choice of the pressure transducer	- Use an absolute transducer with a good *linearity* (better than ±0.04% FS)	- Use an absolute transducer with a good expanded relative uncertainty (better than ±0.06% FS) and an internal volume as small as possible	- Use a differential transducer with a good sensitivity
Temperature control	- It is recommended to use a bath that maintains the temperature within ±0.02 °C	- It is recommended to use a bath that maintains the temperature within ±0.02 °C	
Choice of the sample chamber	- Use a screw cap that can be accurately adjusted to the chamber (within ±25 µm for a chamber's length > 100 mm)	- Use a screw cap that can be accurately adjusted to the chamber (within ±25 µm for a chamber's length > 100 mm)	- Use a screw cap that can be accurately adjusted to the chamber (within ±25 µm for a chamber's length > 100 mm)
Choice of the other components	- Use a valve "Z" with an internal volume as small as possible - To determine the volume of solid particles, select a tank whose volume is from 1/3 to 2/3 of the sample-chamber's volume	- Use a piston chamber with a good reproducibility (within ±10 mm^3 for a total volume of >20 cm^3) - To determine the volume of solid particles, select a piston chamber whose volume is from 1/3 to 3/4 of the sample-chamber's volume	- Use a piston chamber with a great reproducibility (within ±10 mm^3 for a total volume of > 200 cm^3) - Use an accurate volume controller (within ±100 mm^3 for a total volume of > 200 cm^3) - A tank whose volume is easily determined from the volume of the other components is required [9]
Pycnometer's handling	- Fill the sample chamber with as many solid particles as possible - Submit the sample chamber to a low initial gas pressure (rough vacuum), then submit the tank to a pressure that matches the highest pressure that the transducer is adjusted to measure (e.g., 0.2 MPa)	- Fill the sample chamber with as many solid particles as possible - Perform a test with the piston chamber closed at the beginning and so that the initial gas pressure matches the highest pressure that the transducer is adjusted to measure (e.g., 0.2 MPa)	- Perform a test with the piston chamber and the volume controller closed at the beginning

[a] *Based on theoretical studies [7-9]*

Fig. 5 *Testing a prototype of constant-volume pycnometer for leakage. The pycnometer (upper left corner of the picture) is connected to a data logger (upper right corner) and to a leak detector (bottom).*

4. FINAL COMMENTS

As suggested by earlier authors [1] and as confirmed by recent studies [7-9], the components and working conditions of gas pycnometers must be carefully selected. It seems possible to use commercially available components for constructing custom gas pycnometers that can determine the volume of solid particles with a relative standard uncertainty smaller than ±0.25%.

The constant-volume pycnometer has a widespread use, probably because it does not require an accurately calibrated pressure transducer (compared against the variable-volume pycnometer) and because it is quite easy to construct (compared against the comparative pycnometer). However, the sample chamber of a constant-volume pycnometer must be filled with as many solid particles as possible for obtaining accurate results (if this is not possible, it may be worth to use a comparative pycnometer, because it is theoretically more accurate at small φ-values).

Finally, it is worth noting that an adequate design is a necessary but not a sufficient condition to warrant that a real gas pycnometer will work properly. After constructing a gas pycnometer, the instrument should be checked for leakage (Figure 5), temperature uniformity and ideal gas behaviour (in practice, it is recommended to use helium).

ACKNOWLEDGMENTS

A slightly modified version of this note has been submitted to the *Journal of Testing and Evaluation*.

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