

THE PRECISION OF GRAIN VOLUME POROSIMETERS

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Abstract

The precision of grain volumes determined by a gas expansion porosimeter is examined by both a theoretical method (stochastic modelling) and an experimental method (repeat experimentation). The results show that the porosimeter is more accurate than would be expected based on published "precisions" for the pressure transducer that it uses. This is because this "precision" is actually an accuracy. Because systematic errors are calibrated out during operation of the instrument, the true precision of the device is much better than the quoted precision of the transducer. The results indicate that a reference chamber to sample chamber volume of 0.25 to 0.50 is optimal, and that grain volume to sample chamber volume should be greater than 0.5. Experimental evidence is given to show that grain volumes found using helium are consistently larger than those found using nitrogen. This is likely due to adsorption effects.

Introduction

In this paper, the accuracy and precision of a helium porosimeter, as used for grain volume determination, are examined. Although common English usage rarely distinguishes between "accuracy" and "precision", scientific usage does. Consider the situation where the value of a certain property ψ is known to be ψ_o ; this value is referred to as the "true" value of ψ . Whenever attempts are made to measure this value, experimental uncertainty (*i.e.* errors of observation, off-calibration instrumentation) ensures that the experimentally obtained value of ψ will not be ψ_o . The experimentally obtained value will be denoted by ψ_e . If many measurements of ψ are performed, the values of ψ_e may be averaged to obtain $\overline{\psi_e}$. The accuracy of the measurements is defined as the difference between the mean of the experimental values and the true value, that is, $\overline{\psi_e} - \psi_o$. The precision of each measurement is the difference between the mean of the experimental values and any single experimental reading, that is, $\psi_e - \overline{\psi_e}$. The average or overall precision of the instrument is usually expressed in terms of the "root-mean-square deviation" of the experimental values from the mean experimental value:

$$\Delta\psi = \sqrt{\frac{\sum (\psi_e - \overline{\psi_e})^2}{N}}, \quad (1)$$

where N is the number of experimental observations. Accuracy is concerned with systematic errors, errors which may be corrected only by careful calibration. Precision, on the other hand, is concerned with such things as repeatability and hysteresis of an instrument. A standard reference for these definitions is Topping [1].

For the present paper, two investigative techniques were used: stochastic simulation and repeat experimentation. Stochastic simulation is a technique which involves mathematically modelling the performance of the porosimeter including “errors of observation” (precision) of the pressure transducer used in the apparatus. As applied here, these errors were assumed to be distributed in a Gaussian manner, a large number of simulated experiments were performed, and the resulting errors in the “measured” grain volumes were determined. The experimental approach used a typical porosimeter. Combinations of various sized ball-bearings were used as calibration standards, and cylindrical, aluminum billets of various lengths were used as model samples. Several hundred measurements were performed, and the results were analysed statistically to determine the precisions of the determined billet volumes.

Basic Operating Principles

A schematic diagram of a gas expansion porosimeter is shown in Figure 1. It comprises a sample chamber, a reference chamber, a three-way valve, a gas source, a shut-off valve, and a pressure transducer. In principle, the volumes of the two chambers (sample chamber volume, V_c , reference chamber volume, V_r) are known.

The apparatus is operated as follows:

1. The sample is placed in the sample chamber which is vented to atmosphere.
2. The sample chamber is sealed.
3. The reference chamber is pressurized by means of the gas source.
4. The shut-off valve is closed.
5. Once the system comes to equilibrium, the gauge pressure in the reference chamber is recorded (p_{1g}).
6. The three-way valve is opened between the reference chamber and the sample chamber.
7. Once the system has re-equilibrated, the gauge pressure of the system, p_{2g} is measured.
8. The grain volume, V_g of the sample is calculated from the equation (see Appendix 1 for a detailed derivation):

$$V_g = (V_c + V_r) - \frac{p_{1g}}{p_{2g}} V_r . \quad (2)$$

The uncertainty (error) in V_g may be found from Equation 2 using standard error analysis techniques. However, there is actually more uncertainty in this equation than is

first apparent. It has been assumed that the values of V_c and V_r are known. In fact, the values of these two parameters are normally found by calibration. The procedure is as follows:

1. Using a number of samples with known grain volumes, a series of experiments are performed to obtain a set of pressure ratios.
2. By means of linear regression, this data set (V_g versus p_{1g}/p_{2g}) is used to obtain calibrated values for V_c and V_r (actually $(V_c + V_r)$ and V_r).

Because these calibrated values will contain error, it is difficult to obtain a closed-form solution for the total error caused by the application of Equation 2. In order to overcome this difficulty, a simple stochastic model of Equation 2 was constructed.

The Stochastic Model

The procedure used to construct the stochastic model was as follows:

1. True values for V_c , V_r and a number of grain volumes (henceforth referred to as “standard”) were assumed.
2. Using all but one of the standard grain volumes (the one not used will be referred to as the “omitted standard grain volume”), and the standard values for V_c and V_r , Equation 2 was used to predict ideal values of p_{2g} that would result for each of the standard grain volumes. Here, p_{1g} was assumed to be fixed. This resulted in a set of p_{1g}/p_{2g} data for each standard grain volume.
3. The pressure data (both p_{1g} and p_{2g}) were “corrupted” by adding to them Gaussian errors with a standard deviation equal to the quoted precision of the pressure transducer. This resulted in a set of pseudo-experimental data.
4. The pseudo-experimental data were used to “calibrate” the apparatus (*i.e.* calculate values of $(V_c + V_r)$ and V_r).
5. The ideal pressure response for the omitted standard grain volume was determined. This pressure response was then corrupted, and the calibrated equation was used to calculate a grain volume.
6. The true value of the omitted sample was used along with the “experimental” value to calculate an error.
7. This procedure was repeated 1000 times and root-mean-square deviations were calculated for each standard grain volume.

The design parameters for the porosimeter used in the experimental study are given in Table 1. These were also the parameters used in the stochastic model. The “precision” quoted in Table 1 is not entirely a function of errors of observation. This value is more a measure of guaranteed accuracy under specified operating conditions. Because the pressure

transducer when used in the porosimeter need not be accurate but only repeatable (the pressures are used in a regression equation and systematic inaccuracies will be calibrated out), the quoted value of precision may be inappropriate for the present analysis. For this reason, the model was run for a range of precisions. The results are given in Figure 2 in the form of fractional root-mean-square errors (root-mean-square deviation divided by the true grain volume).

In order to obtain grain densities that are within the "industrial standard tolerance" of $\pm 10 \text{ kg/m}^3$, grain volumes must be determined to at least 1 part in 250 or a fractional error of 0.004. The data in Figure 2 demonstrate that the quoted "precision" for the transducer (0.0025) implies that the instrument only marginally meets the standard required for grain volumes over 90 cc, and does not meet the standard at all for smaller grain volumes. In fact, these results are optimistic because they show only root-mean-square error. Maximum deviations can be much larger: if a large number of tests are performed, approximately 5% of them will give errors that are twice as large as the root-mean-square error. The above results are at first discouraging because they imply that a precise porosimeter would be very expensive, requiring very high quality pressure transducers. However, as previously indicated, quoted precisions for transducers are actually accuracies, and take into account typical (industrial) operating conditions. All that is important in the porosimeter is the repeatability of the transducer. This parameter is typically an order of magnitude smaller than the quoted "precision" for the type of transducer used in the present study. For a precision of 0.00025, the predicted deviations are well below the standard of 0.004.

Calibration and Accuracy

Accuracy depends on calibration. Calibration depends on having samples for which true values are known. In the case of grain volumes, the calibration standards used most commonly are ball bearings. The reason for this is that ball bearings are manufactured to very close and well documented tolerances. The poorest grade of ball bearing deviates no more than 400 μm from its nominal size, while the best grade of ball bearing deviates no more than 0.5 μm from its nominal size. (Ball bearings with tolerances in the range of 50 μm are readily available.) The errors in volumes of a nominally 3.81 cm ball bearing therefore range from 0.00015 cm to 0.032 cm. Using high grade ball bearings, it is easily possible to obtain calibration standards within the 0.004 limit.

Most rock samples are cylindrical in shape; therefore, porosimeter sample chambers are typically cylindrical. The main difficulty in using ball bearings as calibration standards is that, because of their spherical shape, when they are placed in a cylindrical chamber with diameter and length approximately the same as the diameter of the ball, they simulate a sample with a porosity of 33%. One rule of calibration is that the calibration samples should span the entire range of parameter values that will be measured in the instrument. Generally, the chamber has a length greater than its diameter. The porosities simulated by the ball bearings are therefore at the high end of the normally encountered porosity range. In order to properly calibrate the instrument, calibration standards that simulate much lower porosities must be obtained. This problem can be overcome by using a number

of smaller ball bearings, but this makes the calibration process tedious.

In order to overcome the range problem described above, cylindrical billets are usually manufactured for use as standards. The problem then becomes to find the “true” grain volumes of these “standards”. For the purpose of the present study, four aluminium billets were manufactured. Standard samples should be constructed of a material that will not change (corrode) with time. The best choices would therefore be gold or platinum, but these are very expensive materials. Aluminum was chosen because it is easy to obtain and work with, corrosion occurs in only a very thin layer on the surface, and it is inexpensive. If the billets were manufactured from a pure material, their volumes could be found in a very straightforward manner by finding their masses and calculating their volumes using documented values for the density of the pure substance. However, it is very difficult to obtain pure materials, and because the error range to be achieved is less than 0.004, compositional changes of 1% may cause significant errors.

Various means of measuring the true grain volumes of the aluminum billets were attempted:

1. Calipers: The lengths and diameters of the samples were measured and the volumes were calculated. The cylinders were manufactured with a smooth surface and as right cylinders. However, the accuracy of a caliper measurement can be no better than ± 0.0025 mm and the surface can never be made completely smooth. Therefore, it was accepted from the beginning that this method was inadequate.
2. Archimedes' Method: The billets were weighed in air and then weighed while submerged under water. The buoyancy principle was then used to calculate their volumes.
3. Porosimetry: The porosimeter was calibrated using combinations of ball bearings, then used to measure the volume of the billets. This technique was applied in two different ways: with the chamber volume fixed at the value used to perform the main study (3.81 cm diameter, 7.62 cm length); and with the chamber volume reduced to optimize the measurement of each billet.
4. By Mass Using Composition Specified by Manufacturer: The masses were obtained, the density of the aluminum was calculated using the composition specified by the manufacturer of the aluminum (see Reference 1 for procedure), and the volumes were calculated using this density.
5. By Mass Using Measured Composition: The masses were obtained, the density of the aluminum was calculated using the composition measured by chemical analysis, and the volumes were calculated using this density.

The most reliable method should be Method 5 above. The deviations of the billet volumes from the volumes obtained using Method 5 are shown in Figure 3. The billet volumes based on the manufacturer's specifications all deviate by the same percentage because they are all based on the same (erroneous) density. Table 2 shows the compositions used in

Methods 4 and 5. The two analyses are actually quite similar, yet sufficiently different to cause major deviations in the calculated grain volumes. The caliper based values (the average of five replicates) are systematically high, and are outside of the 0.004 limit. Except for the smallest billet, the Archimedes' results (the average of five replicates) agree well with the chemical analysis based numbers. The porosimeter based values are very poor when a large chamber was used, but much improved when smaller chambers were used. The agreement between the Archimedes' values, the small chamber porosimeter values, and the chemical analysis based values were taken as evidence that accurate "true" values had been obtained.

In light of the above discussion, some comments on bulk volume determination are in order. Bulk volumes of small samples are typically found using either calipers or Archimedes' principle. The above results indicate that for typical samples (in the 70 to 100 cc bulk volume range), the Archimede's principle method is clearly preferred. Except in the case where large surface vugs preclude the use of the Archimedes' technique (in which case small samples are inappropriate anyway), caliper measurements should not be used to determine bulk volumes of plug samples.

Precision

In order to measure the precision of the instrument, an experimental procedure equivalent to the stochastic procedure outlined above was performed. The steps were as follows:

1. A series of experiments were run with different combinations of billets and ball bearings in the sample chamber.
2. Using data from all but one of the runs (the "omitted run"), the porosimeter was calibrated.
3. The calibration was used to calculate the grain volume of the sample used in the omitted run.
4. Using the true value for the grain volume for the sample in the omitted run, the error was calculated.
5. The procedure was repeated for a total of 9 replicates and root-mean-square deviations were calculated for each combination of billets and ball bearings.

The results of this procedure are shown in Figure 4. Also shown are the theoretical (stochastic) precision curves. It is clear from this figure that the actual performance of the instrument is much better than that predicted by theory based on the quoted precision of the transducer (0.0025). As suggested previously, the reason for this is that the quoted precision is actually an accuracy — the guaranteed agreement between the measured value and the true value under the specified operating conditions. When used in a porosimeter, the pressure transducer need only be able to reproduce readings and have a linear response with little hysteresis. If these conditions are fulfilled, then the calibration procedure will take care of any systematic errors that lead to inaccuracies.

The data show that as the grain volume becomes smaller than 50% of the chamber volume, the precision of the instrument deteriorates rapidly. (This behaviour is also evident in Figure 3 in the curve for the large chamber porosimeter.) A porosimeter is normally operated with the chamber volume essentially filled by the sample; that is, the bulk volume of the sample is only slightly smaller than the sample chamber volume. The grain volume limit of 50% implies a porosity of 50%. Because most core analysis samples do not approach these high values, the 50% limit has no impact on a typical core analysis. However, in other applications, such as determining grain volumes of fibres such as insulation, this limit should be observed if precise results are required.

Figure 5 shows the precisions that result when the calipered grain volumes of the aluminum are used in the data reduction scheme. Much larger values of error are apparent. This implies that the caliper values of the volumes are in error. These errors in volume lead to errors in calibration which are propagated through to errors in the measured grain volumes. The importance of obtaining accurate values for the volumes of the calibration samples is evident.

In order to obtain some preliminary results on how the choice of the working gas will affect the results, the experimental process was repeated using nitrogen. The results are shown in Figure 6. The errors here are very similar to those shown in Figure 4. This implies that either helium or nitrogen could be used in a gas expansion porosimeter. However, the usual criticism of the use of nitrogen is that nitrogen adsorbs to surfaces, thereby causing erroneously low measurements of grain volume. Because the surface areas of the aluminum samples are small compared with those found in actual core samples, adsorption effects would not be expected in these experiments.

A preliminary study using sandstone samples was conducted to further explore the use of nitrogen in place of helium. Table 3 shows a comparison of the results. In all but one case, the grain volumes determined using nitrogen were less than those determined using helium, and in this exceptional case, the deviation is small. If adsorption is occurring, the adsorbed nitrogen would lead to an greater pressure reduction, hence a lower calculated grain volume. These results do suggest such a mechanism. The results in Figure 4 and 6 suggest that the precision of the instrument should be less than 0.001. Deviations between helium and nitrogen results are larger than this value, ranging up to 0.003; however, because the differences in the test results are similar to the precision of the porosimeter, no firm conclusion as to adsorption can be based on these results. Still the systematic trend and the magnitudes of the differences are suggestive.

Design Criteria

Experience gained with the experimental data suggests that the precision of the pressure transducer as used in a typical gas expansion porosimeter is approximately 0.0001. This result was used with the stochastic method in order to gain some insights into the optimum design of gas expansion porosimeters. Of particular interest were the effects of the reference chamber volume to sample chamber volume ratio and the initial reference volume pressure. A sample chamber volume of 110 cc was assumed for these studies.

The results for the volume ratio study are given in Figure 7. If the volume ratio is small, the precisions at low values of grain volume are affected. However, once the grain volume exceeds 50% of the sample chamber volume, the precisions are essentially the same for all reference chamber volumes. Close inspection of the results shows that there is a weak minimum in the error in the region between V_r/V_c 's of 0.25 and 0.5. Whether this weak minimum has any meaning for an actual porosimeter is questionable in light of the observed scatter of the experimental precision data (Figure 4).

The results for the initial pressure study are given in Table 4. For these results, V_r was 27.5 cc. Clearly, the effect of the initial pressure on the precision is minimal. However, this is based on an important assumption — that the pressure gauge is chosen such that the initial pressure is equal to the full range of the gauge. Because precisions of pressure transducers are expressed as fractions of full range, if the full range is greater than the initial pressure, the precision of the porosimeter will deteriorate.

The porosimeter constructed for the present study was designed with a fine threaded endcap. This endcap design ensured that each time the chamber was opened or closed, the volume of the chamber would be the same to within a very small tolerance. This feature is essential if precise results are to be expected. However, the design is not well suited to routine operation, with large numbers of samples, in a dusty environment. In the authors' experience, the design of a rapid closing endcap that will repeatedly reproduce the same chamber volume is one of the most problematic aspects of porosimeter design.

Conclusions

The present work supports the following conclusions:

1. Gas expansion porosimeters should not be operated with the following restrictions:
 - $V_g/V_c > 0.5$
 - $0.25 < V_r/V_c < 0.5$
2. The precision of grain volumes obtained using a gas expansion porosimeter that is operated within the limits specified in 1. should be less than ± 0.001 .
3. Helium is the preferred gas for use in the porosimeter.
4. If nitrogen is used in the porosimeter, systematically low values of the grain volume may result. For this reason, nitrogen should not be used in gas expansion porosimeters.

References

1. Topping, J., Errors of Observation and Their Treatment, Fourth Edition, Chapman and Hall Science Paperbacks, London, England, 1972.
2. —, Aluminum Standards and Data, Tenth Edition, the Aluminum Association, Inc., Washington, D.C., U.S.A., 1990

Appendix

The reference volume, V_r , is initially filled with a gas, usually helium, at an absolute pressure of p_1 . The sample chamber, V_c , contains the sample, and is initially filled with air at ambient pressure, p_a . The number of moles of helium in V_r will be denoted by n_h and is given by

$$n_h = \frac{p_1 V_r}{RT}, \quad (A1)$$

where R is the ideal gas constant and T is the temperature. The number of moles of air present is denoted by n_a and is given by

$$n_a = \frac{p_a (V_c - V_g)}{RT}. \quad (A2)$$

When the valve is opened, the system will come to equilibrium, at which time the following equations will hold:

$$p_{2h} (V_r + V_c - V_g) = n_h RT, \quad (A3a)$$

$$p_{2a} (V_r + V_c - V_g) = n_a RT, \quad (A3b)$$

and

$$p_{2h} + p_{2a} = p_2, \quad (A3c)$$

where p_{2h} is the final helium partial pressure, p_{2a} is the final air partial pressure, and p_2 is the final total pressure. Combining Equations A1 through A3:

$$p_2 (V_r + V_c - V_g) = p_1 V_r + p_a (V_c - V_g). \quad (A4)$$

In the laboratory, gauge, not absolute pressures are usually measured. Since

$$p_1 = p_{1g} + p_a \quad (A5a)$$

and

$$p_2 = p_{2g} + p_a, \quad (A5b)$$

Equation A4 may be rewritten in the form

$$p_{2g} (V_r + V_c - V_g) = p_{1g} V_r \quad (A6)$$

or

$$V_g = (V_r + V_c) - \frac{p_{1g}}{p_{2g}} V_r. \quad (A7)$$

Table 1
Porosimeter Design Parameters

Parameter	Value	Units
Nominal Sample Chamber Volume, V_c	114.1	cc
Nominal Reference Chamber Volume, V_r	25.9	cc
Initial Pressure	100.0	psig
Pressure Transducer "Precision"	± 0.0025	of full scale
Working Gas	Helium	—

Table 2
Composition of Aluminum Used in Billets

Component	Manufacturer's Specifications	Chemical Analysis
Aluminum	0.9264	0.9296
Copper	0.0643	0.0456
Manganese	0.0072	0.0058
Magnesium	0.0021	0.0135
Iron	—	0.0028
Silicon	—	0.0012
Zinc	—	0.0012
Chromium	—	0.0003

(Aluminum fraction by difference.)

Table 3
A Comparison of Helium and Nitrogen Porosimetry

Sample	Helium V_g (cc)	Nitrogen V_g (cc)	Fractional Deviation
R2	40.43	40.30	-0.0033
S1	66.02	65.95	-0.0009
N6B	45.12	45.14	+0.0005
Y1	43.37	43.28	-0.0023
B3	42.37	42.37	0.0000
R6B	40.71	40.58	-0.0031
GTS5	38.50	38.49	-0.0003
S2	56.68	56.67	-0.0001

Table 4
Effect of Initial Reference Volume Pressure

Grain Volume (cc)	Fractional Deviation ($p_{1g} = 100 \text{ psi}$)	Fractional Deviation ($p_{1g} = 50 \text{ psi}$)	Fractional Deviation ($p_{1g} = 25 \text{ psi}$)
50	0.00060	0.00060	0.00061
60	0.00039	0.00038	0.00042
70	0.00027	0.00026	0.00027
80	0.00017	0.00017	0.00017
90	0.00012	0.00013	0.00015
100	0.00011	0.00011	0.00011

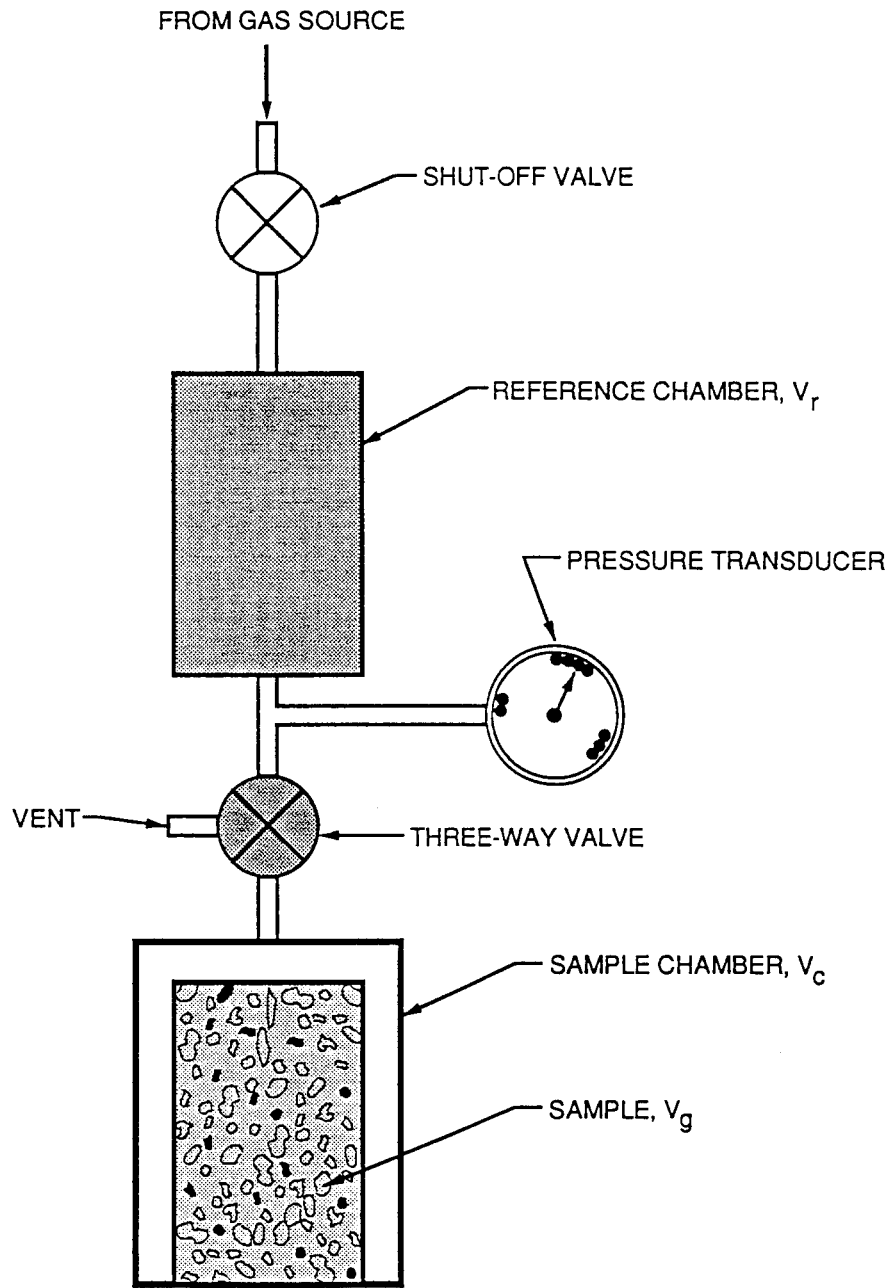


Figure 1. Gas Expansion Porosimeter

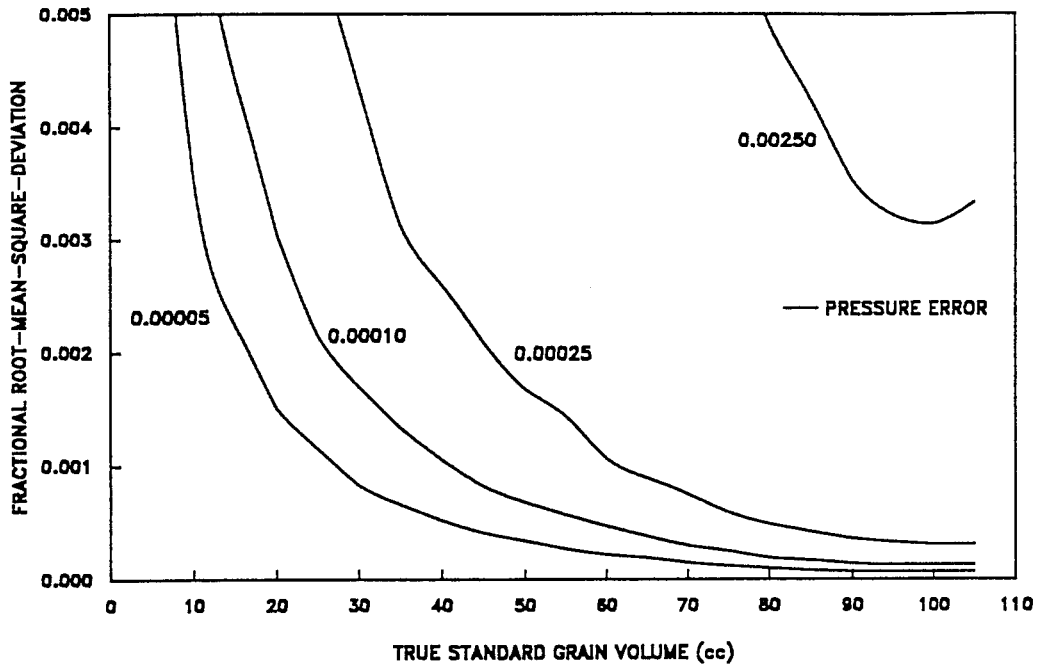


FIGURE 2 STOCHASTIC MODEL POROSIMETER PRECISIONS

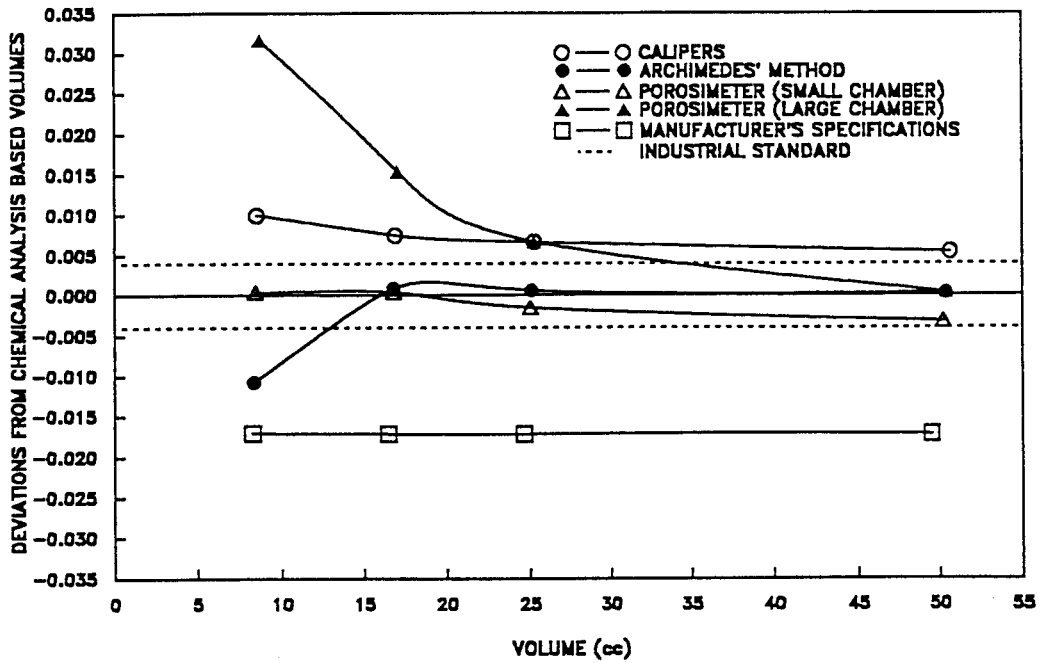


FIGURE 3 ACCURACIES OF METHODS FOR DETERMINING GRAIN VOLUMES

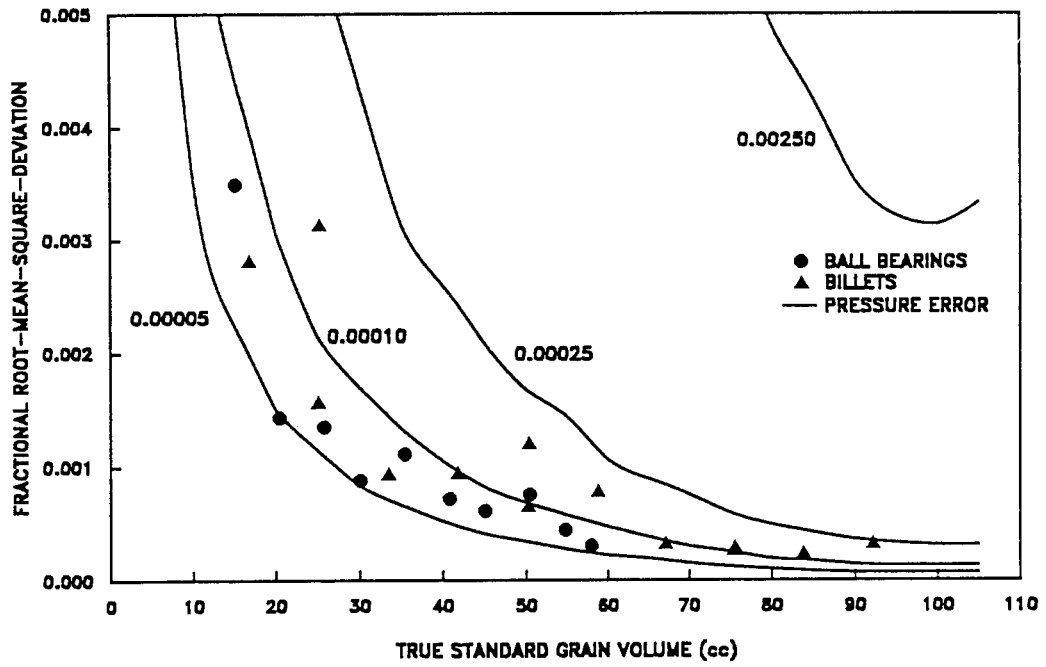


FIGURE 4 PRECISION OF THE TYPICAL HELIUM POROSIMETER

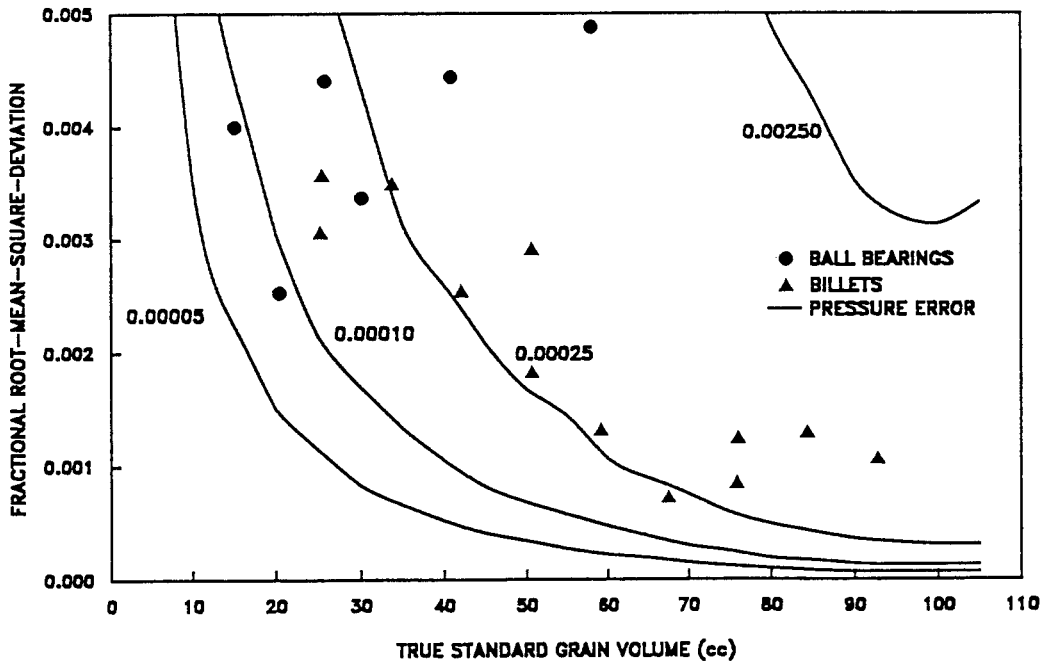


FIGURE 5 PRECISIONS RECALCULATED USING CALIPER DERIVED BILLET VOLUMES

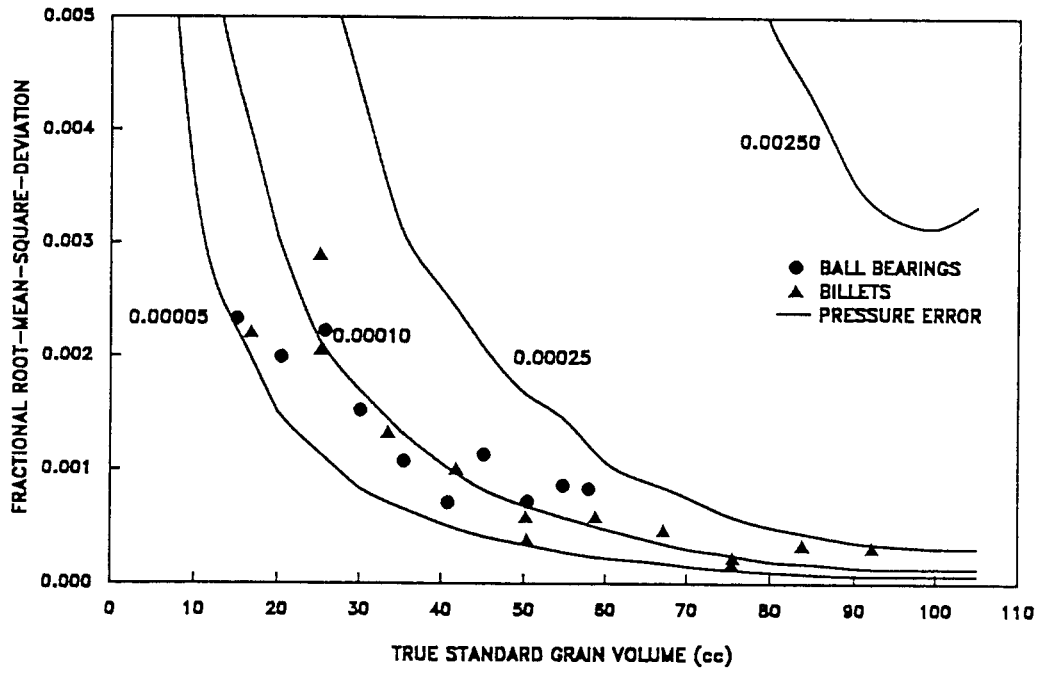


FIGURE 6 PRECISIONS OF THE TYPICAL NITROGEN POROSIMETER

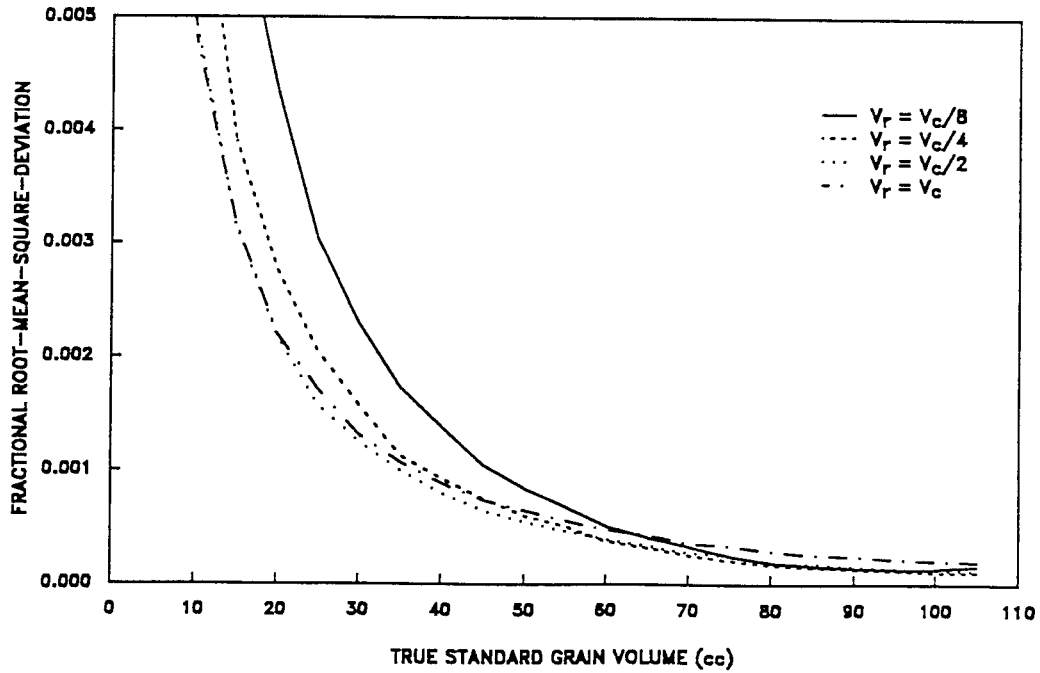


FIGURE 7 VARIATION OF PRECISION WITH REFERENCE CHAMBER VOLUME TO SAMPLE CHAMBER VOLUME RATIO

