

DETERMINATION OF THE DENSITY OF SOLIDS BY MEANS OF A SOLID PYCNOMETRIC SUBSTANCE

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A new method has been developed for determination of apparent density of porous powdered materials, which uses a suitable plastic solid substance as the pycnometric medium. In this method a mixture of the tested and pycnometric substances is compressed in a pressing device up to the pressure, at which the pycnometric substance undergoes plastic deformation and fills completely all intergranular voids between particles of the tested material. The rheologic properties of the pycnometric substance prevent its penetration into coarse pores, which makes the method especially suitable for determination of apparent density of coarsely porous materials. The method can be used also for determination of true density of non-porous powdered materials.

The porous structure of solid substances may be characterized by the total volume of pores V_p

$$V_p = (d_t - d_a)/d_t d_a, \quad (1)$$

or by the porosity e

$$e = (d_t - d_a)/d_t, \quad (2)$$

where d_t is the true and d_a the apparent density of the porous material.

There exists no universal method for the determination of apparent density applicable to substances with different pore distributions and particle sizes. For lump materials, the most suitable and, at the same time, the most precise is the stereometric method, based on measurement of dimensions of a geometrically regular body cut out of the sample.

For water-insoluble substances with grain size over 10 mm, the displacement method¹⁻⁴, with water used as pycnometric medium, gives practically the same results as the stereometric method and is simple and very precise.

For substances with finer grain size, which do not react with mercury, the pycnometric method with mercury is generally used^{5,6}. As the capillary depression of mercury, after wetting the grain surface, must be overcome by external pressure, certain volume of the largest pores is always filled, thus distorting the actual value of the apparent volume. Therefore, the apparent density determined in this way is usually denoted as "mercury density".

Problems associated with the interaction of pycnometric liquid with tested material, with the effect of penetration on the value of apparent density, as well as with the limited possibility to measure the powdered materials, are eliminated (for substances with grain size below 5 mm) by the new method, which uses solid substances as pycnometric media.

THEORETICAL

When compressing the solid non-porous pycnometric substance in confined space, the substance attains, with increasing pressure, the plastic deformation zone. If the substance is in powdered form, the intergranular voids are gradually filled until at a certain pressure P_t the individual grains associate into a nonporous compact material. After attaining this condition, the bulk density of the relieved compact equals the density of its own solid phase.

If a mixture of a "soft" (pycnometric) substance with low P_t -value (P_{t_1}) and of a "hard" (tested) substance with high P_t -value (P_{t_2}) is subjected to compression by a pressure equal to or only slightly higher than P_{t_1} , the "hard" material is just elastically deformed, while the "soft" substance, subjected to plastic strain, is displaced into voids between the grains of the "hard" substance. In such a case, the "soft" substance — much similarly as the liquid in usual pycnometry — fills completely the void volume between particles and substitutes the function of the pycnometric medium. If the density, weight and volume of the "soft" substance, weight of the "hard" substance, and the volume of the mixture at the pressure P_t , are known, the volume of the "hard" substance can easily be calculated.

EXPERIMENTAL

Apparatus

Because relatively low pressure are required for compacting the tablet (within 250 to 300 MPa approximately) very simple laboratory screw presses may also be used in addition to hydraulic presses. Most suitable is the pressmould (Fig. 1) with a cylindrical cavity, in which both the piston and the packing piece on the mould bottom must fit with minimum tolerance, in order to prevent leaking of the pycnometric substance from the mould within the creep range.

Preliminary Determinations

The density of the non-porous solid pycnometric substance d_p is determined in an inert liquid. Increasing pressures are used to produce a number of tablets from the solid pycnometric substance. The pressure P_{t_1} , at which the density of the tablet reaches the density d_p , i.e. the pycnometric substance turns from powder into compact material, is then used for compacting of tablets in the determination of densities.

The materials with creeping at a relatively low pressure which can be prepared in powdered form are suitable as pycnometric substances. With these claims comply some synthetic organic

polymers, very soft metals, hard waxes and some by-products of the heat treatment of coal and crude oil. For the practical application, the coal tar pitch and petroleum asphalts have the largest significance.

Procedure

The investigated porous substance (weight m_s) and the pycnometric substance (weight m_p) are weighed into a vial, the ratio m_p/m_s being between 1.5 and 2. The total amount of the mixture should be sufficient for preparation of a 2 to 3 cm³ tablet. The mixture is homogenized in the closed vial by slow rotation around its longitudinal axis. The mixture is then carefully poured into the mould to avoid perceptible segregation of the two components. If the segregation cannot be avoided because of the large difference in the densities of the investigated and pycnometric substance, a known small amount m_b of the pycnometric substance is first poured into the empty mould and then the mixture of the two substances is added on the top of this auxiliary layer.

The powder mixture is gradually compressed by pressure P_{t1} , or slightly higher, and is maintained under this pressure for 15 to 20 seconds. After relieving the pressure, the tablet is carefully removed from the mould, weighed (m_t) and its geometric dimensions are determined with the accuracy ± 0.05 mm (with the aid of a micrometer screw). The dimensions are used to calculate the tablet volume V_t .

Density of the porous substance, d_s , is calculated as

$$d_s = \frac{m_t m_s d_p}{(V_t d_p - m_b)(m_s + m_p) - m_t m_p} \quad (3)$$

If use is not made of the auxiliary layer of the pycnometric substance itself, $m_b = 0$. If the investigated substance is non-porous, the density d_s is equal to its true density d_i ; for porous substances d_s is equal to the apparent density d_a . Equation (3) takes into account that not the whole

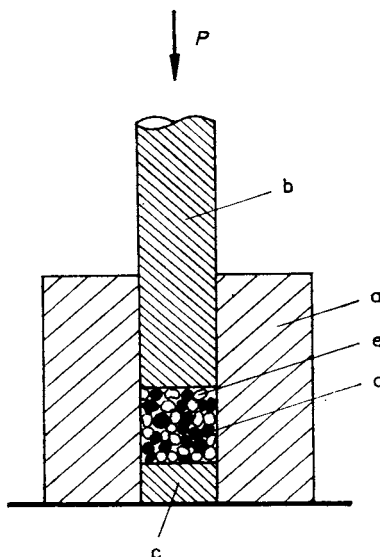


FIG. 1

Scheme of the pressmould. a Thick-walled jacket, b piston, c packing piece, d grains of the investigated material, e grains of the pycnometric substance

weighed mixture was necessarily transferred into the mould, i.e. that the weight of the tablet need not be the same as that of the mixture.

Very thin layer of MoS₂ was applied to the walls of the mould in order to decrease the friction during compression. In this way a uniform consolidation of powder layer is achieved and the extrusion of tablets is easy.

RESULTS AND DISCUSSION

In developing this method, the polymerized glycerol-1-monostearate, was used as the solid pycnometric substance. This substance was in the form of monodisperse

TABLE I

Comparison of densities determined by conventional method (CM) and with the solid pycnometric substance (SPS)

Sample	Form	$d_s, \text{g cm}^{-3}$	
		CM	SPS ^d
Steel	monodisperse balls $r = 0.239 \text{ cm}$	7.810 ^a	7.810 ± 0.001 ^e
Glass	monodisperse beads $r = 0.113 \text{ cm}$	2.450 ^b	2.447 ± 0.005
Mg	powder <0.1 mm	1.878 ^b	1.888 ± 0.004
Al	powder <0.1 mm	2.675 ^b	2.672 ± 0.005
Charcoal 1	grains 3–5 mm	0.813 ^c	0.814 ± 0.005
	powder <0.06 mm	—	0.943 ± 0.003
Charcoal 2	grains 3–5 mm	0.981 ^c	1.000 ± 0.003
	powder <0.06 mm	—	1.219 ± 0.005
Charcoal 3	grains 3–5 mm	0.557 ^c	0.565 ± 0.006
	powder <0.06 mm	—	0.626 ± 0.003
Charcoal 4	grains 3–5 mm	0.756 ^c	0.758 ± 0.003
	powder <0.06 mm	—	1.095 ± 0.004
Silica gel	grains 3–5 mm	1.310 ^c	1.310 ± 0.002
Coke	grains 3–5 mm	1.250 ^c	1.242 ± 0.008
	1–3 mm	1.290 ^c	1.296 ± 0.003
	0.5–1 mm	1.323 ^c	1.330 ± 0.005
	<0.2 mm	1.368 ^c	1.380 ± 0.003
Pycnometric substance	grains 0.5 mm	1.036 ^b	1.036 ± 0.001

^a Stereometry; ^b pycnometry; ^c Hg porosimetry; ^d $P_1 = 245 \text{ MPa}$; ^e the values of $d_s(\text{SPS})$ are given with standard deviations.

spherical particles of diameter 0.1 mm and density $d_p = 1.036 \text{ g cm}^{-3}$. Plastic flow started at $P_{ti} = 245 \text{ MPa}$. Certain penetration of this solid pycnometric substance into macropores cannot be a priori excluded. Therefore, the possibility of penetration was verified on glass capillaries with known opening size. It was found that at pressure 250 MPa, capillaries with openings smaller than $30 \mu\text{m}$ were not penetrated. It is evident, that the diameter of the smallest penetrated macropore depends strongly on the rheologic properties of the used pycnometric substance.

Determination of true density was performed with steel balls, glass beads and powdered metals; apparent density was determined for silica gel, active carbons and cokes. The obtained results are compared with data from conventional methods in Table I.

The developed method is suitable for determination of true density of non-porous substances and of apparent density of porous substances with particle sizes below 5 mm. The accuracy of the determination depends on the precision of weighing and determination of dimensions of the tablets.

Advantages of the described method are following: *a)* The apparent volume includes pores with diameters up to $30 \mu\text{m}$. *b)* Mercury is not used. *c)* The pycnometric substance is chemically inert, thus, there is no interaction with the tested material. *d)* No evacuation of the sample is necessary. *e)* Temperature control is not necessary because the determined quantities are temperature insensitive. *f)* The volume of tablets is determined with high accuracy. *g)* Substances containing moisture can be processed, which is of considerable practical importance.

LIST OF SYMBOLS

d_s	density of investigated sample, g cm^{-3}
d_p	density of the pycnometric substance, g cm^{-3}
m_p	weight of the pycnometric substance in the mixture, g
m_s	weight of the investigated sample in the mixture, g
m_b	weight of the auxiliary layer of the pycnometric substance, g
m_t	weight of the tablet, g
V_t	volume of the tablet, cm^3

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