

## Understanding the Uncertainty and Precision Specifications for the AccuPyc

A frequently asked question is, “What is the accuracy of the densities reported by the AccuPyc?” And that is a good question. The problem is that, though the AccuPyc reports the skeletal density of the sample under test, it actually determines the skeletal volume,  $V$ , of the test portion. It uses the sample mass,  $M$ , entered by the user, to calculate the density,  $\rho$ , using equation (1).

$$(1) \quad \rho = \frac{M}{V}$$

This means that the uncertainty, or error, in the density is going to be a combination of the uncertainty in the mass of the sample determined using a balance and the uncertainty of the volume determined using the AccuPyc. Actually the relative uncertainty,  $\epsilon_\rho$ , in the density will equal the sum of the relative uncertainty in the volume,  $\epsilon_V$ , and the relative uncertainty in the mass,  $\epsilon_M$ , as shown in equation (2). Note that it is the relative uncertainties that are additive, not the absolute uncertainties.

$$(2) \quad \epsilon_\rho = \epsilon_V + \epsilon_M$$

Most laboratories use analytical balances with readability to 0.1 mg, or 0.0001 g, typically with the uncertainty of the mass in the last decimal place. Assuming that the uncertainty is 0.0005 g, and with a test portion mass of 10.0 g, the relative uncertainty is 0.0005/10.0 or 0.00005. Expressed as a percentage,  $\epsilon_M$  is 0.005% for this example.

So what about the relative uncertainty in the volume determined by the AccuPyc? How is that determined? There is an absolute accuracy specification,  $V_\epsilon$ , not a relative uncertainty, for the various AccuPyc models based upon the nominal volume of the AccuPyc,  $V_N$ , and the volume of the sample under test,  $V_S$ , determined using equation (3).

$$(3) \quad V_\epsilon = \pm 0.03\% \times (V_N + V_S)$$

The same formula is used for all of the AccuPyc models. These are available in standard nominal volumes of 1 cm<sup>3</sup>, 10 cm<sup>3</sup>, 100 cm<sup>3</sup>, 350 cm<sup>3</sup>, and for the CorePyc, 2000 cm<sup>3</sup>. These are the nominal volumes,  $V_N$ , to be used in equation 3 as the pycnometer component of the determined volume uncertainty. The sample portion simply depends on the amount under test,  $V_S$ . The relative uncertainty in the volume measurement,  $\epsilon_V$ , then is given by equation (4).

$$(4) \quad \epsilon_V = \frac{V_\epsilon}{V_S}$$

And so the volume uncertainty depends on which AccuPyc is being used, and how much sample is under test. To help better understand, an example of a sample of glass beads analyzed using both a 100 cm<sup>3</sup> and a 10 cm<sup>3</sup> AccuPyc is shown in Table 1 below.

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AccuPyc Volume, $V_N$ (cm <sup>3</sup> )	Sample Mass, $M$ (g)	Sample Volume, $V_S$ (cm <sup>3</sup> )	Sample Density, $\rho$ (g/cm <sup>3</sup> )	Volume Uncertainty, $V_\epsilon$ (cm <sup>3</sup> )	Mass Uncertainty, $M_\epsilon$ (g)	Density Uncertainty, $\rho_\epsilon$ (g/cm <sup>3</sup> )
100	115.5789	46.6811	2.4759	0.0440	0.0005	0.0023
10	12.5693	5.0752	2.4766	0.0045	0.0005	0.0023

Table 1. Analysis of one test portion of glass beads using two different AccuPyc models.

Using equation (1) to calculate density, equation (2) to calculate the relative uncertainty in the density reported from the relative uncertainties in volume and mass, the absolute uncertainty in the sample density is calculated simply by multiplying the reported density by the density relative uncertainty. Note that the density uncertainty for both of these examples is essentially the same, and is driven mostly by the uncertainty in the volume determined by the AccuPyc. Since the relative amount under test is the same, with 46.68 cm<sup>3</sup> under test in the 100 cm<sup>3</sup> AccuPyc, and 5.07 cm<sup>3</sup> under test in the 10 cm<sup>3</sup> AccuPyc, the relative volume uncertainty is essentially the same for the two

experiments. The volume uncertainty is basically a function how much of the AccuPyc sample cup is filled by the sample.

As further illustration, different amounts of the glass beads were analyzed using the 100 cm<sup>3</sup> AccuPyc. Three analyses were performed with the cup approximately filled. For the next analysis, approximately 80% of the mass used in the filled-cup experiment was used, followed by one analysis each of 60%, 40%, and 20% of the mass used in the filled-cup experiment. Finally three analyses were performed using 10% of the mass used in the filled-cup experiment. The results are given in Table 2 below.

AccuPyc Volume, $V_N$ (cm <sup>3</sup> )	Sample Mass, $M$ (g)	Sample Volume, $V_S$ (cm <sup>3</sup> )	Sample Density, $\rho$ (g/cm <sup>3</sup> )	Volume Uncertainty, $V_\epsilon$ (cm <sup>3</sup> )	Mass Uncertainty, $M_\epsilon$ (g)	Density Uncertainty, $\rho_\epsilon$ (g/cm <sup>3</sup> )
100	115.5789	46.6811	2.4759	0.0440	0.0005	0.0023
100	113.6955	45.9215	2.4759	0.0438	0.0005	0.0024
100	111.3100	44.9590	2.4758	0.0435	0.0005	0.0024
100	90.6356	36.6284	2.4745	0.0410	0.0005	0.0028
100	67.8304	27.4402	2.4719	0.0382	0.0005	0.0035
100	45.6852	18.5110	2.4680	0.0356	0.0005	0.0048
100	22.3716	9.1215	2.4526	0.0327	0.0005	0.0089
100	11.5790	4.7846	2.4201	0.0314	0.0005	0.0160
100	11.1499	4.5796	2.4347	0.0314	0.0005	0.0168
100	11.8456	4.8587	2.4380	0.0315	0.0005	0.0159

Table 2. Analysis of different size test portions of glass beads using a 100 cm<sup>3</sup> AccuPyc.

Notice that the Density Uncertainty, in g/cm<sup>3</sup>, increases as the amount of sample under test decreases. Recall that the AccuPyc contribution to the volume uncertainty is constant, while the contribution due to the sample is directly related to the amount of sample under test. As the amount of sample under test is increased, the contribution due to the AccuPyc, while a constant absolute amount, becomes a smaller relative uncertainty. Since it is the relative volume uncertainty that is used to determine the relative density uncertainty,

minimizing the impact of the AccuPyc volume on the analysis results, by increasing the sample amount, will decrease the overall uncertainty in the density reported by the AccuPyc. The same information shown in Table 2 above is repeated in Table 3 below, except that the relative uncertainties are listed for the volume, mass, and density. Note that Percent of cup filled refers to the percentage of the cup volume filled by the sample and void space, not that the sample volume was equal to 100% of the cup volume of 100 cm<sup>3</sup>.

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AccuPyc Volume, $V_N$ (cm <sup>3</sup> )	Percent of cup filled	Sample Mass, $M$ (g)	Sample Volume, $V_S$ (cm <sup>3</sup> )	Sample Density, $\rho$ (g/cm <sup>3</sup> )	Relative Volume Uncertainty $\varepsilon_V$	Relative Mass Uncertainty, $\varepsilon_M$	Relative Density Uncertainty, $\varepsilon_\rho$
100	100%	115.5789	46.6811	2.4759	0.000943	0.000004	0.000947
100	100%	113.6955	45.9215	2.4759	0.000953	0.000004	0.000958
100	100%	111.3100	44.9590	2.4758	0.000967	0.000004	0.000972
100	80%	90.6356	36.6284	2.4745	0.001119	0.000006	0.001125
100	60%	67.8304	27.4402	2.4719	0.001393	0.000007	0.001401
100	40%	45.6852	18.5110	2.4680	0.001921	0.000011	0.001932
100	20%	22.3716	9.1215	2.4526	0.003589	0.000022	0.003611
100	10%	11.5790	4.7846	2.4201	0.006570	0.000043	0.006613
100	10%	11.1499	4.5796	2.4347	0.006851	0.000045	0.006896
100	10%	11.8456	4.8587	2.4380	0.006475	0.000042	0.006517

Table 3. Analysis of different size test portions of glass beads using 100 cm<sup>3</sup> AccuPyc.

Notice that the relative volume uncertainty increases with decreasing test portion size, as discussed above. The relative mass uncertainty also decreases with sample amount as it is based on a fixed 0.0005 g absolute uncertainty for each sample amount, however, it is generally two orders of magnitude less than the relative volume uncertainty, assuming that a good analytical balance is used for mass determinations. And so both the relative and absolute uncertainties in the reported density decreases with increased sample amount.

A similar set of experiments was conducted using a 10 cm<sup>3</sup> AccuPyc. The results of these analyses are shown in Table 4 below, with the uncertainties expressed as absolute values rather than relative values. Note that the density uncertainties are essentially the same for the two pycnometers when the cups are filled to approximately the same capacity of bulk sample under test.

AccuPyc Volume, $V_N$ (cm <sup>3</sup> )	Percent of cup filled	Sample Mass, $M$ (g)	Sample Volume, $V_S$ (cm <sup>3</sup> )	Sample Density, $\rho$ (g/cm <sup>3</sup> )	Volume Uncertainty $V_\varepsilon$ (cm <sup>3</sup> )	Mass Uncertainty, $M_\varepsilon$ (g)	Density Uncertainty, $\rho_\varepsilon$ (g/cm <sup>3</sup> )
10	100%	12.5693	5.0752	2.4766	0.0045	0.0005	0.0023
10	100%	12.8731	5.1971	2.4770	0.0046	0.0005	0.0023
10	100%	12.3061	4.9685	2.4768	0.0045	0.0005	0.0023
10	80%	10.2633	4.1445	2.4763	0.0042	0.0005	0.0027
10	60%	7.5421	3.0472	2.4751	0.0039	0.0005	0.0033
10	40%	5.1660	2.0902	2.4715	0.0036	0.0005	0.0045
10	20%	2.4842	1.0067	2.4678	0.0033	0.0005	0.0086
10	10%	1.1971	0.4889	2.4485	0.0031	0.0005	0.0168
10	10%	1.3603	0.5549	2.4514	0.0032	0.0005	0.0149
10	10%	1.2785	0.5208	2.4549	0.0032	0.0005	0.0158

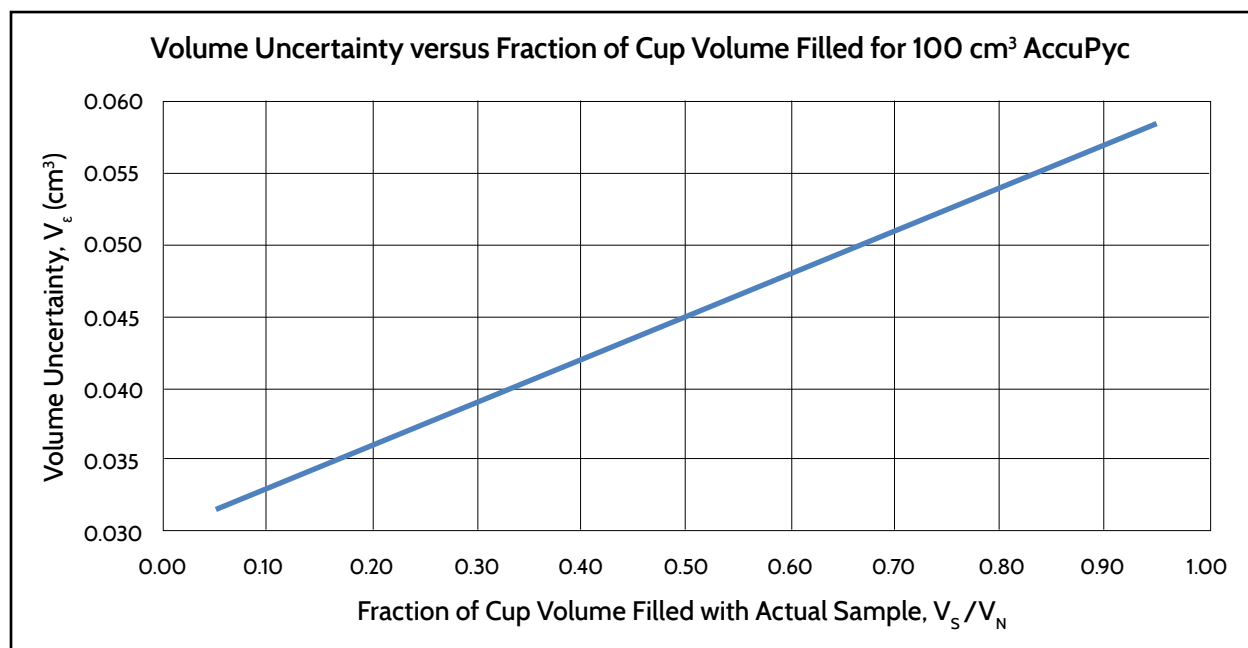
Table 4. Analysis of different size test portions of glass beads using 10 cm<sup>3</sup> AccuPyc.

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And so, the answer to the opening question of “What is the accuracy of densities reported by the AccuPyc?” is that it depends on the amount of sample under test. Therefore to minimize the uncertainty in the density reported, analyze a test portion that will fill the sample cup. Now the tables above contain values for the density uncertainty, and yet the question to answer dealt with the accuracy of the densities. When the sample under test has a known density, from some reference method such as X-ray diffraction, the values determined using the AccuPyc should agree to within the density uncertainty of that theoretical or reference density, assuming essentially a perfect sample, that is, one that has a high degree of purity, does not include any closed porosity or other inclusions, is free of adsorbed vapors, including water, and has the same crystal structure as the reference sample. Assuming all of these to be valid, then the density reported by the AccuPyc should be accurate to within the density uncertainty as calculated above. Note that these values are the maximum uncertainty expected for a properly operating

AccuPyc and a properly prepared and analyzed sample. Actual results likely will be better as the AccuPyc being used likely is operating to a better degree than given by the maximum uncertainties calculated here. In order to determine the actual uncertainty for a particular AccuPyc, a sample of known volume can be analyzed, such as one of the calibration spheres.

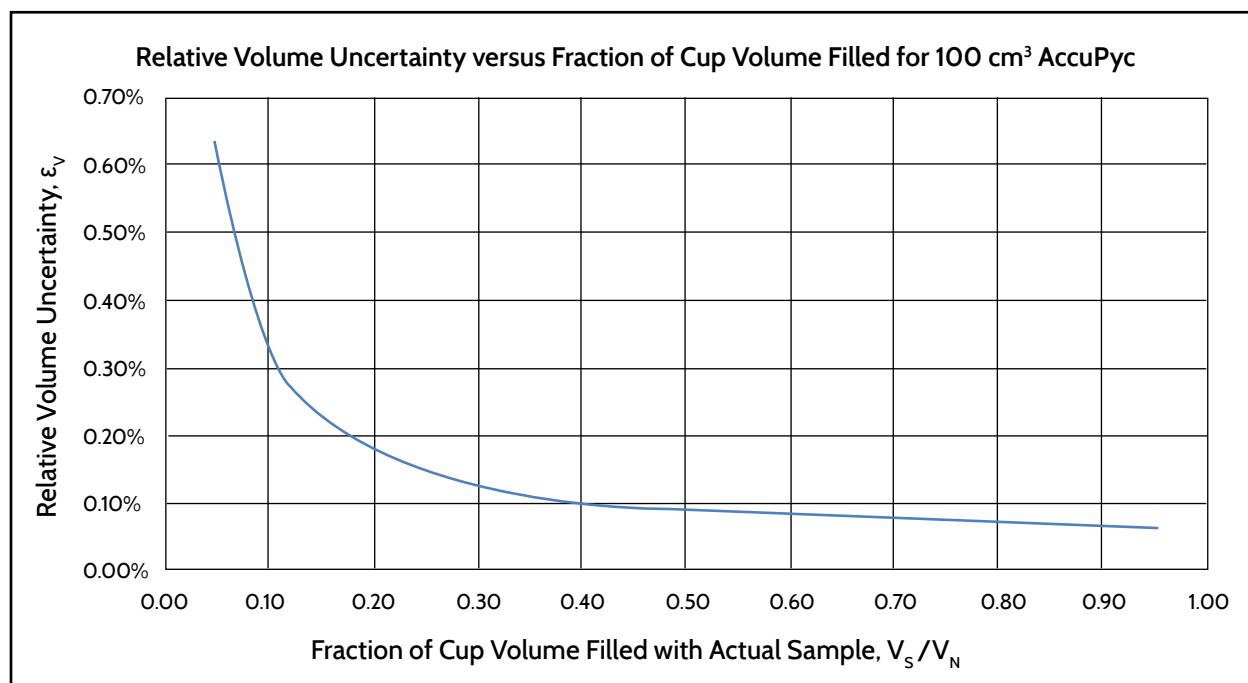
In the above examples, with the sample cup essentially filled with bulk sample, only about 50% of the total cup volume was occupied by the sample. The remaining cup volume was the void space between the glass beads. For powdered samples that pack differently, more or less of the cup volume will be filled with sample when as much sample that the cup will hold is under test. Samples that have a wide particle size distribution, where small particles can fill the space between larger ones, frequently can fill upwards of 70% or more of the cup volume. In the first example, for the 100 cm<sup>3</sup> sample cup, Graph 1 illustrates the relationship between volume uncertainty and the fraction of the cup filled with actual sample, not including the void space of the powder bed.



Graph 1. Volume uncertainty versus fraction of cup volume filled with actual sample for 100 cm<sup>3</sup> AccuPyc.

Graph 2 illustrates the relationship between the relative volume uncertainty and the percentage of the sample cup actually occupied by the sample. Note that in this study, the sample beads occupy just under ½ of the cup volume when the bulk of the sample essentially fills the cup.

Thus, about ½ of the bulk volume is void space between these glass beads. This is to be expected as the particle size distribution for these beads is quite narrow, spanning from 149 μm to 210 μm, based upon sieve size classification.



Graph 2. Relative volume uncertainty,  $\epsilon_v$ , versus percentage of sample cup filled with actual sample,  $V_s/V_N$ .

A second obvious, and good, question concerning the AccuPyc performance is, “What is the precision of the densities reported by the AccuPyc?” Since precision can be interpreted as repeatability, as reproducibility, or as both, from the perspective of the AccuPyc operation, precision refers to repeatability of individual determinations for the current sample under test. The absolute repeatability specification for each of the AccuPyc models is given by equation (5). Note that since a single value of sample mass is being used for each individual determination, repeatability is strictly a function of volumes determined by the AccuPyc, with no contribution from the sample. Thus the relative repeatability of the density will be equal to the relative repeatability of the volume under test.

$$(5) \quad r_v = \pm 0.02\% * V_N$$

Note that only the nominal volume of the AccuPyc is used to determine the expected absolute repeatability specifications for the AccuPyc. The amount of sample under test directly impacts the relative repeatability as it is determined by dividing the absolute repeatability from equation (5) by the volume under test, and the relative repeatability of the reported density is equal to that of the volume.

The values for volume and density in Tables 1 through 4 above are averages of 5 individual analysis cycles of the particular sample test portion. The instrument is programmed to conduct a number of purge cycles to help clean the sample and AccuPyc of other vapors, and then to perform a number of analysis cycles from which to calculate average values for skeletal volume and density, along with a standard deviation for each. Up to 999 purge and analysis cycles can be programmed, as desired. In the current investigation, only 5 analysis cycles were used.

The individually determined volumes of the 5 analysis cycles for each glass bead test portion analyzed with the 100 cm<sup>3</sup> AccuPyc are shown in Table 5. The repeatability specification for the 100 cm<sup>3</sup> AccuPyc, determined using equation (5), is  $\pm 0.0200$  cm<sup>3</sup>. This absolute repeatability value is then used to determine the relative volume repeatability. Table 6 shows the densities determined for each of the analyses for each test portion, along with the expected absolute density repeatability specification based upon the relative volume repeatability values from Table 5.

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AccuPyc Volume, (cm <sup>3</sup> )	Percent of cup filled	Sample Mass (g)	Volume Cycle 1 (cm <sup>3</sup> )	Volume Cycle 2 (cm <sup>3</sup> )	Volume Cycle 3 (cm <sup>3</sup> )	Volume Cycle 4 (cm <sup>3</sup> )	Volume Cycle 5 (cm <sup>3</sup> )	Average Volume (cm <sup>3</sup> )	Relative Volume Repeatability
100	100%	115.5789	46.6764	46.6749	46.6793	46.6853	46.6894	46.6811	0.00043
100	100%	113.6955	45.9184	45.9226	45.9191	45.9203	45.9272	45.9215	0.00044
100	100%	111.3100	44.9476	44.9550	44.9644	44.9621	44.9659	44.9590	0.00044
100	80%	90.6356	36.6208	36.6312	36.6244	36.6331	36.6325	36.6284	0.00055
100	60%	67.8304	27.4352	27.4438	27.4441	27.4385	27.4392	27.4402	0.00073
100	40%	45.6852	18.5016	18.5151	18.5087	18.5106	18.5193	18.5110	0.00108
100	20%	22.3716	9.1226	9.1256	9.1247	9.1226	9.1119	9.1215	0.00219
100	10%	11.5790	4.7620	4.7661	4.7982	4.7933	4.8034	4.7846	0.00418
100	10%	11.1499	4.5719	4.5815	4.5777	4.5838	4.5830	4.5796	0.00437
100	10%	11.8456	4.8453	4.8557	4.8670	4.8692	4.8562	4.8587	0.00412

Table 5. Skeletal volume determined for five repeat analysis cycles of different glass bead test portions using 100 cm<sup>3</sup> AccuPyc.

AccuPyc Volume, (cm <sup>3</sup> )	Percent of cup filled	Sample Mass (g)	Density Cycle 1 (g/cm <sup>3</sup> )	Density Cycle 2 (g/cm <sup>3</sup> )	Density Cycle 3 (g/cm <sup>3</sup> )	Density Cycle 4 (g/cm <sup>3</sup> )	Density Cycle 5 (g/cm <sup>3</sup> )	Average Density (g/cm <sup>3</sup> )	Absolute Density Repeatability (g/cm <sup>3</sup> )
100	100%	115.5789	2.4762	2.4763	2.4760	2.4757	2.4755	2.4759	0.0011
100	100%	113.6955	2.4760	2.4758	2.4760	2.4759	2.4756	2.4759	0.0011
100	100%	111.3100	2.4764	2.4760	2.4755	2.4756	2.4754	2.4758	0.0011
100	80%	90.6356	2.4750	2.4743	2.4747	2.4741	2.4742	2.4745	0.0014
100	60%	67.8304	2.4724	2.4716	2.4716	2.4721	2.4720	2.4719	0.0018
100	40%	45.6852	2.4693	2.4675	2.4683	2.4681	2.4669	2.4680	0.0027
100	20%	22.3716	2.4523	2.4515	2.4518	2.4523	2.4552	2.4526	0.0054
100	10%	11.5790	2.4316	2.4294	2.4132	2.4157	2.4106	2.4201	0.0101
100	10%	11.1499	2.4388	2.4337	2.4357	2.4325	2.4329	2.4347	0.0106
100	10%	11.8456	2.4447	2.4395	2.4339	2.4328	2.4393	2.4380	0.0100

Table 6. Skeletal density determined for five repeat analysis cycles of different glass bead test portions using 100 cm<sup>3</sup> AccuPyc.

Notice that the maximum expected repeatability limits for a properly operating 100 cm<sup>3</sup> AccuPyc improves as the size of the sample test portion increases. Recall that the repeatability specification for the AccuPyc is independent of the amount of sample under test, and so as the amount of sample increases, the expected repeatability tolerance

decreases proportionately, both for the relative volume repeatability, and the absolute density repeatability.

The individual analysis cycle results for the analyses performed using the 10 cm<sup>3</sup> AccuPyc are shown in Tables 7 and 8. For this pycnometer capacity, again using equation (5), the absolute

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volume repeatability specification is  $\pm 0.0020 \text{ cm}^3$ , an order of magnitude smaller than that for the  $100 \text{ cm}^3$  AccuPyc, but since the cup capacity for the  $100 \text{ cm}^3$  pycnometer is ten times larger than that for the  $10 \text{ cm}^3$  AccuPyc, the relative volume repeatability for a given filled-cup percentage will be

the same for both pycnometers. And since the relative density repeatability is the same as that for the volume, and since the same sample, in this case glass beads, is being analyzed, the two pycnometers will produce results of the same quality, so long as the sample cup is filled to the same extent.

AccuPyc Volume, (cm <sup>3</sup> )	Percent of cup filled	Sample Mass (g)	Volume Cycle 1 (cm <sup>3</sup> )	Volume Cycle 2 (cm <sup>3</sup> )	Volume Cycle 3 (cm <sup>3</sup> )	Volume Cycle 4 (cm <sup>3</sup> )	Volume Cycle 5 (cm <sup>3</sup> )	Average Volume (g/cm <sup>3</sup> )	Relative Volume Repeatability
10	100%	12.5693	5.0742	5.0747	5.0762	5.0751	5.0758	5.0752	0.00039
10	100%	12.8731	5.1969	5.1976	5.1965	5.1973	5.1970	5.1971	0.00038
10	100%	12.3061	4.9681	4.9691	4.9680	4.9684	4.9686	4.9685	0.00040
10	80%	10.2633	4.1448	4.1447	4.1442	4.1445	4.1444	4.1445	0.00048
10	60%	7.5421	3.0463	3.0470	3.0479	3.0472	3.0477	3.0472	0.00066
10	40%	5.1660	2.0899	2.0899	2.0897	2.0905	2.0911	2.0902	0.00096
10	20%	2.4842	1.0066	1.0054	1.0068	1.0073	1.0072	1.0067	0.00199
10	10%	1.1971	0.4897	0.4877	0.4889	0.4891	0.4892	0.4889	0.00409
10	10%	1.3603	0.5554	0.5548	0.5552	0.5552	0.5540	0.5549	0.00360
10	10%	1.2785	0.5208	0.5213	0.5210	0.5200	0.5209	0.5208	0.00384

Table 7. Skeletal volume determined for five repeat analysis cycles of different glass bead test portions using  $10 \text{ cm}^3$  AccuPyc.

AccuPyc Volume, (cm <sup>3</sup> )	Percent of cup filled	Sample Mass (g)	Density Cycle 1 (g/cm <sup>3</sup> )	Density Cycle 2 (g/cm <sup>3</sup> )	Density Cycle 3 (g/cm <sup>3</sup> )	Density Cycle 4 (g/cm <sup>3</sup> )	Density Cycle 5 (g/cm <sup>3</sup> )	Average Density (g/cm <sup>3</sup> )	Absolute Density Repeatability (g/cm <sup>3</sup> )
10	100%	12.5693	2.4771	2.4768	2.4761	2.4767	2.4763	2.4766	0.0010
10	100%	12.8731	2.4771	2.4767	2.4773	2.4769	2.4770	2.4770	0.0010
10	100%	12.3061	2.4770	2.4765	2.4771	2.4769	2.4768	2.4768	0.0010
10	80%	10.2633	2.4762	2.4762	2.4766	2.4763	2.4764	2.4763	0.0012
10	60%	7.5421	2.4758	2.4752	2.4745	2.4751	2.4747	2.4751	0.0016
10	40%	5.1660	2.4718	2.4719	2.4721	2.4712	2.4705	2.4715	0.0024
10	20%	2.4842	2.4679	2.4709	2.4675	2.4661	2.4665	2.4678	0.0049
10	10%	1.1971	2.4447	2.4546	2.4483	2.4478	2.4469	2.4485	0.0100
10	10%	1.3603	2.4493	2.4519	2.4503	2.4499	2.4553	2.4514	0.0088
10	10%	1.2785	2.4551	2.4526	2.4538	2.4586	2.4545	2.4549	0.0094

Table 8. Skeletal density determined for five repeat analysis cycles of different glass bead test portions using  $10 \text{ cm}^3$  AccuPyc.

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A detailed look at the data in tables 6 and 8, where the repeatability of the individual density determinations are listed, shows that all of the individual density determinations, except for one, fall within the repeatability specification listed for each experiment. The first determination of the eighth analysis using the 100 cm<sup>3</sup> AccuPyc, with 11.5790 g under test, is lower than the expected repeatability tolerance for that experiment by 0.0014 g/cm<sup>3</sup>. This is the first of the three test portions analyzed with only 10% of the filled-cup amount of sample. A quick look shows that the skeletal volume of the sample is only 4.7846 cm<sup>3</sup> (average of the five cycles), and this is less than 5% of the capacity of the AccuPyc. It is due to the way that the beads pack in the sample cup that when essentially

filled the skeletal volume of the sample is only about 50 cm<sup>3</sup> rather than 100 cm<sup>3</sup>, and that when only 10% of the filled-cup amount is analyzed, the amount under test represents only 5% of the AccuPyc capacity. Thus the bulk density of the glass beads is only about 1/2 of the skeletal volume.

And so once again we answer the question, in this case, "What is the precision of the densities reported by the AccuPyc?" And as with the question about accuracy, or uncertainty, it depends upon the amount of sample under test, for both the 100 cm<sup>3</sup> and the 10 cm<sup>3</sup> AccuPyc. The same can be said for the other AccuPyc models as the same accuracy and repeatability equations (3) and (5), respectively, are used for AccuPyc models of all nominal capacities.