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DENSITY DETERMINATION OF POWDERS BY LIQUID DISPLACEMENT METHODS.

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ABSTRACT

The densities of a number of powders were determined by liquid pycnometry and flotation as well as the more usual method of gas pycnometry. Replicate samples showed more variation when determined by liquid methods. However large differences between results obtained from liquid and from gaseous methods were not obtained. The significance of these differences in terms of powder compression and porosity calculations was assessed. The sample size and degree of ultrasonic agitation was shown to affect the value of density obtained by liquid pycnometry.

INTRODUCTION

Compression equations relating applied pressure to the porosity of the resultant compact are widely used in powder compaction studies[1]. Some calculations for tablet tensile strength also include a correction for tablet porosity[2].

In order that porosity can be calculated, both the apparent and true densities of the compact must be available. The former is readily calculated from tablet dimensions, but the latter is normally determined by gas pycnometry, a technique which uses an apparatus which though not complex is fairly expensive. In a recent publication[3], true density was determined by liquid pycnometry, a method using simple and cheap apparatus. These authors report significant differences between densities obtained by gas and liquid pycnometry.

A subsequent publication (Duncan-Hewitt and Grant[4]) reported the use of gas and liquid pycnometry and a flotation method for the determination of the densities of samples of adipic acid doped with oleic acid. This study was primarily to investigate the crystallinity of the samples.

The aim of this work is to compare gas and liquid pycnometry plus a flotation method for their usefulness in determining the densities of powder particles prior to their compaction. The data so obtained will be used in compression equations and the precision of the data will be assessed with this use in mind.

EXPERIMENTAL

Powders: Avicel PH102 (microcrystalline cellulose, Honeywell and Stein, London), Emcocel (microcrystalline cellulose, Forum Chemicals, Reigate), Lactose DC11 (Spray-dried lactose, DMV, Veghel), Microtal (compressible sucrose, Tate and Lyle, London), paracetamol (Sterling Organics, Newcastle), Emcompress (directly compressible dicalcium phosphate dihydrate, Forum Chemicals). All were used as received.

Liquids: The liquids used in the displacement and flotation studies are given in Table 1. In all cases, a saturated solution of the solid in the appropriate liquid was prepared.

Gas pycnometry was carried out on a Beckman Model 930 Gas Comparison Pycnometer, using air as the gaseous medium.

A 10ml glass pycnometer was used for liquid pycnometry determinations. Ultrasonic agitation, where used, was carried out in a Mettler Model ME11 ultrasonic bath, with the pycnometer containing the powder sample and about 5 ml of the liquid. After agitation, the apparatus was allowed to return to ambient temperature before filling and weighing.

For density measurements by flotation, mixtures of the appropriate liquids were prepared in 5ml vials. About 0.2g of the solid was added and the mixture shaken. The suspension was then drawn up into a vertical 5ml pipette, and the movement of the particles observed. The composition of the liquid was changed until the particles remained stationary. The density of the liquid mixtures was determined by density bottle.

RESULTS AND DISCUSSION

The determination of density by any liquid method demands that the solid is relatively insoluble in and effectively wetted by the liquid in question. Also for the flotation method, the two liquids used should have fairly similar densities, one somewhat less than and one somewhat greater than that of the solid in question.

Density data for the three methods are given in Table 1.

The effect of sonication was evaluated by subjecting samples to a range of sonication times and also using different quantities of solid. Specimen results for Emcompress with water are shown in Figure 1. With shorter sonication times, the time and sample size affect the result, but after about 8 minutes, results were independent of experimental conditions. For all the data quoted in Table 1, a sonication time of 10 minutes and a sample size of 0.5g were employed. The variation within groups of replicate samples showed no dependence on sample size or sonication time.

Carstensen and Hou [3] reported that sonication increased the density of granular tricalcium phosphate from 1.91 to

TABLE 1

Densities of Powders (gcm^{-3}) determined by Air Pycnometry, Liquid Pycnometry and Flotation.
A = Avicel, El = Emcocel, L = Spray-dried lactose, M = Microtal, P = paracetamol, Em = Emcompress.
SD = standard deviation, CV = coefficient of variation.

(a) By Air Pycnometry

	A	El	L	M	P	Em
Mean	1.546	1.552	1.533	1.573	1.306	2.230
n	11	5	5	4	4	3
SD $x10^{-3}$	4.55	6.43	1.79	1.50	3.88	0.85
CV(%)	0.29	0.41	0.12	0.10	0.30	0.09

(b) By Liquid Pycnometry

	A	El	L	M	P	Em
Mean	1.456	1.494	1.536	1.646	1.310	2.376
n	5	5	5	5	5	5
SD $x10^{3}$	20.7	30.9	32.4	17.8	43.8	18.2
CV(%)	1.76	2.07	2.11	1.09	3.34	0.77
Liquid	Water	Ether	Chloroform	Chloroform	Ether	Water

(c) By Flotation, using chloroform:carbon tetrachloride mixtures.

	A	L	M
Mean	1.557	1.531	1.570
n	10	10	10
SD $x10^{-3}$	8.41	9.01	7.62
CV(%)	0.54	0.59	0.49

(d) By Flotation, using 1-bromonaphthalene:carbon tetrachloride mixtures

	A	L	M
Mean	1.562	1.539	1.579
n	10	10	10
SD $x10^{3}$	10.52	9.05	6.41
CV(%)	0.67	0.59	0.41

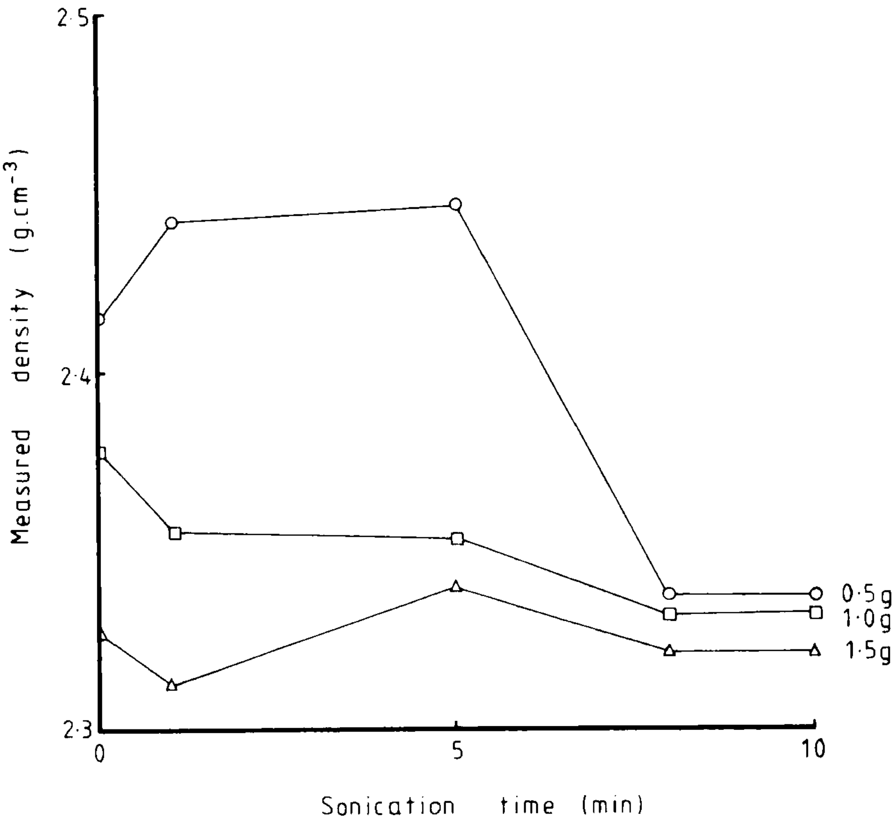

FIGURE 1
The effect of sample size and sonication time on the value of powder density measured by liquid pycnometry.

3.1 gcm . These workers did not describe their experimental conditions, but even so, such changes far exceed those found in the present study for any of the solids examined. It must be concluded that the change in density brought about by sonication of tricalcium phosphate is related to the granular nature of that material and is not applicable to all solids.

Comparison of the two pycnometry methods shows that liquid pycnometry is a less precise method than air pycnometry, the coefficients of variation of the former invariably being greater than those of the latter. Replicate measurements of the densities of the suspending fluids by liquid pycnometry always gave coefficients of variation of less than 0.1%. It must therefore be concluded that variations in the liquid pycnometry technique derive from slight variations in wetting and/or the entrapment of occluded air. With both air and liquid pycnometry, the coefficients of variation obtained from all powders are of the same order for any particular technique, thus suggesting that the precision of that technique is independent of the nature of the material.

Even though liquid pycnometry does in some cases give a different particle density from that given by gas pycnometry, the significance of these differences must be evaluated. In the case of Avicel, the difference in density (0.09gcm) is the greatest for all the powders examined. If the air pycnometry value is assumed to be "correct" at 1.546gcm , then the significance of a measured density of 1.456gcm must be assessed.

Figure 2 is derived from a series of Avicel tablets compressed at a range of pressures (P). Apparent densities were calculated from tablet dimensions, and a series of notional values between 1.2 and 3.0 gcm are used for the "true" density. The relative density (D, the ratio between apparent and true densities) is calculated and the data

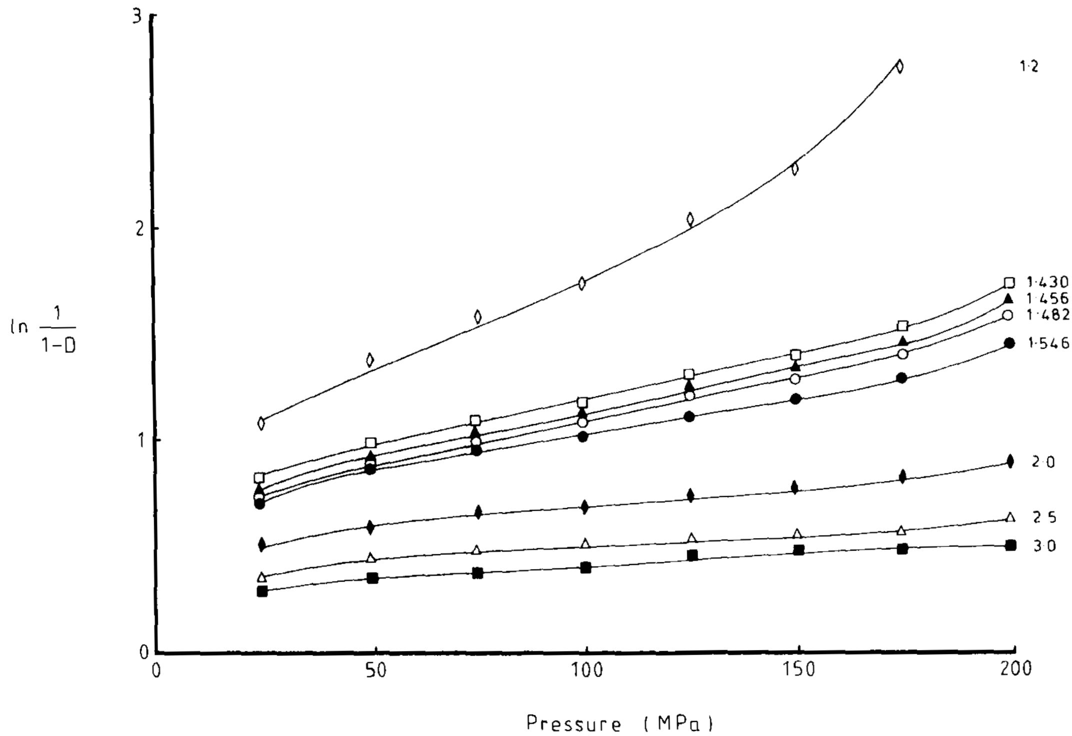

FIGURE 2
Compression data manipulated according to the Heckel equation and using a range of values for the assumed density of the powder.

expressed by means of the Heckel equation (Equation 1).

$$\ln 1/(1-D) = kP + A \qquad \text{Equation 1}$$

Linear regression analysis over the range 50-150 MPa gives the constants k, the slope of the line, and A, the intercept on the ordinate. The variation of these parameters with the assumed value of the true density is shown in Figure 3.

The values of both intercept and slope decrease in a non-linear manner as the assumed density is increased.

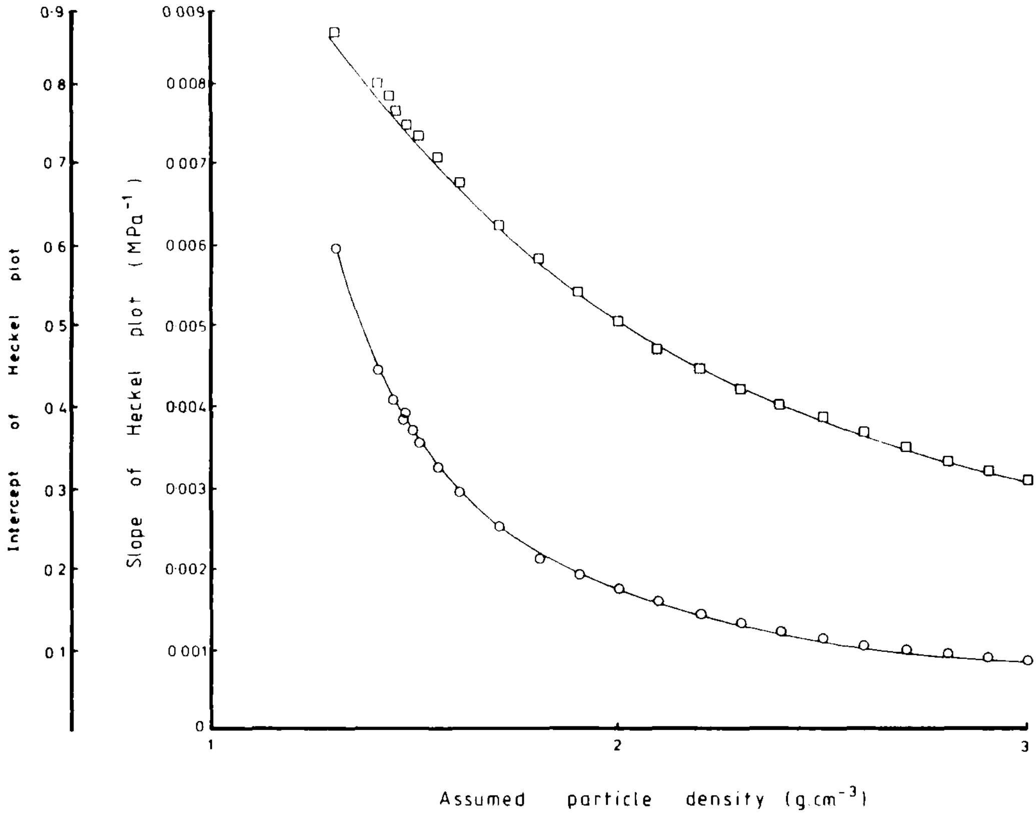

FIGURE 3
Values of slopes and intercepts of Heckel plots derived from data shown in Figure 2.

The change in both is less at higher densities i.e. a given error made in determining the true density will have a more serious consequence with low density solids. The linear correlation coefficient remained constant at 0.998 between assumed densities of 1.4 and 3.0 gcm^{-3}, in contrast to the increased linearity reported by Carstensen and Hou .

The effect brought about by the relative imprecision of liquid pycnometry is also shown in Figures 2 and 3. The mean density of Avicel by liquid pycnometry is 1.456 gcm^{-3}, with a standard deviation of $0.026gcm^{-3}$. The Heckel plots, using densities of 1.430 and $1.482gcm^{-3}$ i.e mean $\pm$ 1 standard deviation, are shown.

The densities of Avicel, Microtal and direct compression lactose were determined by the flotation technique, using two liquid media, namely carbon tetrachloride with either chloroform or 1-bromonaphthalene. Reproducibility and density results were comparable to those given by gas pycnometry, a result in agreement with that given by Duncan-Hewitt and Grant[4]. However such precision may not be obtained if it were necessary to use two liquids which differed considerably in density. Such a situation may obtain in the examination of solids of relatively high density such as calcium phosphate. The latter has a density of about 2.3 gcm^{-3}, and there is a limited choice of liquids of about this density but with suitable volatility, stability and lack of toxicity. The flotation technique is also more time-consuming than liquid pycnometry.

CONCLUSION

From the data presented here, gas pycnometry would appear to be the most precise technique. Nevertheless, liquid pycnometry and flotation techniques can be used to determine particle densities with reasonable reproducibility. As with any analytical technique, the errors associated with it must be considered in the context for which the data are required. Nevertheless, in view of the cheapness and availability of the apparatus needed, powder density measurements by liquid technique appear worthy of investigation

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