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Application Notes

压汞仪的空白和样品压缩校准

摘要

美国麦克仪器的 AutoPore 压汞仪系列产品是使用压汞法分析材料孔径分布的一款仪器。在测试过程中，由于样品性质或操作不当等问题可能会遇到 BaseLine Error，即基线错误，会对样品测试及测试结果产生一定的影响。基线错误是与样品材料的性质息息相关的，本文从基线错误产生的原因和对结果产生的影响开始，详细介绍了在不同情况下，如何解决基线错误的问题，并讨论了如何进行错误补偿，以便获取高精度的测试数据。

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Blank And Sample Compression Corrections for Mercury Porosimetry

Instrument Type: 9220

Technique: Hg Porosimetry

“Baseline” errors in AutoPore II 9220 data are errors that occur even when no sample is placed in the sample bulb and when a zero intrusion or extrusion volume of mercury would be expected as the pressure is increased to 60,000 psia and then decreased again.
The material which follows relates the causes of these errors and discusses ways to minimize and compensate for them when maximum accuracy is required.

Baseline Errors

When the AutoPore II 9220 applies pressure (up to 60,000 psia) to the mercury, penetrometer, and surrounding high pressure oil, compression occurs.

Compressibility effects account for a substantial portion of the baseline errors. The penetrometer bulb and capillary are made of glass which decreases in linear dimensions by about 0.8% and in volume by 2.3% at 60,000 psia. If the mercury were incompressible, a typical penetrometer having a 400 microliter capillary and a 5 milliliter bulb would experience a rise of mercury in the capillary of about 124 microliters or 31% of the capillary. Fortunately, mercury compresses also, but slightly more than glass such that the capillary actually falls some as the pressure is increased. The compressibility amounts to about 150 microliters in this example leaving a net fall of 26 microliters or about 6% of the capillary. The oil which surrounds the penetrometer and transmits the pressure to the mercury compresses at more than 10 times the rate

of the mercury and occupies only 3/4 the original volume at 60,000 psia. Some of the oil is in the electric field of the capacitor, especially around the sample bulb and its connection to the exterior. The dielectric constant of the oil increases with its density. This contributes an increasing capacitance which cancels some of the decrease due to the net fall of mercury with compression.

Other effects caused by compression arise from the plastic insulators which are used on the penetrometer bulb base to prevent an electrical short circuit. Not only does the plastic compress almost as much as the oil, but it lags behind and only slowly assumes its final density. This is especially pronounced upon release of pressure where the plastic may continue to increase in dimensions for almost an hour. It also tends to increase the dielectric constant and capacitance with increasing pressure. The pressure vessel expands as the internal pressure is increased and, like the plastic, requires considerable time to stabilize. The resulting changes in spacing from the sample bulb to the walls and bottom causes a decrease in capacitance. Micromeritics has minimized this effect by making the initial spacings as large as is practical.

Another effect, and the one most difficult to predict, arises from the similarity of the penetrometer to a thermometer. This would not be troublesome if its temperature could be maintained constant, but compression of the surrounding oil causes a temperature rise of nearly 50°C in the oil and a smaller change in the glass and mercury. How quickly this heat is transferred to the mercury depends upon how rapidly the pressure is being increased, the relative amounts of oil and mercury present, and how recently the vessel has been previously cycled and the metal and oil warmed relative to the penetrometer. Release of the pressure causes the inverse effect, chilling the oil and setting up a reversal of the heat flow. The

thermal gradient across the glass of the penetrometer may be considerable such that little benefit may be derived from precisely equalizing the temperature coefficients of the mercury and glass. As might be expected this problem is worst when the sample bulb is large and the capillary volume small. Choosing the right penetrometer helps minimize this effect. Make sure the sample nearly matches the size of the sample bulb and that the capillary volume is large enough to satisfy intrusion.

Approaches to Error Compensation

Situations arise where the typical errors of about 1.0% of capillary volume are significant or where the errors exceed this level due to unfavorable sample characteristics. Most commonly, this happens when one of the following is encountered: 1) The amount of sample available is so limited that the intrusion volume is only a small fraction of the smallest diameter capillary; 2) adequate sample is available but the porosity is so low that a limited amount of the smallest capillary is used even though the largest sample bulb is filled; 3) the sample is of small or moderate porosity and its compressibility or thermal properties differ considerably from those of mercury; 4) accuracy and reproducibility specifications have been imposed at levels tighter than the typically expected levels for mercury porosimetry. In such cases "blank corrections" may be used to advantage.

Micromeritics' AutoPore II 9220 provides four different ways to apply blank corrections. The first, and simplest, is by use of stored formulas based upon averages of large numbers of blank runs on mercury-filled penetrometers under varying rates of pressure build and release. No provisions are made for entering compressibility data or thermal data since these numbers are seldom known and the formulas would become very complex. Typical examples of blank runs are shown in Figures 1, 3

and 7. Typical examples of formula blank correction of data are shown in Figures 2 and 6. It is very important that trial blank runs be made when applying these formulas to ensure that a reasonable degree of correction is actually attained under the running conditions being used.

The second technique is apt to be much more useful. It permits the user to run a blank run, store the results using the exact run conditions and penetrometer type to be used for the real sample, and subtract this result from other runs. Examples of correction by subtracting a blank run file are shown in Figures 4 and 8.

The third technique provides the highest degree of compensation possible and can be attained when the exact penetrometer to be used later is loaded with a non-porous sample of the same weight and material as the porous sample to be run later. When analyzed, the non-porous sample will expose all the aforementioned compressibility effects which can then be subtracted from the porous sample run. This third technique has the advantage of compensating for differences in compressibility and thermal effects between mercury and the sample material. Care should be exercised that the interval between runs, oil temperature, and penetrometer temperature, and any other initial conditions are made as nearly identical as possible. Figure 9 is a typical baseline run so obtained. Figure 10 is a subsequent blank run corrected using the Figure 9 data and shows the actual degree of correction attained.

Besides running blank runs, correction files may be created by manually entering the data. This fourth technique allows entry of the average of several blank runs, assuring a representative correction.

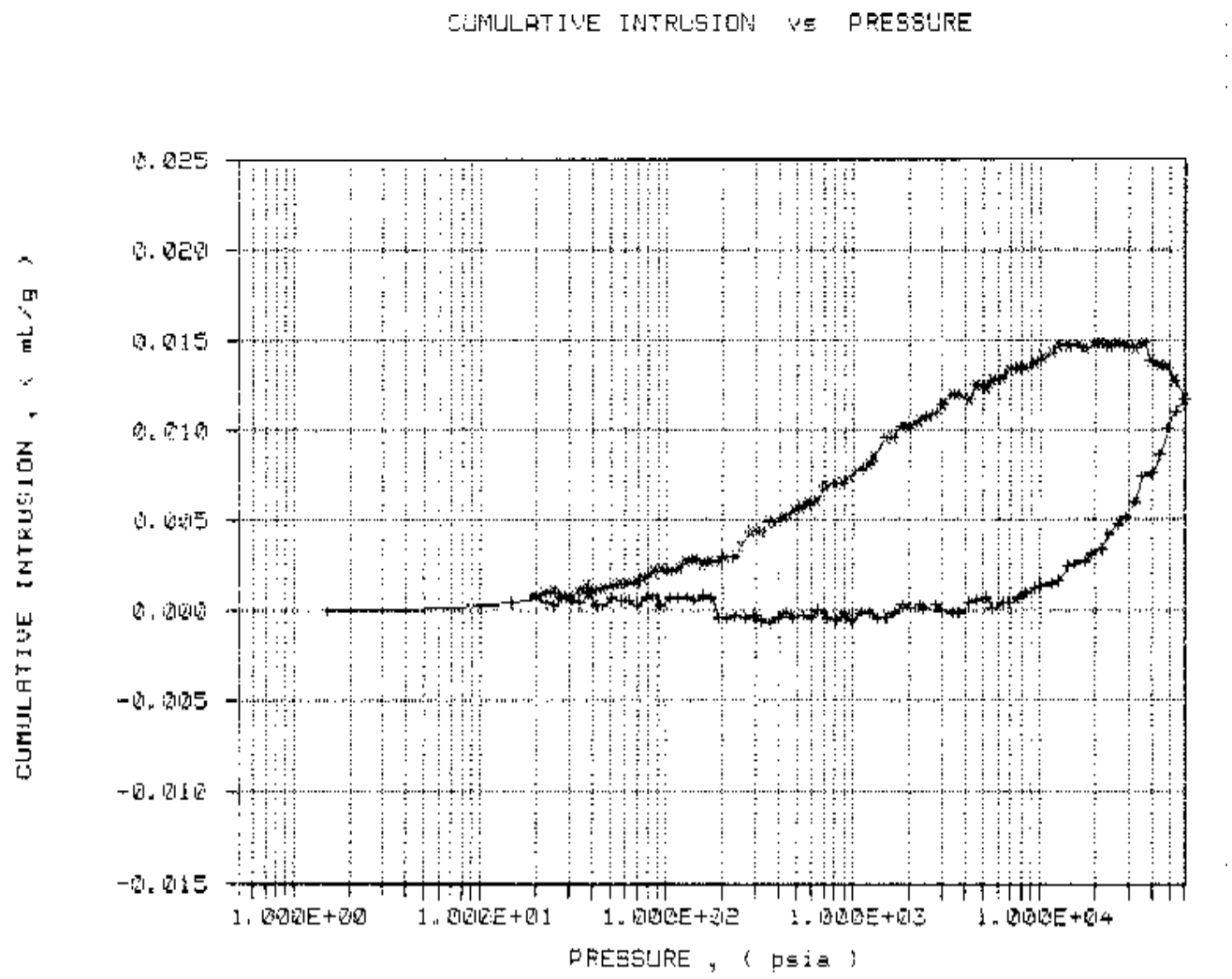

Figure 1

A blank run on a 5mL powder penetrometer with a 1.1 mL stem volume. The rise in the initial depresurrization data is primarily caused by thermal effects. As the hydraulic fluid is allowed to expand, it cools. This in turn cools the mercury in the penetrometer, causing it to contract and recede in the stem, giving the appearance of positive intrusion during depressurization

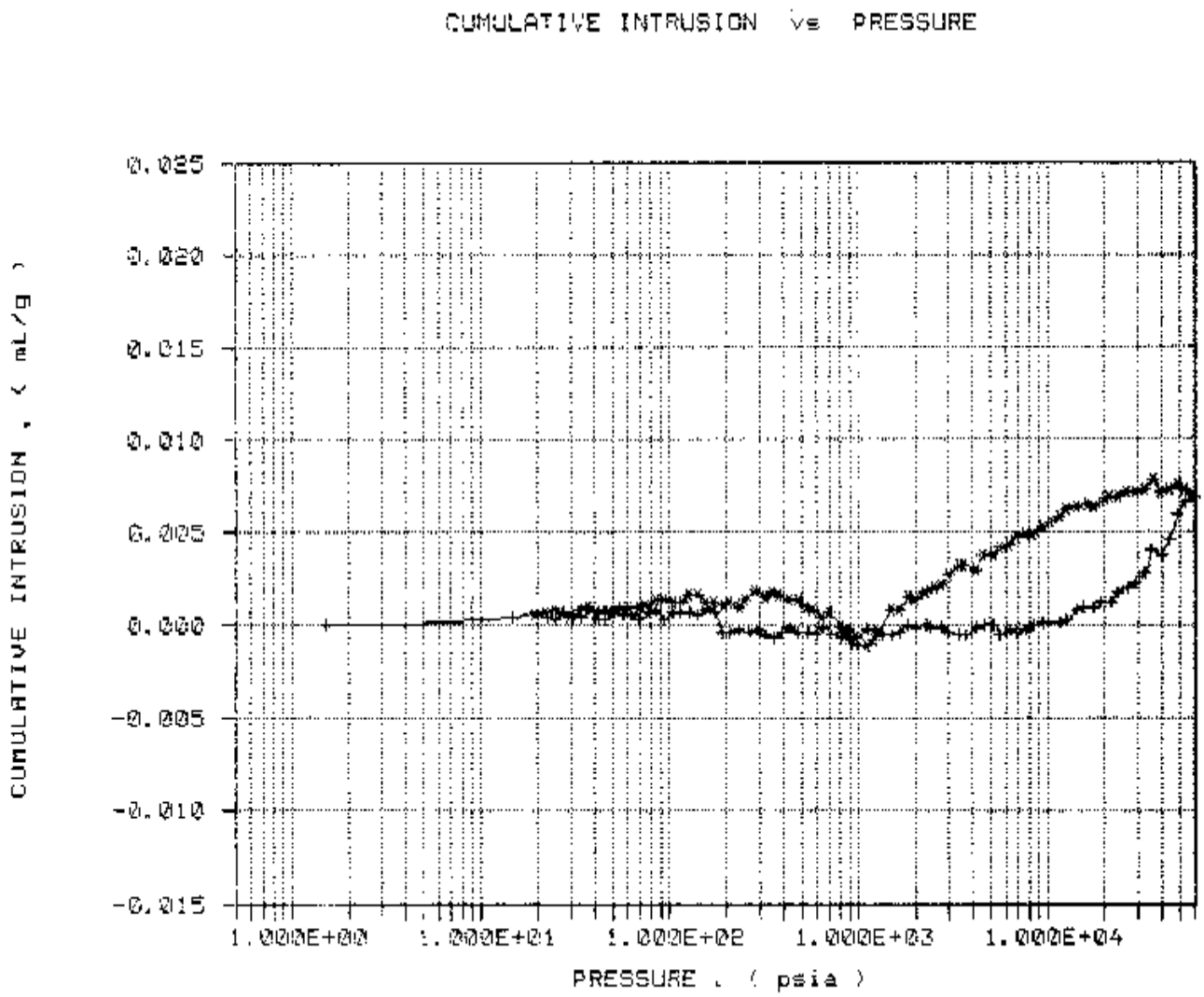

Figure 2

The difference between the blank data in Figure 1 and the formula blank correction for a run under the same conditions. The formula cancels some of the error, but does an imperfect job in this case.

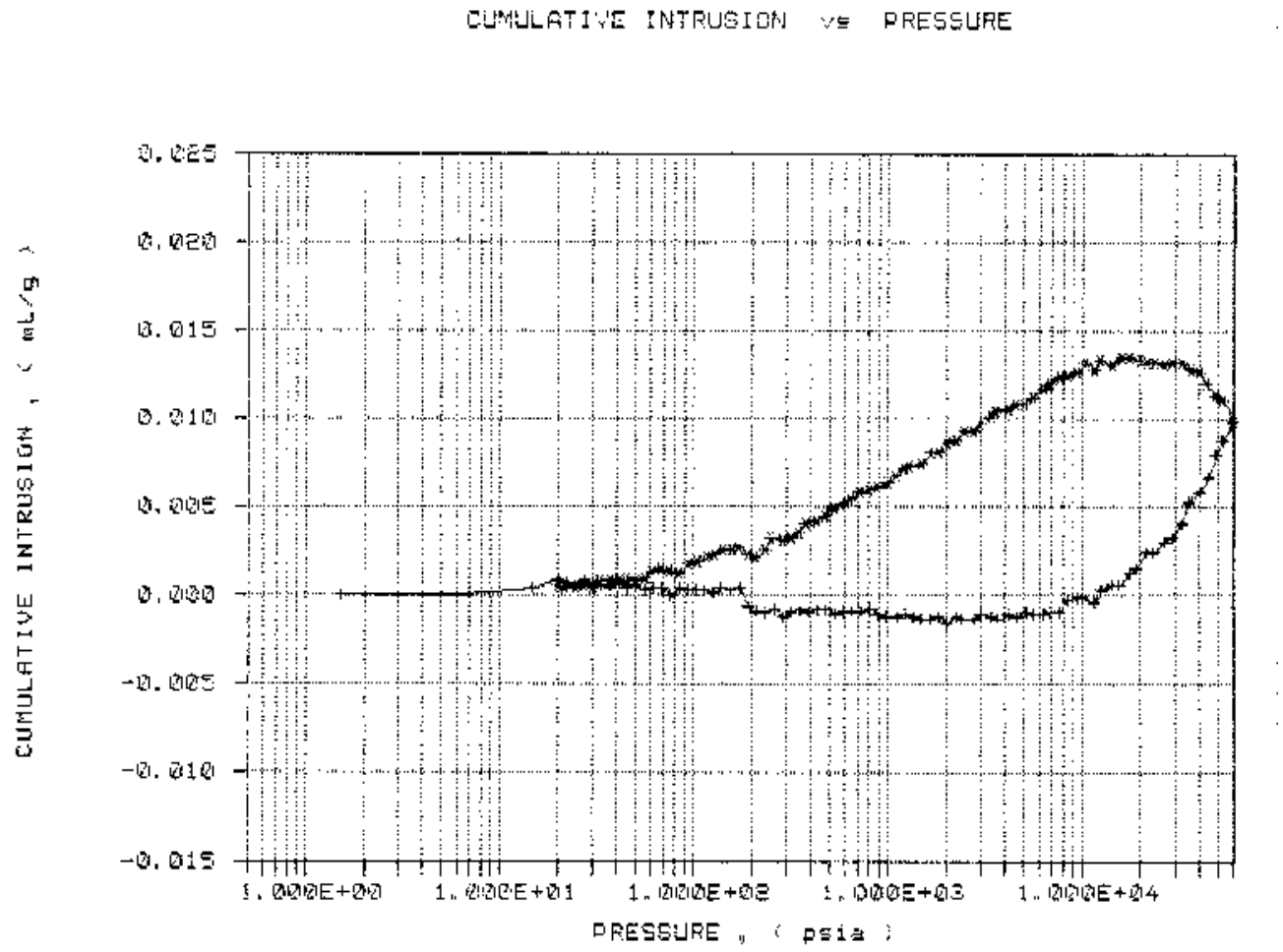

Figure 3

Another blank data set taken under identical conditions to those for Figure 1. The similarity between the two blank data sets is an indication of the excellent repeatability of blank runs

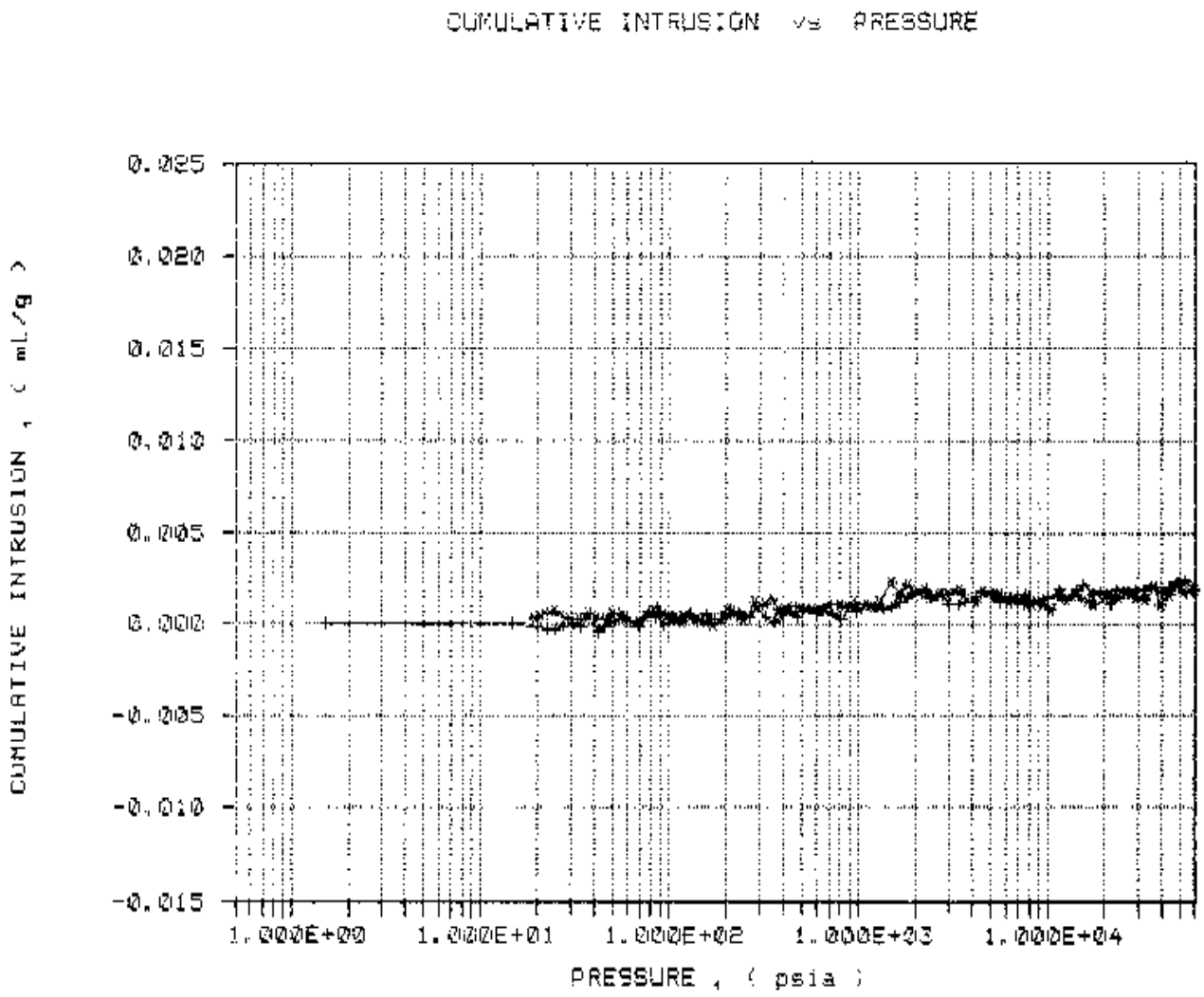

Figure 4

The difference between the blank data from Figure 1 and the blank data from Figure 3. This demonstrates that blank data collection and subtraction is a powerful method for accurately removing blank error from sample data.

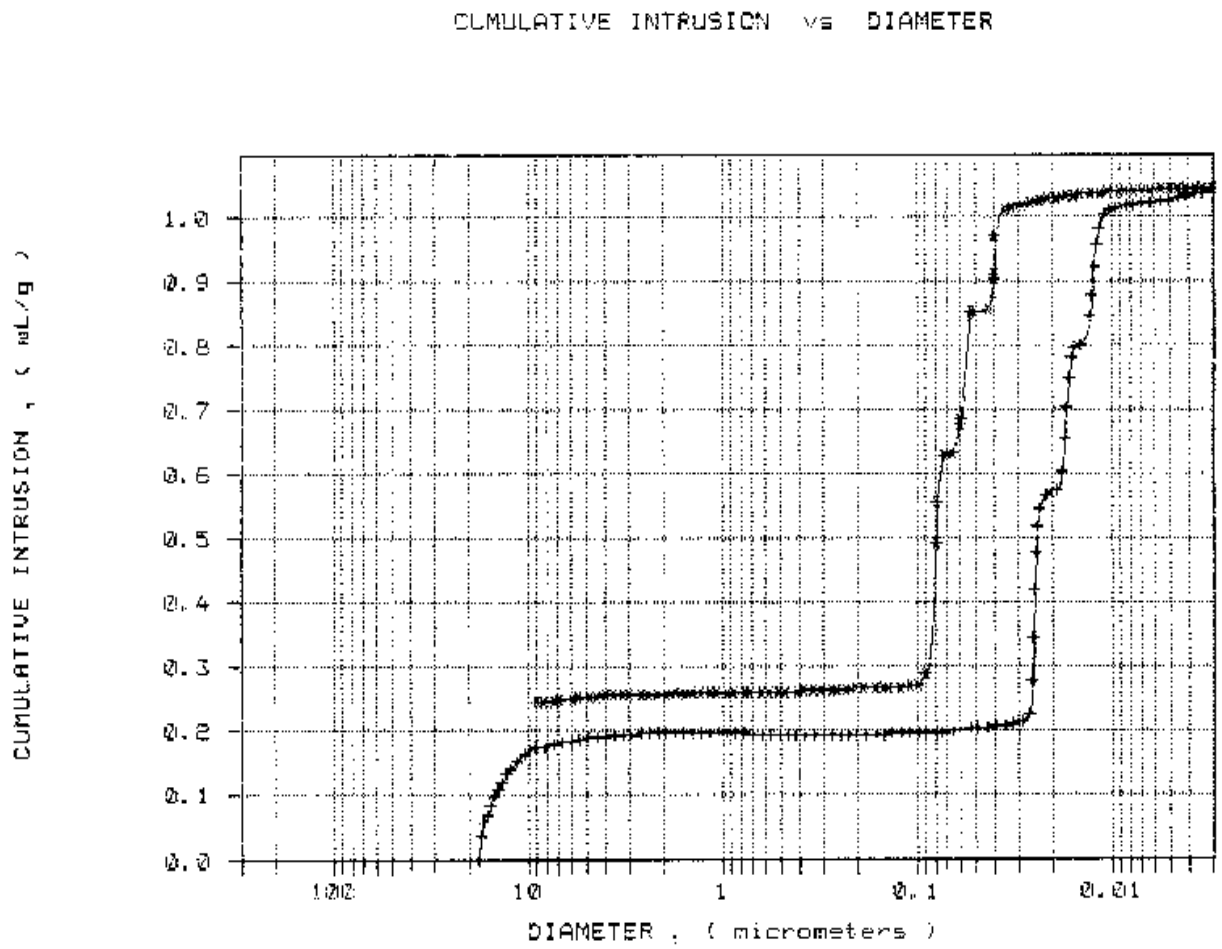

Figure 5

Uncorrected data from analysis of a sample of controlled pore glass made of a mixutre of three pore sizes. Note the three distinct regions of intrusion between 0.03 and 0.01 micrometers on the pressurization curve, and the corresponding extrusion regions. The apparent intrusion at sizes above 10 micrometers is due to interparticle filling. The apparent intrusion between 0.01 and 0.003 micrometers, and the "loop" in the extrusion curve from 0.04 to 0.003 micrometers, are due to a combination of sample compression and blank error. There is no actual intrusion in this region.

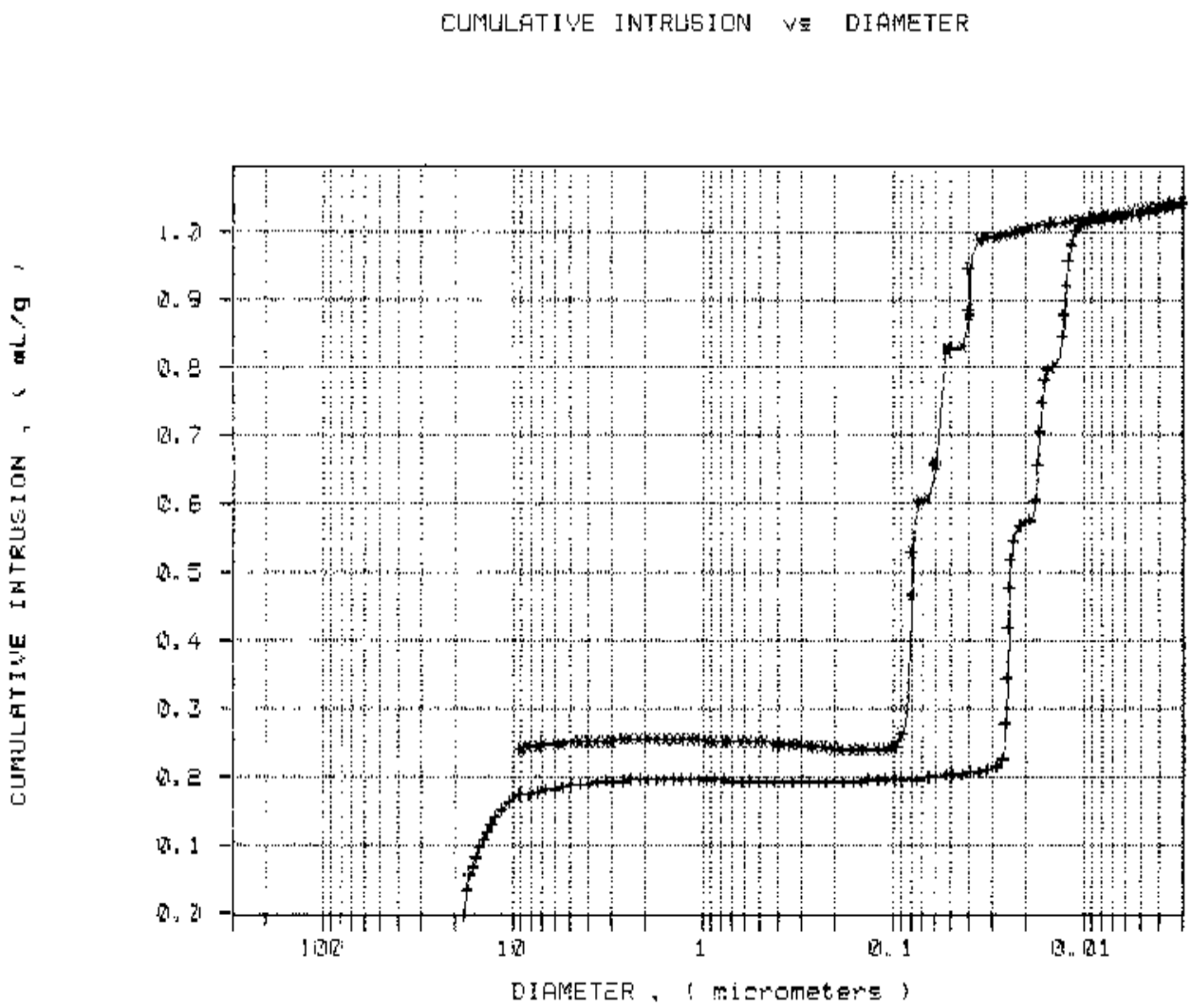

Figure 6

The data from Figure 5 with the formula blank correction applied. Note that the rise at the top due to blank error has been removed, but the apparent intrusion due to sample compression remains. This is because the formula makes no attempt to account for sample compression.

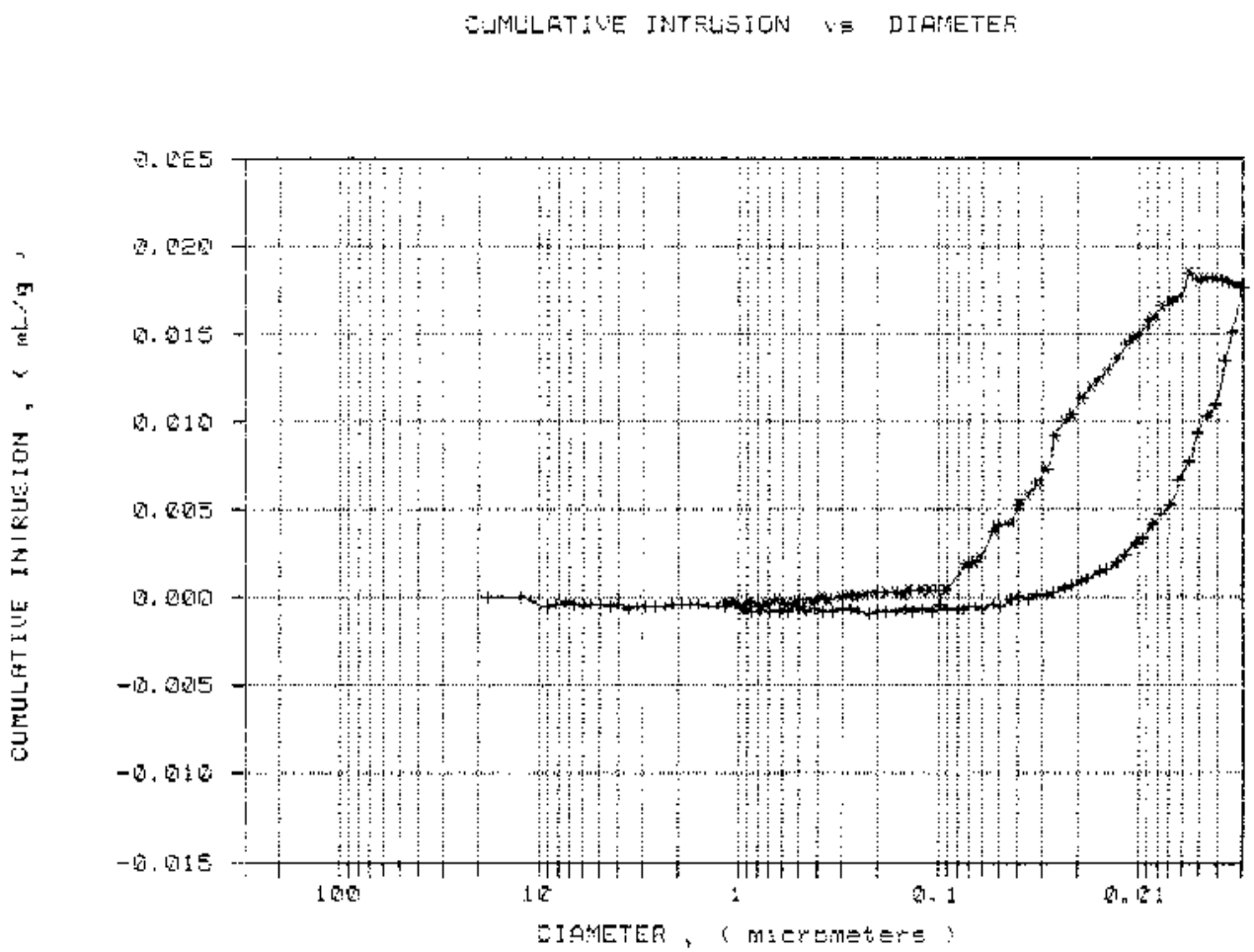

Figure 7

A blank run with the same type of penetrometer under the same conditions as the sample in Figure 5. It is dominated by the initial increase between pressurization and depressurization, primarily due to thermal effects.

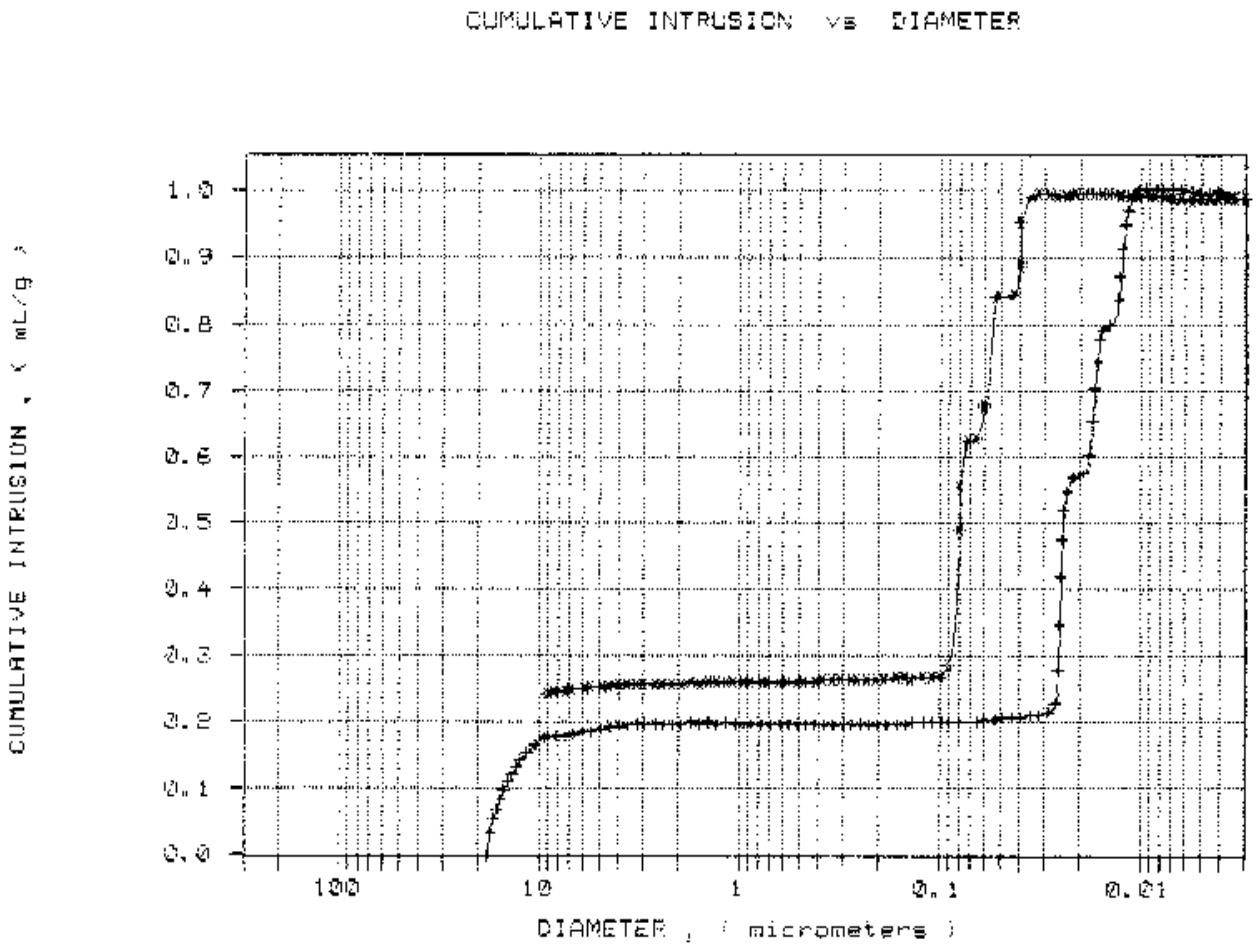

Figure 8

The sample data from Figure 5 corrected by subtracting the blank data from Figure 7. Note that practically all of the blank error and compression data have been removed, leaving only the filling curve and the actual intrusion. The sample compression is effectively cancelled because the compression coefficient of mercury is close to that of the controlled pore glass used as sample. Many solid materials have compression coefficient fairly close to that of mercury, making this a very effective means of blank correction in many cases.

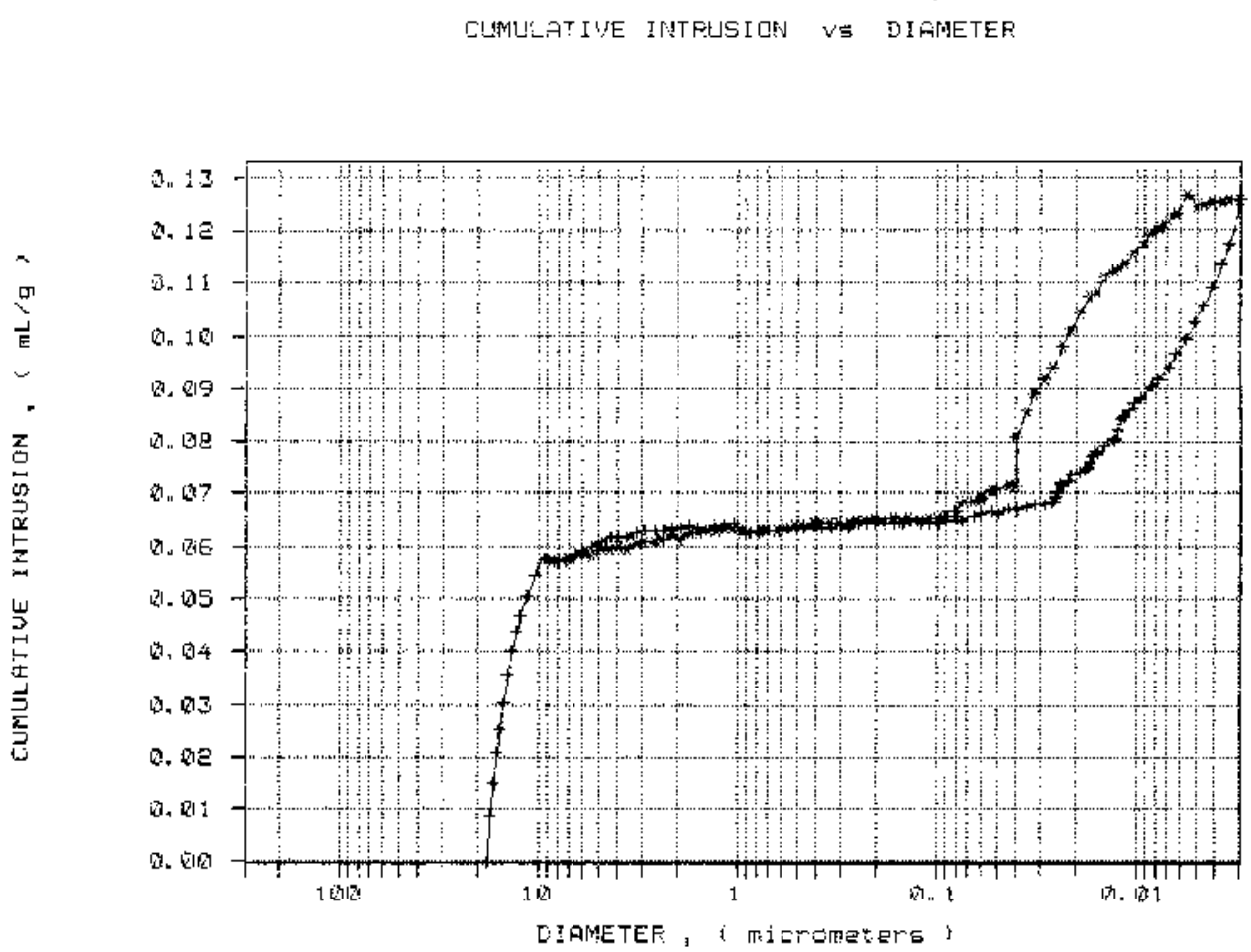

Figure 9

Uncorrected data from an essentially non-porous sample of the same type of glass shown in Figure 5. The weight of sample used was approximately equal to the weight of porous sample analyzed, so that the same volume was occupied. Note the filling curve and the blank error "loop". The slight incline of the intermediate plateau and the angle of the "loop" are due to compression of the sample.

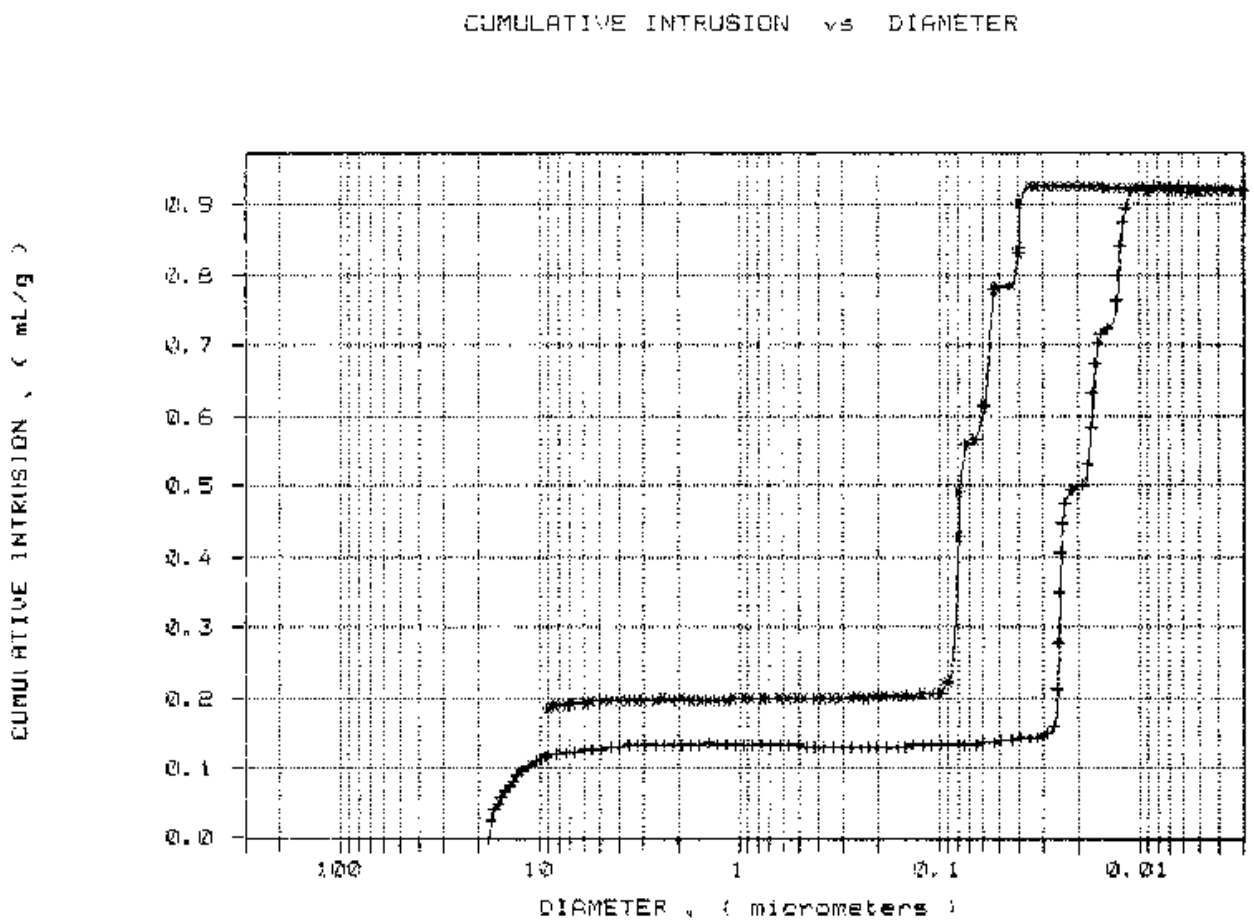

Figure 10

The difference between the porous sample data of Figure 5 and the non-porous sample data of Figure 9. Some of the filling curve has been removed, as well as all blank error and sample compression effect, leaving an accurate picture of the actual intrusion. This is the preferred method of blank correction, especially for materials with compression coefficients substantially different from that of mercury, and where maximum accuracy is desired