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AN INVESTIGATION OF DENSITY DETERMINATION METHODS FOR POROUS MATERIALS, SMALL SAMPLES AND PARTICULATES

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Abstract – Three new density measurement techniques have been devised and evaluated for the measurement of non-standard objects, namely porous material samples, small solid samples, powders and particulates. Hydrostatic weighing has traditionally been used to determine the density of solid artefacts. This method is not, however, suitable for porous objects since they will adsorb water making weighing in water unstable and possibly detrimental to the material samples. A method, weighing the artefacts in inert gas, has been developed for this application. The density determination of small solid artefacts cannot be achieved by conventional hydrostatic weighing techniques due to limits on the accuracy with which the weight-in-water can be determined A density gradient column method for such measurements, delivering very low uncertainties, has been developed and evaluated. A liquid pyknometry method has also been investigated as an alternative to traditional helium and mercury pyknometry. The technique offers improved accuracy and a precise determination of thermal coefficient of the sample under test.

1. INTRODUCTION

The density determination of solid materials has been traditionally performed by hydrostatic weighing techniques [1]. With care and using appropriate temperature controlled baths and mass comparators of high resolution, accuracies of parts in 10^5 can be achieved. However, not all materials are suitable for density determination by this method. In particular porous material samples, small solid samples, powders and particulates require different measurement techniques to determine their densities.

2. DENSITY OF POROUS MATERIALS

2.1 Weighing in vacuum, dry air and inert gas.

The apparatus used for these measurements consisted of a Mettler HK1000MC mass comparator (capacity 1 kg, resolution 0.1 micrograms) inside a vacuum chamber. The balance environment can be pressure controlled to vary the density of the air (or inert gas) inside the chamber. Pressure, temperature, relative humidity and carbon dioxide concentration sensors are fitted inside the vacuum chamber to monitor the ambient conditions around the balance. The apparatus is shown in figure 1.

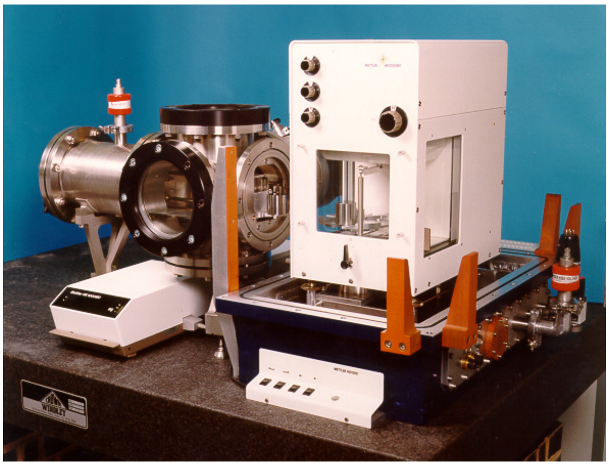

Fig. 1. Mettler HK1000MC mass comparator with base of vacuum chamber and load-lock mechanism.

The apparent mass of a sample under test is compared with the mass of a standard of known volume. By making measurements over a range of controlled pressures (and gas densities) the volume of the test sample can be determined with relation to the volume of the standard.

2.2 Measurements and uncertainty budget

Figure 2 shows typical results for the comparison of a stainless steel kilogram standard of unknown volume with a similar standard with a previously calibrated volume.

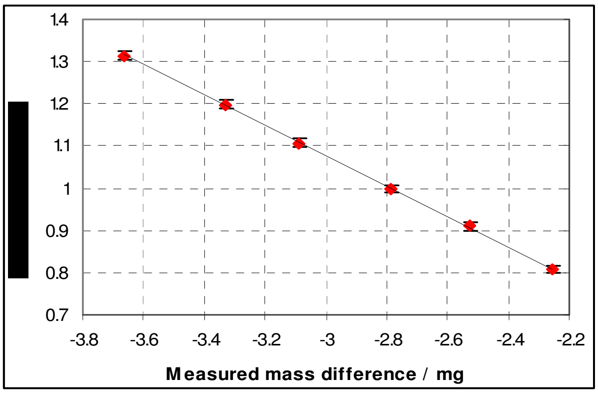

Fig. 2. Results from the comparison of stainless steel kilogram standards under controlled ambient conditions.

The relationship between the volumes and apparent masses of the artefacts being compare is given by;

$$m_1 - m_2 = \rho_{gas}(v_1 - v_2) \qquad (1)$$

The (inverse of the) slope of a graph of mass difference plotted against gas density is thus equal to the volume difference between the artefacts compared. Table 1 gives a typical uncertainty budget for a volume determination by this method, based on the measurement of the volume of a 1 kilogram stainless steel mass standard.

Table 1. Typical uncertainty budget for volume determination.

Uncertainty component	Value	Units	Sensitivity coefficient	Uncertainty contribution cm^3
Data fit (type A)	0.020	cm^3	1	0.020
Volume of std.	0.002	cm^3	1	0.002
mass comp.	0.005	mg	2.88	0.014
Density of gas	0.001	kg/m^3	8.06	0.008
			Total (k=1)	0.026

The relative contributions of the uncertainty components will depend on several factors, in particular how well matched the volumes of the standard and test artefact are. To obtain uncertainties at the level shown the standard and test artefact need to be of similar materials (and mass values). By extending the range of pressures over which the measurements are made, the type A uncertainty contribution may be reduced but care needs to be taken to ensure the accurate calculation of gas density for pressures which are not near to ambient. By performing a mass comparison at vacuum, the true mass difference of the artefacts is determined and the data fit uncertainty contribution reduced. However, care should be taken to account for surface effects (desorption of water from the surface of the weight) when moving between ambient pressures and vacuum.

2.3 Validation of technique

The technique was validated by measuring the density of artefacts of platinum-iridium, stainless steel and silicon whose density (and volumes) had been previously determined by hydrostatic weighing. The results of these measurements are given in table 2.

Table 2. Comparative measurements of hydrostatic and gas based measurement techniques.

Artefact	Hydrostatic determination		Gas based determination		Diff.
	Volume cm^3	Unc. cm^3	Volume cm^3	Unc. cm^3	cm^3
1 kg Pt-Ir	46.416 0	0.000 4	46.415 8	0.043	0.000 2
1 kg SS	124.231 2	0.001 9	124.228 1	0.060	0.003 1
500 g SS	63.707 6	0.001 4	63.699 8	0.042	0.007 8
500 g Si	106.693 9	0.000 7	106.699 4	0.054	0.005 5

The agreement between the two techniques is well within the combined uncertainties giving confidence in the results of the gas based density determination technique.

2.4 Applications of the gas based measurements

Having validated the gas based technique it has been used to determine the density of a number of mass standards and samples. Because it does not require the weighs to be immersed in water, this technique can be used to determine the density of mass standards without affecting the surface of the weights and losing the history of their calibration values.

Many materials are unsuitable to have their density determined by immersion in water. Many metals and alloys react with water and thus their densities cannot be determined by hydrostatic weighing. Porous materials are also unsuitable for density determination by liquid immersion techniques.

Among the samples measured using this new technique were a number of samples of concrete and grout for the construction industry. The new technique allowed the density determination of large samples (40 mm diameter x 50 mm high) of the materials which could subsequently be used for tests on their structural integrity. The new test method allowed uncertainties of 1 part on 10^3 to be achieved on the samples and led to a significant improvement in the modelling of the performance of the materials and the effect of heat treatment on their density and structural integrity.

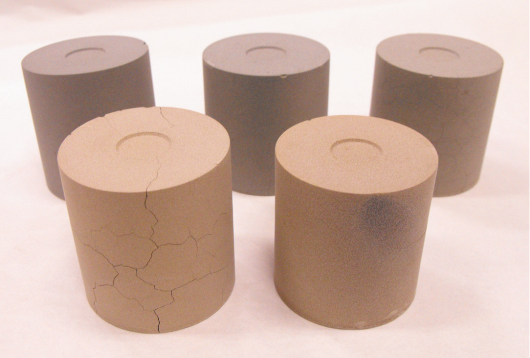

Fig. 3. Grout and concrete test samples for density determination.

3. DENSITY OF SMALL SOLID SAMPLES

3.1 Density Gradient Column

Traditionally, density gradient columns have been set up using two (or more) liquids of dissimilar density in such a way as to create a vertical density gradient [2]. The density of small objects can be determined to accuracies of typically 1 part in 10^3.

Experiments have been performed using a 1.4 metre long column, setting up a density gradients with a very small range. This, combined with sub-milliKelvin temperature control, could potentially increase the resolution and therefore the accuracy of this measurement method by two to three orders of magnitude.

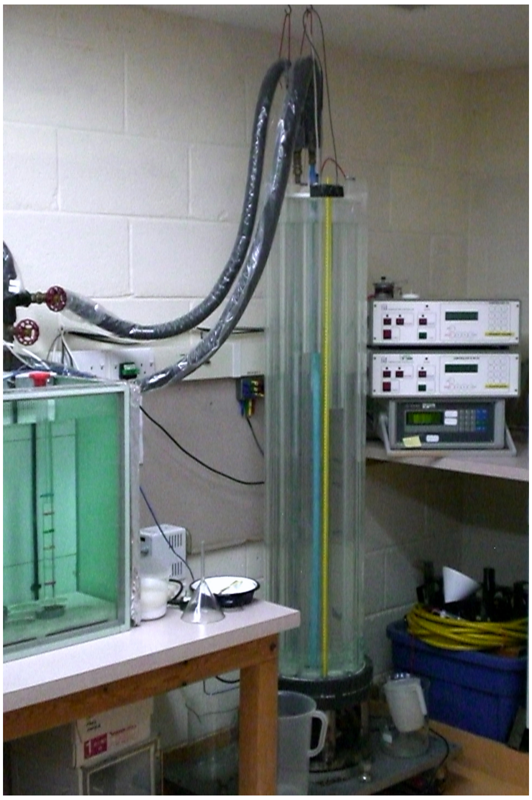

Fig. 3. Long-range (1.4 m) density gradient column

The development of this measurement technique was undertaken with the aim of providing a method for the determination of the density of natural diamonds (mean value approximately 3520 kg/m^3) to accuracies approaching 1 in 10^6. Measurements to this accuracy would allow investigation into the causes of colour variations in natural diamonds and also into the differences between natural and synthetic diamonds.

A density gradient column filler was designed using two peristaltic pumps capable of very low flow rates under computer control. Initially columns were set up with sodium bromide solution to validate the concept of producing stable density columns with very small density ranges. Figure 4 shows the repeatability achieved between 2 column fills.

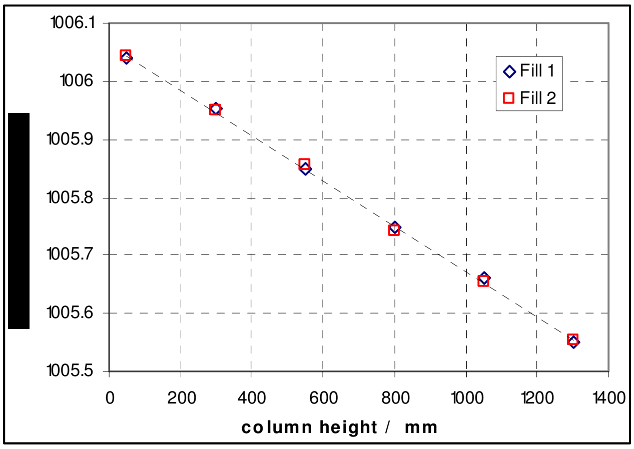

Fig. 4. Repeatability of column fills with NaBr solution

The results demonstrate the feasibility of achieving a resolution of 1 in 10^6, a vertical change of 2.5 mm being equivalent to 0.001 kg/m^3 change in liquid density. The repeatability of the column fill is of the order of 0.005 kg/m^3 demonstrating the robustness of the column construction technique.

Experiments have been performed with sodium hetero-polytungstates dissolved in water at densities in the range 2 500 kg/m^3 to 2800 kg/m^3. It has proved feasible to set up density columns in this range but the columns have been less linear than those achieved at lower densities, possibly due to stripping of the larger (heavy) solute molecules by the pumping process.

4. DENSITY OF PARTICULATES AND POWDERS

4.1 Liquid pyknometry

A technique using liquid pyknometry has been developed for the characterisation of powders used in the food industry. Traditionally helium pyknometry has been used to measure the density of powders and particulates. Accuracies of between 1% and 0.1% are generally achieved [3]. Additionally helium pyknometry does not usually allow temperature-controlled measurement. The liquid pyknometry technique allows close temperature control of the material under test so thermal coefficient as well as density values can be measured. Additionally, for this application the effective density of the powders measured in liquid rather than in gas provided data which was of more relevance to the end user in this case.

Fig. 4. 100 mL and 50 mL glass pyknometers

The liquid pyknometry technique uses a standard 100 mL glass pyknometer. The volume and thermal expansion of the pyknometer was initially characterised by filling with water and controlling at temperatures between 10 °C and 80 °C. To measure the densities of the powders under test a suitable liquid for the suspension of the powder was required. The liquid needed to be incompatible with the powder (i.e. it would not dissolve it) and needed to be stable over the time period (and temperature range) of the experiment. Isooctane was selected as a suitable liquid and its density was characterised over the required temperature range (10 °C to 80 °C) using a Paar DMA 5000 vibrating element density meter, which had previously been characterised with water and a series of certified reference liquids. Iso-octane was then used to re-calibrate the volume of the pyknometer. It is important that the volume is measured with the liquid which will be used for the calibration since different liquids will give different apparent volumes for a pyknometer, due mainly to meniscus effects. Having characterised the pyknometer with the test liquid it was emptied and cleaned, filled with a measured mass of powder and a suitable volume of the incompatible liquid (depending on the temperature at which the powder density is to be determined). Care must be taken that no air is trapped in the pyknometer, spinning the pyknometer as the liquid is added assists in the de-aeration of the powder/liquid mixture. The pyknometer is then placed in a temperature-controlled bath and allowed to reach equilibrium. It is critical that the temperature of the liquid inside the pyknometer is checked before the pyknometer is sealed by insertion of the stopper, as there may be a differential in temperature between the bath and the liquid in the pyknometer. It is also crucial that none of the powder under test is lost when performing the sealing process.

4.2 Measurement results for liquid and gas pyknometry

With care, uncertainties of better than 1 in 10^3 can be achieved with this measurement method. Table 3 shows the results of measurements of powder density by liquid and gas pyknometry methods. The results are plotted in figure 5.

Table 3. Density measurements by liquid and gas pyknometry.

Measurement method	Temperature °C	Measured density $g\,cm^{-3}$	Estimated uncertainty $\pm g\,cm^{-3}$
Liquid pycnometry	20.0	1.208 6	0.002
	30.0	1.206 1	0.001
	50.0	1.201 5	0.004
	70.0	1.195 2	0.001
Helium pycnometry	26.5	1.240 5	0.020

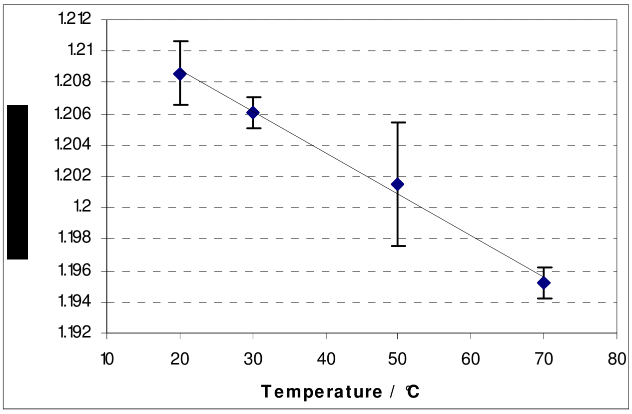

Fig. 5. Liquid pyknometry results for powder density at temperatures in the range 20 °C to 70 °C.

The results show an uncertainty of 1 in 10^3 is achievable with the liquid pyknometry technique. The technique also allows close control of the measurement temperature and the results in the range 20 °C to 70 °C show good consistency. This allows the calculation of a thermal coefficient for the powder which had not been possible with other measurement methods. A significant difference can be seen between the results of the liquid and gas pyknometry methods. Helium pyknometry will give a value for the "skeletal density" (solid material including closed pores). The value measured by liquid pyknometry will be closer to the "effective density" (solid material including open and closed pores).

5. CONCLUSIONS

Techniques for the measurement of the density of porous materials, small samples and particulates have been developed and evaluated. A gravimetric method involving the weighing of larger samples of porous material (10 grams to 1 kilogram) in gas of known density has been used to measure the volume of mass standards to uncertainties of parts in 10^4 without the need for immersion in liquid. The method has also been used to determine the density of materials not suitable for hydrostatic weighing.

The feasibility of using a density gradient column for the accurate determination of the density of small samples of material to an accuracy of parts in 10^6 has been demonstrated for densities below 2500 kg/m^3. Further work is underway to adapt the technique to allow the measurement of samples with densities of about 3500 kg/m^3.

Liquid pyknometry measurements have been adapted to allow the determination of the density of powders for the food industry. The technique has advantages over the usual helium pyknometry method in that it allows close temperature control of the measurements and therefore the calculation of a thermal coefficient of expansion for the powder. An in-liquid calibration method may also be more appropriate for powders used in certain applications where apparent density in liquid is the required measurand.

ACKNOWLEDGEMENTS

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REFERENCES

[1] "A comparison of hydrostatic weighing methods used to determine the density of solid artefacts", Downes and Elandaloussi, NPL report MOT 3.

[2] "Use of a density gradient column to measure the density of microspheres" Canada and Laing, *Anal. Chem.*, **1967**, *39* (6), pp 691–692.

[3] "About pyknometric density measurements" Viana et al, Talanta, vol. 57 (3), 2002, pp 583-593