

# High-Precision Density Measurements of Energetic Materials for Quality Assessment

Dirk Herrmannsdörfer<sup>\*[a]</sup> and Thomas M. Klapötke<sup>[b]</sup>

**Abstract:** Even though helium pycnometry is considered a very precise method of density determination, its use to analyse factors influencing crystal quality (e.g. solvent inclusions, amorphous states, crystal defects...) is limited due to the unknown inherent accuracy of the method. Previous studies have attempted to identify the best possible accuracy of helium pycnometry. However, no robust method has been proposed to validate even the precision obtained. This means that the often occurring, seemingly random density deviations have never been satisfactorily explained. In this study the influencing factors on density measurements of the CL-20/HMX cocrystal and phase stabilised ammonium nitrate carried out with an AccuPyc 1340 TEC were

quantified and a robust method of data analysis was developed to judge with certainty the quality and significance of the data obtained. This study shows that statistical tests such as the t-test and ANOVA cannot be utilised to differentiate between samples or repeat measurements, even though the density data points exhibit a normal distribution. By utilising confidence intervals and quantifying the three major sources of error (sampling error, change in barometric pressure during the measurement, and weight in error), a repeatability of 0.015% was achieved and a method was developed that enables differentiation between samples with a certainty as good as 0.05%.

**Keywords:** ANOVA · CL-20 · Density · Gas pycnometry · HMX

## 1 Introduction

The skeleton density of solids is a useful tool in chemical industry and research for the detection of, for example, processing efficacy [1], composition [2], or for characterisation [3]. Specifically in the field of energetic materials, the density can be utilised to calculate the detonation velocity [4], assess the explosive's quality [5], or the success of the generation of a pressed composition.

The skeleton density is most commonly obtained by gas pycnometry which is considered to provide the closest approximation of the skeleton density [6]. Of the available density determination techniques of solids, gas pycnometry is one of the most user friendly due to the availability of easy to operate consumer grade devices lending it an air of simplicity that invites people to regard gas pycnometry as a standard analysis method. The high precision of pycnometry is strongly dependent on the measurement conditions as has been shown previously [6]. And even under optimised conditions, errors to the measurements remain, and in-depth analysis is required to judge with confidence whether a repeat measurement is valid and whether one sample is significantly denser than another. Viana *et al.* [6] have published what is probably the most in-depth analysis of the influences on and optimal conditions for pycnometric density determination. Since then, some studies have used ANOVA [7] or confidence intervals [3] to analyse their results, but no fundamental analysis of the statistical character of the pycnometric measurement and the impact

of the varying influences on the measurement have been published. So, to this date it is unexplored what the true accuracy of a pycnometric measurement is and whether the nature of the obtained data points even allows for the use of statistical tests. Here we expand on some of the previously reported challenges to a successful density measurement and the steps to optimise it and present additional challenges and the necessary data analysis of the results. Viana *et al.* [6] concerned themselves mostly with the quest for maximum accuracy of the data and closed their paper with the assessment that for the differentiation of products of different crystallinity, hydration, and polymorphic form


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very close density values must be compared and that this comparison is greatly influenced by the calibration of the device. Therefore, the first step in optimising gas pycnometric measurements on the quest for highest discriminatory power of samples must be to maximise the precision of repeat measurements but leave reproducibility for future studies. This study aims to explore the precision limits of helium pycnometry by investigating which errors dominate the density measurement, how to minimise these, and whether statistical test such as the t-test and ANOVA are applicable to optimised pycnometric density measurements to allow for statistically backed discrimination between samples under repeat conditions. If sufficient precision is achieved, helium pycnometry can be applicable for the quality assessment of the CL-20/HMX cocrystal discussed in this paper. The solvent content of the cocrystals, which depends on the crystallisation technique, ranges from traces of solvent (C3) through to 0.07% (C2) and up to 0.3% (C1), which correlates with an expected density difference of 0.0018 g/cm<sup>3</sup> for C3-C2 and 0.0097 g/cm<sup>3</sup> for C3-C1. While it is obvious from literature data that a difference of 0.0097 g/cm<sup>3</sup> is detectable, it is unclear whether 0.0018 g/cm<sup>3</sup> or even smaller differences can be resolved. Detection of such differences would make it possible to utilise gas pycnometry as a valuable tool for quality assessment of energetic materials of highest quality, a role that was formerly reserved for more sophisticated but hard to operate and time consuming methods such as density flotation [8].

## 2 Material and Methods

Sample mass was determined using a Kern 770 analytical balance (accuracy 0.1 mg).

The pycnometer was operated and reports compiled utilising the AccuPyc 1340 Windows Software.

Density measurements were carried out using a micromeritics AccuPyc 1340 TEC 10 cm<sup>3</sup>. This configuration includes a temperature-controlled Peltier element. The heating/cooling element was set to 19.8 °C for all measurements to achieve an average chamber temperature close to 20 °C (the chamber temperature can vary depending on the room temperature by about 0.4 K for the measurements presented here). Two chamber inserts can be utilised to reduce the chamber volume from 10 cm<sup>3</sup> to 3.5 cm<sup>3</sup> and 1 cm<sup>3</sup>, respectively. Sample cups were fitted with AccuPyc filter caps (10 µm pore diameter) to prevent the fluidation and discharge of sample material during measurements. The basic measurement principal is described elsewhere [6,9]. He 5.0 was used as measurement gas. Between 1 and 100 purging cycles were carried out before measurement (see supporting information for specifics on each measurement). For most measurements, a fixed equilibration time of 60 seconds was utilised.

All utilised statistical methods have been carried out using OriginPro version 2019 9.6.0.172, OriginLab Corporation, Northampton, MA, USA.

ε CL-20 (lot number 573598) was obtained from SNPE. The chemical purity has been determined via <sup>1</sup>H NMR and HPLC to be 98.3 and 99.4%, respectively. Further analysis details are found in the supporting information. β HMX (lot number NSI 00E 000 E004) was purchased from Chemring Nobel. The chemical purity has been determined via <sup>1</sup>H NMR and HPLC to be 98.7 and 99.3%, respectively. Further analysis details are found in the supporting information. Ammonium nitrate 99.86% (LA 84802524) was purchased from Borealis Agrolinz Melamine GmbH. The Ni and NH<sub>3</sub> content of the PSAN was 2.5% and 0.9%, respectively.

## 3 Results and Discussion

In the following paragraph challenges to an accurate density measurement of energetic materials and ways to face them are presented. This list is likely not exhaustive, but it is based on the findings of Viana *et al.* [6], the ISO12154 [9], and the result of the measurements carried out of the abovementioned materials. In all likelihood additional challenges might occur with different materials such as for example extremely porous or amorphous substances. It is important to note that the aim of this study is to maximise the precision of the measurements to push the limit of significant comparison of samples as far as possible. Following the terminology of DIN ISO 5725 [10], if

$$y = m + B + e$$

with  $y$  being the measurement result,  $m$  the calculated mean,  $B$  the laboratory bias under repeatability conditions and  $e$  the random error occurring in every measurement under repeatability conditions, most of the optimisations presented here aim to minimise  $e$ . Minimising  $e$  maximises the precision of the measurements, but has only a partial influence on the accuracy of  $y$ . Therefore, samples can only be compared under repeatability conditions i.e. under conditions for which  $B$  is constant. It is obvious that an approach that also minimises  $B$  would be preferable. As, however, for example the varying calibration standard volumes in the study of Viana *et al.* [6] have shown, some factors of  $B$  are possibly uncontrollable and a statistically sound verification of the accuracy is far beyond the scope of this study.

### 3.1 Sample Volume

Chamber and reference volume of gas pycnometers are typically calibrated using calibration standards in form of metal spheres. Maximum precision and trueness are achieved when the sample volume is identical with the volume

of the calibration standard. Often times, however, the bulk density of a material is significantly lower than its skeleton density. Typically, in these experiments a sample volume of less than half of the calibration standard volume was achieved by filling the sample chamber up to 75% (as specified by the manufacturer) and without compaction of the solid. To be able to estimate the resulting increase in standard deviation the calibration standard of the 3.5 cm<sup>3</sup> cell (measurement K1) and the calibration standard of the 1 cm<sup>3</sup> cell (measurement K2) were measured in the 3.5 cm<sup>3</sup> cell. Both measurements achieved an identical volume standard deviation of 0.0004 cm<sup>3</sup>; the density standard deviation of the smaller calibration standard was, however, over three times the standard deviation of the larger calibration standard (0.0088 cm<sup>3</sup> and 0.0023 cm<sup>3</sup>, respectively). This factor 3.8 difference in density standard deviation is the result of the factor 3.5 difference in volume between the standards. One can, therefore, assume that by only obtaining half the calibration volume the standard deviation of the experiments is twice as high as necessary. The achievable sample volume can be increased by compacting the sample (increasing the bulk density) in the process of weighing in and by filling the sample cup higher than the recommended 75% filling height. The recommendation of 75% percent filling height is most likely the attempt of the manufacturer to prevent liability in case of product discharge from the sample cup, as the likelihood of such an occurrence increases with increasing filling height. "Overfilling" the sample cup should, therefore, only be considered if the sample material is certain to not be fluidised by the pressure drop during measurement and if the material is coarse and dense enough to not be carried along by the gas flow. Another very important aspect of the sample volume is that the measured sample density is dependent on the sample volume. Multiple studies [6,7,11] show that with decreasing filling ratio the measured sample density decreases. This trend is shown exemplary in Figure 1 for the measurement

of glass beads carried out by micromeritics [11]. Note that the deviation of the obtained density value from the maximum value is larger than the determined density repeatability for a cup filling percentage of under 40% in this test. Furthermore, it is important to note that 100% of cup filled means no more glass beads could fit in the sample cup, but even then the sample fills only 47 cm<sup>3</sup> of the 100 cm<sup>3</sup> sample cup. Based on the trend in Figure 1 one can assume, that at least for glass beads the sample volume has a small influence on the obtained density if the sample volume is more than half of the sample cup volume.

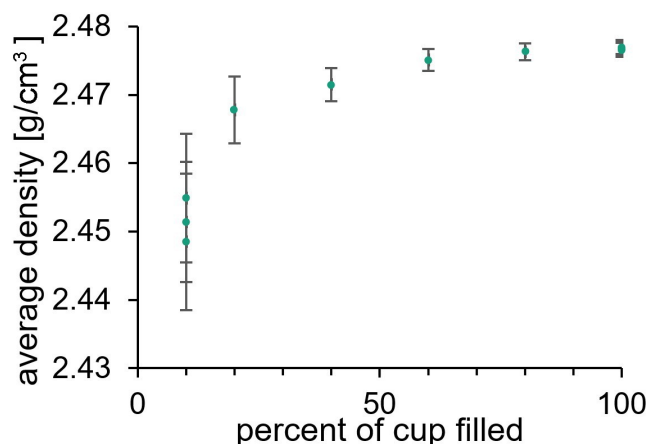
For maximum comparability it is still advisable to match the weight in as much as possible on repeat measurements and sample comparisons.

### 3.2 Chamber Volume

It is essential for the density determination that the measurement chamber volume is constant. Many factors can contribute to a change in chamber volume. In some gas pycnometers the sample chamber lid does not exhibit a defined stop. Here it is important to always apply the same torque when closing the lid. Other pycnometers require the application of vacuum grease to the seal. Here a calibration of the sample chamber volume after application should be carried out to accommodate for the change in grease volume. Furthermore, grease must be applied sparingly even when recalibration is carried out to prevent changing chamber volumes over time as the grease might be squeezed out of the chamber over the course of measurements. Other factors can contribute to a change in chamber volume such as scratches in the sample cup or sample remains in or on the sample cup and chamber. Residues in the mg-scale can already be enough to significantly alter the obtained density value. Therefore, manipulation of the sample cup should always be carried out wearing gloves to prevent water and fat deposition, and thorough cleaning should succeed every measurement.

### 3.3 Calibration

Chamber and reference volume calibration should be carried out with the same level of care as sample measurements. This includes to use the same number of data points (if possible by the programming of the pycnometer) as this increases the quality of the calibration. A calibration should always be verified upon completion. One easy method is to measure the calibration standard. By inserting the standard's volume as the sample mass, a value of 1 g/cm<sup>3</sup> is received that is henceforth called "density". If the determined "density" diverges significantly from 1.0000 g/cm<sup>3</sup>, recalibration is necessary. Typically, a "density" in the region of 0.9999 and 1.0001 g/cm<sup>3</sup> is achievable. An even better validation of the calibration is to utilise an auxiliary volume



**Figure 1.** Measured density of glass beads dependent on the percentage of fill of the sample chamber.

standard, because if the calibration standard itself is damaged or altered, validation with it will still result in seemingly good values. As Viana *et al.* [6] have shown, their calibration standards of the three sample chamber volumes exhibited a correlated increase and decrease in volume over a 6-month period. As it is unlikely that the calibration standards would concerted increase and decrease in volume (except for temperature effects) it is more likely that changes in the pycnometer itself or in the surrounding conditions are responsible. The only true validation of a density value can, therefore, only be obtained by measuring the same sample in different pycnometers.

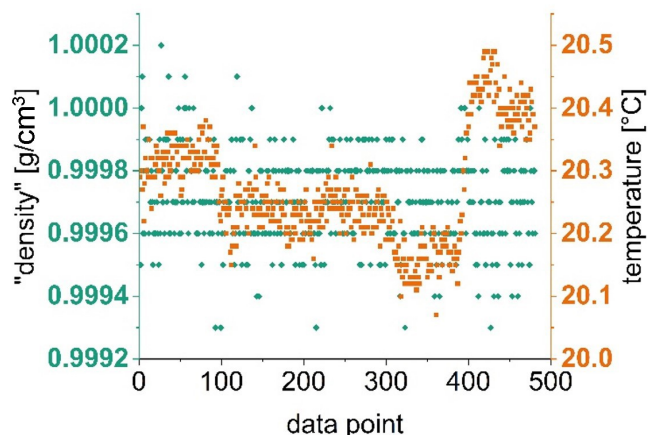
### 3.4 Leak Tightness of the Helium Line

Even though for many substances it is almost irrelevant whether helium or nitrogen is used as measurement gas, it can be very important to ensure that the helium line is free of leakages. This can be most efficiently carried out by utilising specialised portable helium leak detectors. If a helium leak occurs in a non-permanently pressurised part of the helium line, the line will fill with air that is subsequently flushed through the sample chamber in the pycnometer. This can be detrimental if the sample is hygroscopic or reactive towards oxygen or water.

### 3.5 Room Climate

The room temperature can have a significant impact on the quality of a pycnometric measurement, as the density of most materials is temperature dependent. Ideally, a measuring room should be conditioned to 20 °C, and a pycnometer with active temperature control should be employed. If no climatisation is available, varying room temperature in general does not exclude the possibility of high precision measurements. Even under room temperature deviations of 10 K over the course of 24 h, stable density measurements are possible under the condition that the pycnometer is equipped with a heating/cooling device. In Figure 2 the measured “density” of the measurement K3 of the calibration standard of the 3.5 cm<sup>3</sup> cell and the chamber temperature are displayed over the number of data point. The temperature trend is the result of the decreasing room temperature overnight, and the increase in temperature in the morning at around data point 400 was caused by the automated room heating. Even though the room temperature increased by around 5 K over the course of minutes, no influence on the measurement is apparent (the determined “density” of 0.9997 g/cm<sup>3</sup> indicates that a calibration was necessary for following precision measurements).

The other influence of temperature – the decrease of material density with increasing temperature – appears to be too weak for the calibration standard to be noticeable



**Figure 2.** Overlay of the temperature data points (orange squares) and the “density” data points of K3.

here. However, the measurement temperature is not inconsequential. For the cocrystal discussed later, the thermal expansion can be estimated from the cryogenic crystal density of 2.001 g/cm<sup>3</sup> at 95 K [12] and the room temperature density of 1.957 g/cm<sup>3</sup>. By assuming a constant expansion coefficient in this temperature frame, a 1 K temperature difference should amount for a density difference of around 0.0002 g/cm<sup>3</sup> which can be quite significant.

### 3.6 Sample Dryness

Of all the abovementioned factors none is as impactful on the quality of the received data as the sample’s water content and none is as counterintuitive. With the exception of the calibration standards, all measured samples discussed in this paper exhibited a decrease in measured density over the course of 10 to 400 data points. And while it appears obvious that evaporating water could not be responsible, because water evaporation should decrease the sample volume and, therefore, increase the density over time, the opposite is the case [6,7,9,13–15]. As the pressurised helium is virtually free of water the partial pressure of water is also zero. As a result, even strongly hygroscopic material in most cases will release water if no special care has been taken to ensure sample dryness. The continuous evaporation of water will increase  $p_1$  (pressure after charging the sample chamber with helium) and  $p_2$  (pressure after equilibration of the sample chamber pressure and reference chamber pressure) values. Even though both values are increased, only the increase in  $p_2$  influences the volume determination, as an increase in  $p_1$  only offsets the system pressure. An increased  $p_2$  due to evaporating water during the equilibration period seemingly indicates a lower sample volume and, therefore, a higher sample density. It is for this reason, even though the sample loses volume in form of water, the measured sample volume increases with each data point, as

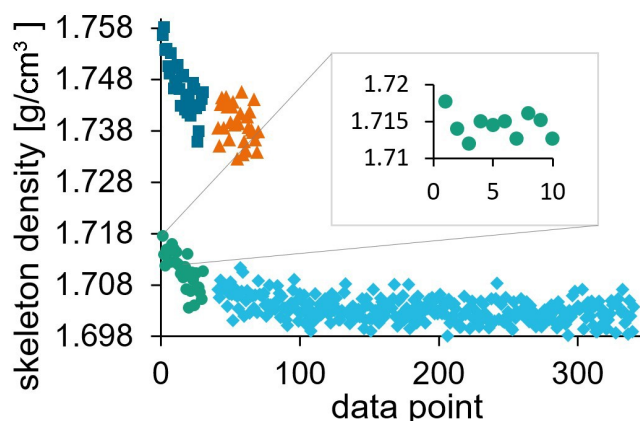


less and less water evaporates over time. The effect of the evaporated water on the measurement is magnitudes stronger than the effect of the loss of condensed water in the sample, because the volume of the gaseous water is several hundred times larger. Kikuchi *et al.* [15] have written a very comprehensive derivation of the density error due to water evaporation.

Insufficient sample dryness can result in multiple different implications for the result of a density measurement. A too wet sample might not be measurable at all, as too much water evaporates constantly and the equilibrium condition is not met within the permitted time frame. A wet but hygroscopic sample might lose water slowly enough that the equilibration condition is met, but does not reach a constant volume for hundreds of purging/measuring cycles [13] and the obtained density in the end is too high, as the sample has lost mass (and, therefore, volume) since it has been weighed in (this can be remedied by additional weighing of the sample after the density measurement and recalculation of the density based on the new sample mass [9]). Even a non-hygroscopic sample might have substantial amounts of water adsorbed especially if the crystalline structure exhibits cracks or pores. In the following, the density trend over time is discussed for two material systems.

### 3.6.1 Phase Stabilised Ammonium Nitrate (PSAN)

Ammonium nitrate is hygroscopic. PSAN [16] typically exhibits a water content of around 0.2% after processing. Sample drying in vacuum, however, could be detrimental to the stability of the instituted amine complex. For a good measurement it is, therefore, required to increase the number of purging cycles to eliminate the initial drop in density. Typical measurements of PSAN are displayed in Figure 3. The blue squares (PSAN1) and orange triangles (PSAN2) data points are two consecutively carried out density measurements on the same sample. The green circles (PSAN3) and teal rhombs (PSAN4) data points are two consecutively carried out density measurements of a sample of a different PSAN batch. The data gap between measurements is the representation of the ten purging cycles carried out at the beginning of each measurement. Several findings can be derived from the data. The density drift for both samples is around  $0.02 \text{ g/cm}^3$  with 20% deviation between the two. The reduction in density appears to exhibit an exponential decline which is congruent with the idea of evaporating water. As a result, no clear endpoint to the drift can be defined. For efficiency reasons it was stated that 60 flushing cycles are sufficient to reduce the density drift to an acceptable level, even though a weak drift appears to be present in the data points of PSAN4 even after 100 data points. While the PSAN1 data points exhibit an obvious drift during the whole measurement, the PSAN3 data points do not. Especially the first 10 data points might mislead an operator to assume density constancy, even though a strong

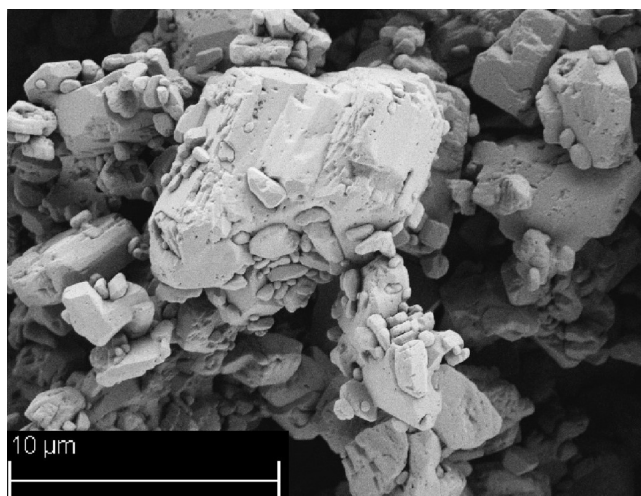


**Figure 3.** Visualisation of the initial density drift of PSAN. PSAN2 (orange triangles) is the direct repeat measurement of PSAN1 (blue squares). PSAN4 (teal rhombs) is the direct repeat measurement of PSAN3 (green circles). The gaps are caused by the 10 flushing cycles before PSAN2 and PSAN4. The first 10 data points of PSAN3 are magnified.

drift is underlying that is just randomly obscured in this case. This highlights the necessity to run measurements of high data point counts when a new material is analysed to end up with a more in-depth insight in the response the material exhibits to the measurement.

### 3.6.2 CL-20/HMX Cocrystal

HMX and CL-20 are non-hygroscopic, insoluble in water, and not easily wettable by water. The cocrystal samples discussed in this paper have been prepared following the previously published procedures [17,18]. Cocrystal 1 (C1, Figure 4) was obtained by slow phase transformation at  $20^\circ\text{C}$



**Figure 4.** REM image of cocrystal 1.

in 2-propanole, while cocrystal 2 (C2, Figure 5) was obtained by reaction cocrystallization at 60 °C in acetonitrile, and cocrystal 3 (C3, Figure 6) was obtained by refined antisolvent crystallisation. The water contents are 0.035%, 0.028% and less than 0.02% for C1, C2 and C3, respectively. Results of the density measurements of the cocrystal samples C1.1 and C2.1 are displayed in Figure 7. C1.1 exhibits a strong density drift (0.008 g/cm<sup>3</sup>), while C2.1 exhibits a drift of 0.0028 g/cm<sup>3</sup>. The drift of C1.1 seems to persist until around data point 300 which is even longer than the drift observed in PSAN while the drift of C2 only persists for about 50 data points. The difference in behaviour between C1.1 and C2.1 lies most likely in the partially porous nature of C1.1 as can be seen in Figure 4, while C2.1 exhibits mostly internal defects and some cracks that propagate through the material. In theory, the drift in density could also be caused by other factors. For example, for C1.1 a vestige of 2-propanol from the crystallisation process could also explain the behaviour. However, a second density measurement carried out after two days on the very same sample

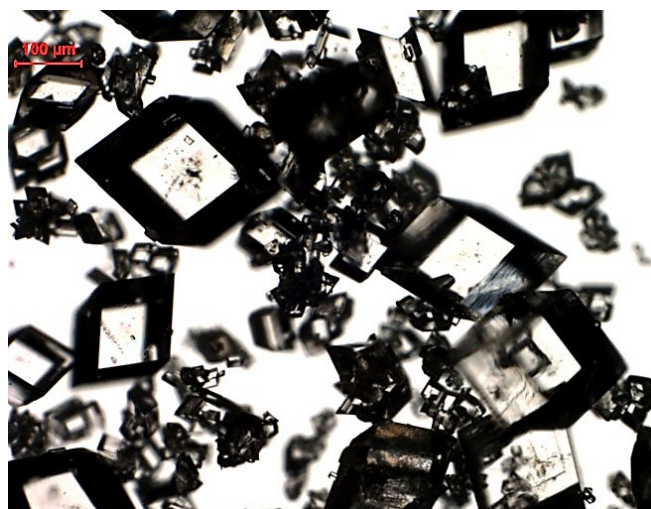


Figure 5. Macroscopic image of typical crystals of cocrystal 2.



Figure 6. Macroscopic image of cocrystal 3.

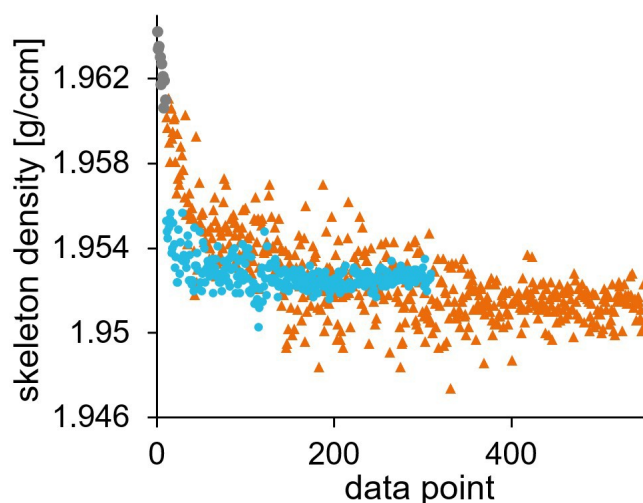
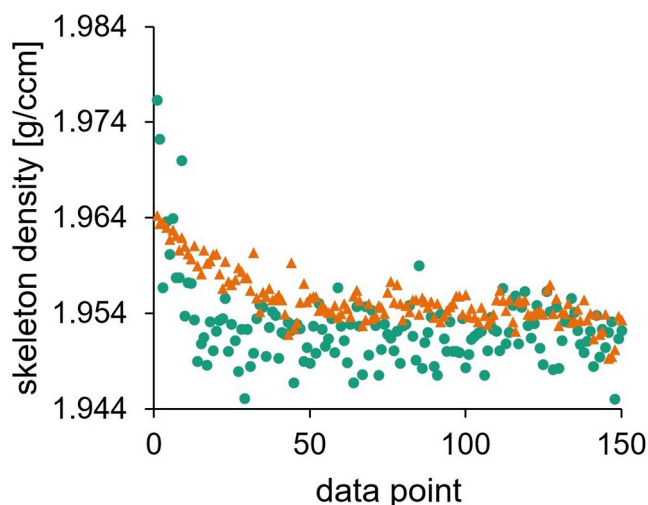


Figure 7. Visualisation of the initial density drift of C1.1 (orange triangles) and C2.1 (light blue circles). The first nine data points of C1.1 are greyed to aid in the comparison of the drift, as C2.1 was preceded by 10 flushing cycles and C1.1 of only one.

material exhibited again a density drift of 0.004 g/cm<sup>3</sup> which indicates that even though the material is non-hygroscopic it appears to collect water from the air most likely because of its porous nature.

The data points of C2.1 start at 10 and the first 10 data points of C1.1 are displayed in grey in Figure 7 to accentuate that the measurement of C1.1 was carried out with one flushing cycle, while the measurement of C2.1 was carried out with ten flushing cycles and to provide better comparability between the two measurements. The reduction of flushing cycles can provide insight into the sample behaviour if the time allows for it, as flushing cycles are around five to ten times faster than measuring cycles. The insight lower flushing cycle numbers can provide is best seen in Figure 8 where the first 150 data points of the measurements of C1.1 and C3.1 are displayed. C3.1 exhibits a substantial drop in density of 0.024 g/cm<sup>3</sup> for the first 10 measurements that is three times larger than even the drop of C1.1. Even with only ten flushing cycles this drop would have been obscured and the sample would have been declared free of any drift. Because C3.1 is virtually free of defects especially on the surface, the most likely explanation for the sample's density drift is traces of water present as a thin film on the surface of the crystals and the sample cup. The comparably high rate of density reduction during measurement is most likely also the result of the smoothness of the crystal surfaces of C3.1 compared to C2.1 and C1.1.

These three different drifts that C1, C2, and C3 exhibited, even though they are the same base material, highlight how important it is to adapt the measuring parameters to the sample if highly time efficient measurements are needed. If time is not of the essence, it always pays to in-



**Figure 8.** Visualisation of the initial density drift of C1.1 (orange triangles) and C3.1 (green circles).

crease the number of data points to increase the information content of the data. A reduction of flushing cycles can also serve to increase the information content, as it provides data about the strength of the initial drift of the sample.

### 3.7 Data Analysis

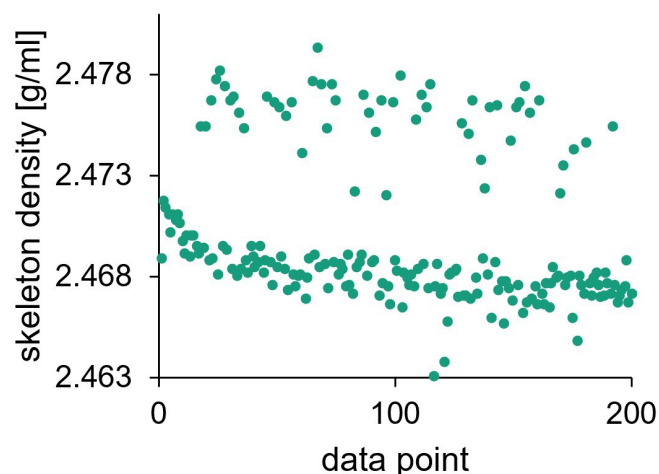
All the abovementioned strategies aim to improve the quality of the density measurement. In themselves they, however, do not provide certainty that the obtained data is correct. "Correct" is in any event the wrong terminology, as it is obvious from the graphs above that every measurement possesses varying degrees of uncertainty. Aside from the standard deviation of the individual measurement, additional errors that affect the repeatability of the measurement can occur. One tends to meet this uncertainty by duplicate measurements and comparison of the obtained average density. A true duplication at this point involves removing the sample from the sample cup, cleaning of the sample cup, and to weigh in the sample anew. Only in doing so the errors stemming from sample inhomogeneities, weight in errors, changes in sample chamber volume, etc. can be statistically comprised. A better way than to simply compare the two received density values is to carry out a true statistical analysis. Thereby one is able to determine whether a difference in the received density averages is likely caused by random sampling error or an underlying additional source of error. Furthermore, one is able to tell whether the amount of data points even allows for such a differentiation. For a duplicate measurement of one sample a t-test [19] is a fitting method, while for the comparison of multiple samples ANOVA with an appropriate post-hoc method is suitable. While non-parametric methods are also

an option, in case of pycnometry, however, all the special requirements that parametric methods demand from the sample data can be met. In the following paragraphs the data requirements for statistical analysis are discussed.

#### 3.7.1 Test for Outliers

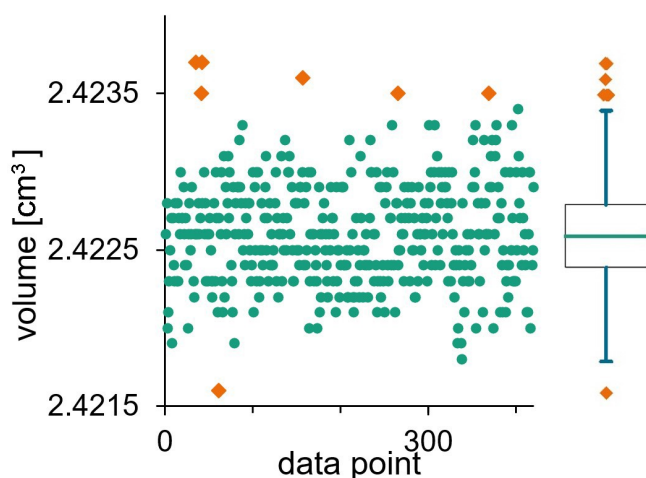
It is proven that ANOVA is affected by extreme outliers [20]. The removal of these outliers should always be considered in a proper density measurement, as no reasonable explanation exists why these values should occur aside from freak measurement error. If, however, a multitude of such outliers occur, this might indicate an underlying issue of the measurement. The first three measurements undertaken with the Accupyc II TEC utilised in this study on spheriglass A2227 exhibited an almost bimodal density distribution as seen in Figure 9.

This effect occurred for three measurements and then disappeared for the following measurements. This was not further studied, but might be related to the gas inclusions close to the surface of the glass beads. Obviously, these extreme outliers are too numerous to be considered freak occurrences and should not simply be removed. The general exclusion of moderate outliers in contrast to extreme outliers is also debatable. A fast and clear visual representation of the data to judge outliers in the data is the box plot [21]. In Figure 10 right, the volume data of K3 on the left is represented by a box plot. The green horizontal line represents the median of the data, the box represents the position of 50% of the data, the blue so-called whiskers indicate the data that lie within 1.5 times the box height (interquartile range IQR), and the orange rhombs visualise the mild outliers i.e. outliers that lie within the region of 1.5 IQR to 3 IQR. Because the reason of the appearance of these mild outliers is unclear, general removal of the data points might



**Figure 9.** The bimodal distribution of the density measurement of spheriglass A2227 is shown.





**Figure 10.** Volume data points of K3 on the left and the corresponding box plot on the right. Outliers are depicted as orange rhombs.

be ill advised. In chapter 3.7.3, however, it is shown that the removal of these mild outliers can significantly improve the normality of the data. Further study is required to develop a general procedure concerning mild outliers.

Based on the gathered data it appears prudent to remove extreme outliers if they appear as singular freak appearances, but to reevaluate the entire measurement if a multitude of extreme outliers occur and to remove mild outliers if appropriate.

### 3.7.2 Underlying Trends

One prerequisite for any meaningful data analysis in this context is that the data points are free of any permanent drift. Due to the differences in sample densities, for best comparability the volume data drift is regarded. Any meaningful drift analysis requires at least around 100 data points. Seven measurements of the cocrystal batches C2 and the calibration standard of at least 150 data points were, therefore, analysed. Most measurements exhibit a volume drift of around  $1 \cdot 10^{-6} \text{ cm}^3/\text{data point}$  and only two of eight measurements exhibit a drift of around  $1 \cdot 10^{-7} \text{ cm}^3/\text{data point}$  (C2.3, K3). The volume drift appears to be mostly independent of the measured material, as the smallest ( $8 \cdot 10^{-8} \text{ cm}^3/\text{data point}$ , C2.3) and second largest ( $2.7 \cdot 10^{-6} \text{ cm}^3/\text{data point}$ , C2.1) volume drift was obtained from the same sample in different runs and the calibration standard achieved an only marginally better drift than average ( $2.6 \cdot 10^{-7} \text{ cm}^3/\text{data point}$ ). Of the seven measurements two exhibited a linear increase in sample volume (C2.5, K3), three a linear decline (C2.1, C2.2, C2.3), and two measurements showed a change in the algebraic sign of the volume drift (C2.4, C2.6). This inhomogeneous behaviour indicates that the volume drift is not a characteristic of the measured

sample, but of the pycnometer itself. It is important to determine whether the monotonically decreasing and increasing volume drifts are indefinitely ongoing. Because if they were, this would render such density measurement meaningless, as the achieved density would be dependent on the length of the measurement. To investigate this, a 900 data point (C3.3) and a 600 data point (C3.4) measurement of C3 were carried out. These measurements took 45 and 31 hours, respectively. It was thus possible to investigate whether the diurnal and semidiurnal barometric pressure cycles that result in a fluctuation of atmospheric pressure of 0.3 to 3 hPa depending on location [22] with a periodicity of around 12 hours each could be the reason for the volume drift. The utilised barometric pressure data was measured at the meteorological station Karlsruhe located around 10 km from the place of experiment. As the AccuPyc 1340 is fitted with a gage pressure sensor, the actual barometric pressure is of lesser importance compared to the rate of pressure change, because a change of barometric pressure between the determination of  $p_1$  and  $p_2$  will influence the measured pressure difference. A reduction in barometric pressure after the determination of  $p_1$  will lead to a relative increase of  $p_2$ . A higher  $p_2$  normally correlates to a sample of lower volume and, therefore, higher density. An increase in barometric pressure accordingly leads to a lower density. A simple recalculation of the sample density based on modified  $p_2$  data was carried out following the formula

$$\rho(\text{sample}) = \frac{p_2 + \Delta p - p_1}{(p_2 + \Delta p)(V_r + V_c) - p_1 \cdot V_c} \cdot m(\text{sample})$$

with the sample chamber volume ( $V_c$ ), the reference volume  $V_r$ , the initial pressure  $p_1$ , the equilibrium pressure  $p_2$ ,  $\Delta p$  the atmospheric pressure change between the measurement of  $p_1$  and  $p_2$ , and the sample mass  $m(\text{sample})$  to investigate whether the magnitude of pressure change is sufficient to explain the density fluctuations. The calculation was carried out under the following assumptions. 0.5 hPa/h was chosen as maximum positive and negative pressure change. This value was derived from the actual atmospheric pressure data for the measurements C3.3 and C3.4. It was assumed, that the time frame of the interference of the pressure change is around 0.03 h of the 0.05 h each individual data point determination took. This resulted in a 1.5 Pa deviation per measurement between the determination of  $p_1$  and  $p_2$ .  $p_1$  was left unmodified and  $p_2$  was increased or decreased in the calculation to receive the maximum and minimum density values, respectively. The calculation was carried out based on actual  $p_1$  and  $p_2$  values of C3.3. The thereby obtained difference in density between maximum and minimum density is  $0.0012 \text{ g/cm}^3$  for this specific sample. This is in remarkable agreement with the actual discrepancy within C3.3 of  $0.0013 \text{ g/cm}^3$ . Assuming that the rate of change of the barometric density fluctuation is about the same for most days its influence in dependence of the utilised sample chamber insert and sample



volume can be estimated. The measurement C2.2 can serve as a realistic scenario for the 10 cm<sup>3</sup> cell. Here the sample volume of 4.3 cm<sup>3</sup> fills the sample chamber volume to about 40% which is a rather good value for most samples due to their low packing density. Here, under the same assumptions as for C3.3 a density deviation of 0.00025 g/cm<sup>3</sup> is calculated. This is also in good agreement with the amplitude of 0.0002 g/cm<sup>3</sup> of a 4<sup>th</sup> order regression curve of the measurement C2.2. The obtained atmospheric pressure data for C3.3 and C3.4 were differentiated and the resulting curves are superimposed with the fitted density curve of the two measurements in Figure 11 to evaluate the correlation between the obtained density values and the change in barometric pressure.

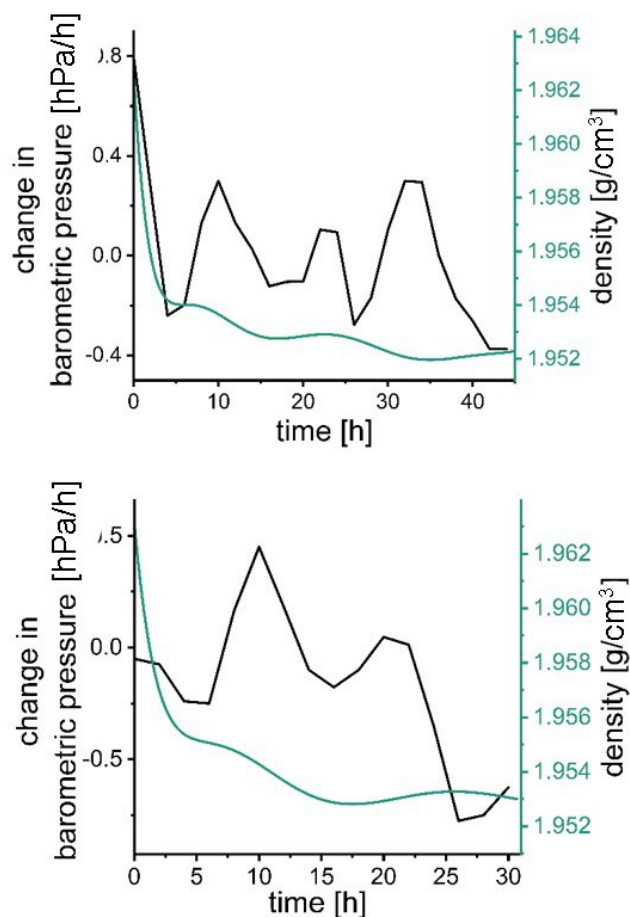
Both density progressions do not seem to fit the change in barometric pressure. This is best seen in the change in correlation of the global minima of the density curve of C3.3 to the barometric pressure change compared to the correlations of the local minima. Also, none of the local

minima of the density curve of C3.4 correlate to the maxima of the barometric pressure change curve. It could be possible that the discrepancies are explained by the spatial distance between the meteorological station and the place of experiment or variations of the length of the individual measurements. Further study is required to explain the lack of correlation.

This, however, does not mean that the calculated influence of the barometric pressure change on the density value is wrong, as this value is derived directly from real pressure change data and is not contradicted by the additional findings. These calculated values can, therefore, still be used for the explanation of some of the occurring error of the density measurements. These values are only valid for stable weather conditions. In case of a superimposed drop or increase of the barometric pressure in addition to the diurnal and semidiurnal barometric pressure cycles a stronger density variation is to be expected. It appears, therefore, advisable to also check the current weather development on performing high precision density measurements, as this might explain an increased drift in measurements or discrepancy between measurements. Furthermore, on the quest for best accuracy one might be tempted to choose stricter equilibration conditions than the standard 35 hPa/min. This could, however, even reduce the accuracy as it increases the measurement time and, therefore, the influence the change in barometric pressure should have on the measurement. It is noteworthy that the influence of the change in barometric pressure should only affect gas pycnometers equipped with gage pressure sensors, as absolute pressure sensors should provide constant pressure values even under changing barometric pressure.

### 3.7.3 Test for Normality

A special requirement of parametric tests is a specific distribution of the data [23] typically a normal distribution [24]. A multitude of test methods for normality exists. Of these it appears that the Shapiro-Wilk test [25] is the most powerful and universal test in most situations [26,27]. It was shown that for normal distributed data the Type I error rate of the Shapiro-Wilk test is independent from the sample size [26], but the test power increases strongly for most non normal distributed data with increasing sample size [26]. The most reliable results should, therefore, be expected at larger sample size. Normality of the density data is thus only discussed for measurements of at least 150 data points. Because of the similar nature of each density measurement one can assume that if the majority of density measurements of more than 150 data points satisfies the normality condition, all data points of proper density measurements are random samples of a normally distributed population, even if the individual measurement's normality is rejected. This assumption might fail if different sample material is probed that possesses a sufficiently dis-



**Figure 11.** Overlay of the rate of barometric pressure change (black) with the smoothed density data points for C3.3 (top) and C3.4 (bottom).

**Table 1.** Summary of the obtained p-values from the Shapiro-Wilk test dependent on the applied data treatment.

designation	nr. of data points	raw data	raw data detrended	recalculated data	recalculated data detrended	polynomial detrended and outliers removed
K3	481	< 0.01	0.26	0.20	0.50	0.20
C2.2	282	0.02	0.05	0.08	0.14	0.19
C2.3	336	0.05	0.06	0.02	0.02	0.17
C2.4	150	< 0.01	0.01	< 0.01	0.01	0.25
C2.5	150	0.21	0.94	0.41	0.73	0.55
C3.3	701	< 0.01	0.43	0.09	0.27	0.17
C3.4	416	< 0.01	< 0.01	0.28	0.45	0.42
average		0.04	0.25	0.16	0.30	0.28

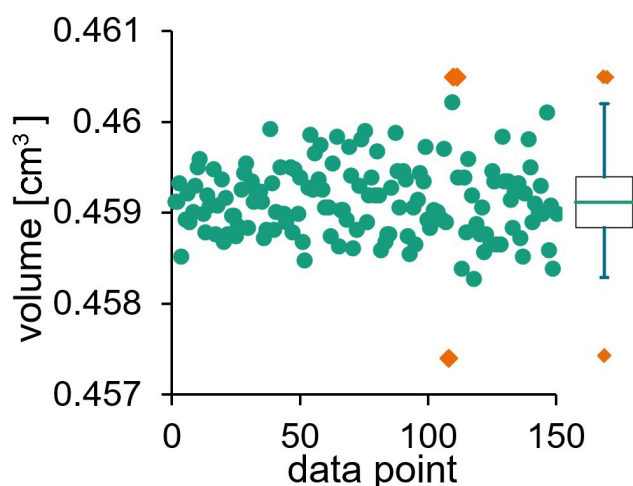
ruptive character to the measurement itself. Which again only highlights the necessity of performing density measurements of high data point count for any new material.

Seven data sets were tested for normality utilising the Shapiro-Wilk test. Only data point regions with a linear volume drift of less than  $2 \cdot 10^{-6} \text{ cm}^3/\text{data point}$  were used. The obtained p-values (probability values) are summarised in Table 1. Of the seven sets only two passed the test unrefined and one of them barely. This indicates that the raw volume data points are not normally distributed. Four data refinements were carried out to investigate whether an improvement of the data is possible. The underlying linear drift of the data was eliminated in such a fashion that the average volume was conserved. The volume was recalculated based on the sample chamber volume  $V_c$ , the reference volume  $V_r$ , the initial pressure  $p_1$ , and the equilibrium pressure  $p_2$  following the formula

$$V(\text{sample}) = \frac{p_2(V_r + V_c) - p_1 \cdot V_c}{p_2 - p_1}.$$

A linear detrending of the recalculated data was undertaken. And the raw data were detrended utilising a regression function typically of 3rd or 4th order while maintaining the average volume followed by removal of all outliers. The comparison of the resulting data sets per measurement allows some conclusions. From Table 1 it is obvious that every data treatment improved the normality of the data on average. The strongest single impact on normality has linear detrending. That recalculation of the data improves the normality seems to indicate that the pycnometer uses additional hidden parameters to calculate the sample volume which influence the normality of the data. Only by combining polynomial detrending and outlier removal do all measurements pass the test.

The impact of outlier removal can easily be identified at C2.4, for which neither the untreated nor the detrended data achieved a satisfactory p-value. On inspecting the boxplot (Figure 12 right) one finds that no extreme outliers are present, but the lower outlier comes close. The removal of this one outlier, however, does not improve the p-value significantly. The additional removal of the two upper outliers increases the p-value of the detrended raw data from 0.01

**Figure 12.** Volume data points of C2.4 on the left and the corresponding box plot on the right.

to 0.23. For this measurement it is easy to identify that the outliers are caused by a disturbance of the measurement and are not part of the regular population. This can be deduced from the temporal closeness of the outliers. This might indicate that every outlier is the result of a disturbance, albeit in many cases a less obvious one. It could, therefore, be argued that every outlier, not only the extreme ones, is to be removed to improve the quality of the data. The poor p-value of C2.3, however, can only be marginally improved by removing the eight outliers. As it was discussed in section 3.7.2 likely due to variations in barometric pressure, density measurements possess a periodic fluctuation. Linear detrending only removes part of its influence. For C2.3 polynomial detrending was, therefore, applied. By polynomial detrending alone a p-value of 0.07 was achieved which is only 0.01 better than linear detrending. By additional removal of the outliers a p-value of 0.17 was achieved which is markedly better than the 0.1 for linear detrending and outlier removal. From Table 1 it can be seen that by removing outliers and the polynomial drift of the data every measurement passes the normality test with typically a quite significant p-value. This indicates that the den-

sity measurement in itself produces normal distributed data points. The normal distribution is, however, heavily influenced by a variety of disturbances. The strengths of these disturbances vary and might lead to measurements that even after post treatment do not fulfil the normality condition. Due to their underlying normality it appears appropriate to extrapolate from the tested measurements that most density measurements are fit for statistical analysis, even though some measurements might benefit from appropriate post treatment such as removal of outliers.

### 3.7.4 Homoscedasticity

The density's standard deviation of a sample measurement appears to be dependent on the sample volume as discussed in section 3.1, but it also seems to be dependent on additional factors. An unexplainable trend of standard deviation occurred in the study of Viana *et al.* [6]. Here three measurements of mannitol in the 10 cm<sup>3</sup> cell have a ten times larger standard deviation than the measurements in the 1 cm<sup>3</sup> cell and a 3.5 times larger standard deviation than the measurements in the 3.5 cm<sup>3</sup> cell, even though the trend should be reverse. For other tested materials (glass beads and quartz) the expected standard deviation trend was observed. In the present study for C3, four measurements were carried out where between measurements the sample chamber was not opened. Measurements C3.1 and C3.2 were carried out directly after one another. Between measurement C3.2 and C3.3 as well as C3.3 and C3.4, however, the sample rested within the sample chamber for 34 hours and 96 hours, respectively. Not only did the initial drift interval increase from 10 data point for C3.1 and C3.2 to about 200 for C3.3 and C3.4, but also the standard deviations of the regions free of strong drift of C3.3 and C3.4 are with 0.001 g/cm<sup>3</sup> and 0.0009 g/cm<sup>3</sup>, respectively, distinctly lower than for C3.1 and C3.2 with 0.0025 g/cm<sup>3</sup> and 0.002 g/cm<sup>3</sup>, respectively. The reason for this different behaviour is unknown and it is unclear whether it is caused by the sample or the device. A similar behaviour is sometimes observed where during a measurement the standard deviation suddenly increases or decreases. This is displayed in Figure 13 for two measurements of C1. For clarity, C1.3 is shifted by 300 data points. C1.2 shows a decrease in standard deviation at about data point 150, while C1.3 shows an increase in standard deviation at about data point 400. It appears unlikely that the samples could exhibit such behaviour and it appears more likely that an external factor, such as a disturbance in the power line, influences the measurements. Direct solar irradiation has disturbed measurements in the past; however, in this case the disturbance has twice started at around midnight which eliminates the sun as causing factor. Besides, the comparably rapid heating of the device by solar irradiation has caused negative density spikes that lasted only around 15 data points instead of a prolonged increase in standard deviation.

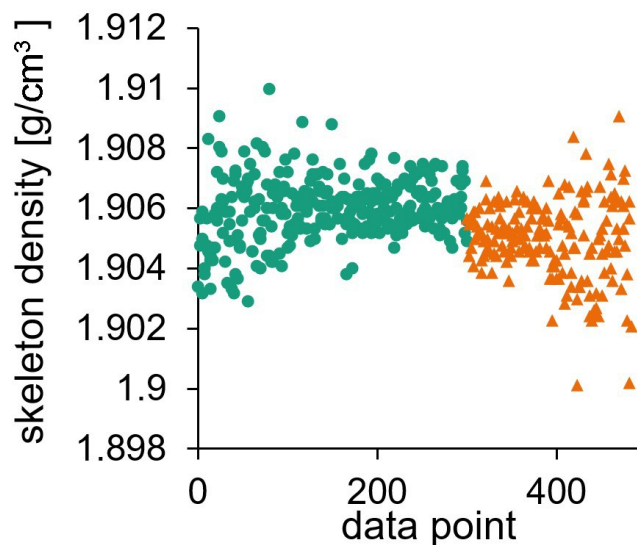


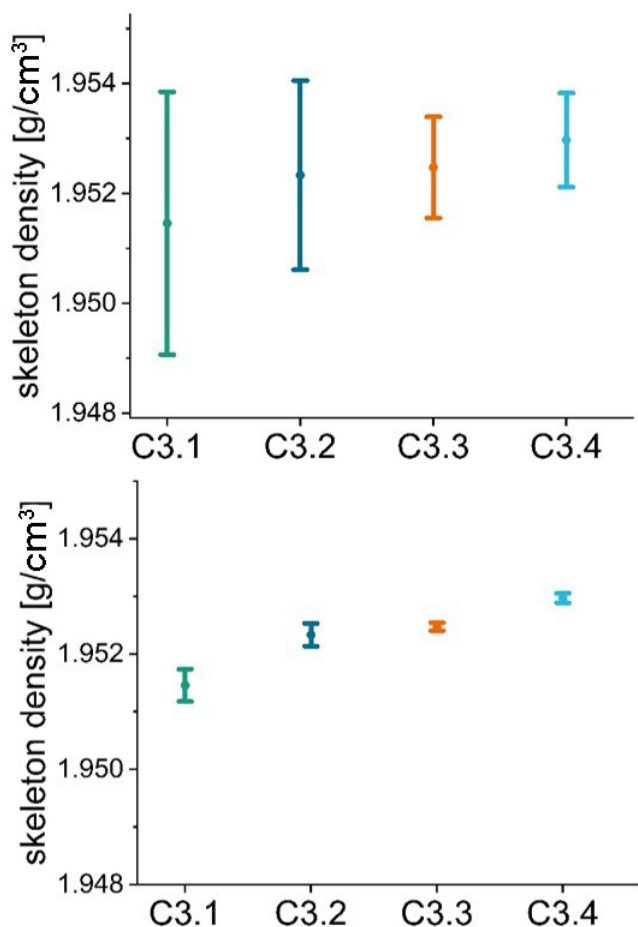
Figure 13. Visualisation of the change in standard deviation within measurements for C1.2 (green circles) and C1.3 (orange triangles).

Fluctuations in the room pressure were also tested as causing factor. The room's air extraction creates a mild vacuum in the room that is equilibrated through the closed door. It is conceivable that this equilibration causes pressure fluctuations that affect the measurement. Two tests (K4 and K5) during which the air extraction was switched on and off for at least 50 data points each showed, however, no effect of the state of air extraction on the standard deviation of the measurements.

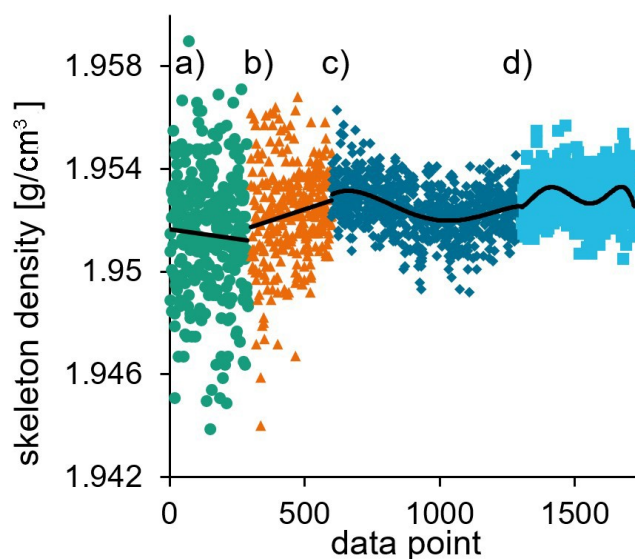
## 4 Repeatability

All the abovementioned aspects serve to enable one to carry out a density measurement that is statistically sound. And in doing so allow for some certainty about the obtained results and their relevance. One simple validation of the quality of measurements is repeatability of the obtained results. In this case the t-test is a suitable method to judge whether the difference in the result of a repeat measurement is only caused by statistical error due to limited sample number. It has been shown in chapter 3.7.3 that influences on the measurements exist that with varying strength influence the data point values and reduce their normality. These influences can also affect the sample average. C3.1 to C3.4 are four repeat measurements that have been conducted in the 1 cm<sup>3</sup> sample chamber without opening the device. It, therefore, would be expected that the sample averages are statistically insignificantly different. Because of the change in standard deviation that was discussed in chapter 3.7.4 between measurement C3.2 and C3.3, Welch's [28] t-test was used to compare the sample means in pairs, but no ANOVA can be carried out.

Of the pairs only C3.2 and C3.3 are identified as originating from the same population with a p-value of 0.19. The power of this test, however, is only 0.38 due to the difference in standard deviations. The lack of sameness of the data means is somewhat surprising when one inspects the raw data or the standard deviation diagram (Figure 14 top), but on considering the 95% confidence intervals [29] of the data (Figure 14 bottom) the result is easily comprehensible. The measurements appear to follow a clear trend of increasing sample density. And this trend could be suspected to cause the lack of similarity. The inspection of the data points, however, draws a different picture (Figure 15). If there was an underlying trend to increase the sample density, it could hardly be explained by evaporation of solvent inclusion as this should lead to a decrease in density during density measurements as discussed in chapter 3.6. Only if the solvent evaporation rate was unchanging over time one could conceive that a slow increase in skeleton density is possible. The data, however, do not support this hypothesis. As discussed for C3.3 and C3.4 in section 3.7.2 fluctuations of the barometric pressure over the course of the day



**Figure 14.** Comparison of the standard deviations of C3.1–4 (top) and the 95% confidence intervals of C3.1–4 (bottom).



**Figure 15.** Visualisation of the density progression from C3.1 (green circles) to C3.4. The measurements C3.2 (orange triangles), C3.3 (blue rhombs), C3.4 (teal squares) have been offset on the x-axis for clarity purposes. Furthermore, at marker a) the first 13 data points of C3.1 have been omitted, at marker c) the first 198 data points of C3.3 have been omitted and at marker d) the first 199 data points of C3.4 have been omitted. Additionally, Measurement C3.2 was started within 10 minutes after the end of measurement C3.1, while 34 h lie between the end of C3.2 and the start of C3.3 and 96 h lie between the end of C3.3 and the start of C3.4.

can influence the density measurements. This influence might explain most of the variation in density as the difference in average density between C3.1 and C3.4 is only 0.0002 g/cm³ larger than the calculated amplitude of the density value resulting from the change in barometric pressure. This pressure drift, however, does not only cause the repeat measurements to be considered different by the t-test, but also the measurements with themselves. This can easily be illustrated by dividing measurement C3.3 into ten equal sections of 70 data points and performing ANOVA on them. Of the 44 pairs, for 21 pairs did the Tukey test [30] reject the null hypothesis. The assumed influence of the change in barometric pressure is much smaller for measurements using the 10 cm³ sample cup as has been shown in chapter 3.7.2. Because the standard deviation of the data points is, however, also reduced, repeat measurements in the 10 cm³ sample cup usually also do not pass the t-test. For example, the t-test of the true repeat measurements C2.2 and C2.3 rejects the null hypothesis even though the mean difference is only 0.00035 g/cm³. Even on parallel translation of the data points of C2.3 to achieve a mean difference of 0.0001 g/cm³ the null hypothesis is rejected.

The failure of a typical repeat measurement to pass the t-test simply shows that the random sampling error of the individual data points due to their limited number is not the only considerable error at play. Besides some prevent-



able errors to a density measurement such as insufficient sample dryness, insufficient sample volume, or markedly different measurement temperature, the following errors that will always affect the measurement remain: sampling error, the weight in error, the error caused by variance in sample chamber volume upon opening and reclosing the chamber, the temperature fluctuation, and the drift of barometric pressure. Of these errors the variance of sample chamber volume and the temperature fluctuations did not show any signs of being relevant in face of the other errors present. For the other three errors, their influence on the obtained density value has been calculated and displayed in Table 2 for the 10 cm<sup>3</sup> and 1 cm<sup>3</sup> sample chamber based on the density measurements discussed in this paper. Insufficient measurements have been carried out in the 3.5 cm<sup>3</sup> sample chamber, but there is no indication that this intermediate chamber should not exhibit intermediate errors. The error resulting from the weight in error was calculated based on a 50% filled sample cup and a sample of density 1.95 g/cm<sup>3</sup>. The error resulting from barometric pressure change was calculated based on an assumed maximum pressure change rate of 0.5 hPa/h, an interference time of 0.03 h per measurement, an about 50% filled sample cup and a sample of density 1.95 g/cm<sup>3</sup>. The sampling error is represented by half of the 99% confidence interval calculated for all discussed measurements in this paper.

It is noteworthy that, technically, the error due to barometric pressure change is to some extent double counted, if the non-detrended data points are used to calculate the confidence interval. It was found, however, for all tested data that detrending and removing the outliers has no influence on the confidence interval within the accuracy of 0.00001 g/cm<sup>3</sup>. No data treatment seems therefore typically necessary for calculating the confidence interval. These obtained values must be viewed in the correct context. Following the terminology of ISO 5725 [10] the error values only represent the precision one can expect and give little information about the trueness of the values. These obtained errors can only be used to compare samples of sim-

ilar volume that were measured in close temporal proximity (and calibration) within the same sample chamber i.e. under repeat measurement conditions [10]. Furthermore, the values are valid for samples of density 1.95 g/cm<sup>3</sup> and can easily be converted for samples of different density. All errors, however, are not necessarily translatable. The assumed weight in error of 0.0002 g is most likely the most universal error. The magnitude of the barometric pressure drift is strongly dependent on the latitude of the measurement location [22]. Better error values can be expected closer to the poles and worse values closer to the equator. The obtained confidence intervals, as can be seen, vary widely for different measurements and samples. These values always have to be determined for the substance of interest and cannot be translated.

Given these error values, it is obvious why in most cases statistical tests such as t-tests and ANOVA will reject similarity of the measurements, as they are only concerned with the error stemming from the data sampling. An alternative procedure to judge whether repeat measurements can be considered the same or whether one sample is significantly denser than another is hence needed. One practical solution is to calculate the sampling error based on the 99%-confidence intervals of the measurements and add the other two error values to obtain a collective measurement error that can be used to compare samples by checking whether their error bars intersect. If the error bars of repeat measurements intersect, the data can be pooled. This pooled data can then be used to compare different samples. The use of the 99%-confidence interval might be beneficial compared to the 95% to remedy some of the alpha error accumulation that is bound to appear upon the comparison of a multitude of samples. Obviously, this methodology lacks the statistical backing of a proper test such as a t-test, but it is still significantly better than to just perform a replicate measurement and judge the data based on scientific intuition. Because it utilises far more data provided by the measurement than for example the three-sigma rule, it is possible to differentiate between far more similar samples. The three-sigma rule would be very lenient towards replicate measurements, but would hardly be able to differentiate between different polymorphs for example. There is no need to fall back to the three-sigma rule, because all of the major contributing error factors are accounted for and the error margin is therefore very well known. Based on the collective measurement error one is able to differentiate between samples of 0.001 g/cm<sup>3</sup> density difference with certainty utilising the 10 cm<sup>3</sup> sample cup. Based on the length of the error bars of 0.0003 g/cm<sup>3</sup> for two samples of a true density difference of 0.001 g/cm<sup>3</sup> the error bars of individual measurements of the two samples can intersect if measurements of both samples are maximum eccentric. It is therefore always advisable to carry out measurements in triplicate. The amount of data points appears to have a less significant impact on the error, as the confidence intervals seem to be relatively unchanged between 30 and 100 data

**Table 2.** Summary of the major sources of error dependent on the chamber volume and the number of data points.

chamber volume [cm <sup>3</sup> ]	nr. of data points	error due to weight in error [g/cm <sup>3</sup> ]	error due to barometric pressure drift [g/cm <sup>3</sup> ]	sampling error [g/cm <sup>3</sup> ]	mean error sum [g/cm <sup>3</sup> ]
10	100	0.00005	0.00013	0.00007–0.00012	0.0003
	30	0.00005	0.00013	0.00011–0.00017	0.0003
1	100	0.00038	0.00060	0.00024–0.00064	0.0014
	30	0.00038	0.00060	0.00045–0.00131	0.0019

points for the 10 cm<sup>3</sup> cell. This means that high precision measurements are possible with relatively short measurement times. And measurements of 100 data points and more are only needed once to assess the samples behaviour during measurement. Furthermore, as the method should only be applied for measurements that were carried out in the same measurement cell with closely matching sample volume, homoscedasticity should be less of an issue here. This comparison should be applicable even under mild discrepancies in the standard deviation of the data sets.

## 5 Conclusion

This study examined the necessary prerequisites and analysis methods to carry out pycnometric density measurements of energetic materials of highest precision. It was shown that the individual data points of the density measurement are normally distributed, which enables one to apply statistical methods such as t-test and confidence intervals to the density data. It was, however, also shown that the measurement is always considerably disturbed presumably by the change of the barometric pressure which causes a density drift over the day, and sometimes disturbed by isolated disturbances that lead to individual outliers. As a result, repeat measurements typically do not pass t-tests or ANOVA even under optimal sample preparation and execution of the measurement, because the sum of the other errors is of the same magnitude as the sampling error. An alternative method to judge the quality of repeat measurements and the significance of density differences has therefore been proposed for general use that considers the contributing errors. Thereby, for the first time enabling one to differentiate with certainty between substances that possess density differences of 0.001 g/cm<sup>3</sup> (0.05 %). It can, however, not be stressed enough that this is the precision of repeat measurements carried out in the same sample chamber with the same calibration. It must not be confused with the accuracy of the obtained density which is affected by even more factors and requires much more effort to be optimised to a level of 0.05 %. This means that under repeat measurement conditions even solvent inclusions of the CL-20/HMX cocrystal of 0.04 % or gas inclusions of 25 µm in a particle with a diameter of 250 µm are detectable via helium pycnometry, which means it can be a valuable tool in the process of quality and sensitivity improvement for energetic materials.

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## Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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