THE INFLUENCE OF SAMPLE MASS AND PARTICLE SIZE ON THE AREA OF THE DTA PEAK IN THE DIFFERENTIAL THERMAL ANALYSIS OF POWDERED MATERIALS

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ABSTRACT

This article presents the results of investigations into the influence of sample mass and particle size on the area of the DTA peak in the differential thermal analysis (DTA) of powdered materials. It was established that for a cylindrical sample, the area of the DTA peak increases linearly with the increase in sample mass up to a certain limit beyond which the linearity breaks down. With further increase in the mass of the sample, the area of the DTA peak increases linearly even further but the straight line obtained has a much smaller slope. A relationship is established between the maximum sample mass, up to which the initial linear relationship of $S = f(m)$ is valid, and the average particle diameter of powder materials studied. This relationship raises the possibility that, based on the average particle diameter of the sample studied, the maximum sample mass usable in quantitative DTA, can be predetermined.

INTRODUCTION

In quantitative differential thermal analysis (DTA), the area of the DTA peak is the basis of all further investigations. Considering the fact that the area of the peak obtained increases with increase in the mass of the sample studied, numerous investigators have studied the relationship of the area of peak obtained with the mass of the sample. Results of a large number of investigations [1—5] show that the area of the DTA peak increases linearly with increase in sample mass up to a certain limit, and that further increase in sample mass does not influence the increase in the area of the DTA peak.

Berg and Egunov [2] have divided the curve $S = f(m)$ into three regions: (a) the region of linear increase in the area of the peak with increase in the sample mass; (b) a transitional region in which the area of the peak increases slightly with increase in sample mass; and (c) the region where the area of the peak does not depend upon the sample mass.

Sementovski [6] states that the linear relationship between the area of the DTA peak and the sample mass does not exist, and Pilojan [7] tries to prove this statement mathematically, stating, at the same time, that linearity exists only for small sample masses.

A large number of investigators [8—14] show that, on the whole, the particle size of the sample under study does not influence the character of the

DTA curve, but concrete considerations of the influence on the area of the peak are very limited.

For the case of the DTA of powdered materials, there is the problem of the bulk density of the sample in the reaction space [15]. Because it is very difficult to provide constant compression of the sample in the reaction space, in the DTA of powder materials, the sample and the reference sample are normally used without compression.

In quantitative DTA, it is required that the maximum sample mass up to which there is a linear increase in the area of the peak with increase in sample mass is known so that quantitative investigations can be carried out up to this limiting sample mass. For the case of powdered samples, where particle size and hence sample geometry, may vary over a wide range for the same mass, this may mean that the limiting sample mass determined for one sample may not be valid for the next sample of the same material. Since this problem has received little attention in the literature, its investigation is of particular interest for the further development of the theory and application of DTA to the quantitative investigation of systems comprising powdered materials.

EXPERIMENTAL

For the experimental investigations, the natural minerals magnesite and calcite were used. These were ground to a pre-determined particle size, and separated into narrow particle size ranges by screening through a series of laboratory screens. The purity of the samples studied was 99.5% and the range of particle sizes was the same as for the determination of the constant gK_s [16].

All investigations were carried out on DTA equipment with the reaction space in a Ni block [16]. Experiments were carried out in air at a heating rate of $10°$ min^{-1}.

RESULTS AND DISCUSSION

Starting with the basic equation for quantitative DTA [16]

$$m\Delta H_T^0 = gK_s \int \Delta T \, dt \tag{1}$$

where m, ΔH_T^0, g, K_s and $\int \Delta T \, dt = S$ represent, respectively, the sample mass, the specific heat of reaction, the constant of geometric shape, the thermal conductivity of the sample and the area of the DTA peak. The area of the DTA peak should increase linearly with increase in sample mass.

To define more closely the relationship $S = f(m)$ for different particle sizes of powdered material, a large number of DTA curves was recorded with different masses and different average particle diameters for samples of $CaCO_3$, $MgCO_3$ and $CdCO_3$. In all cases, the sample investigated was in the form of a cylinder and the particle size of the α-Al_2O_3 reference sample was the same as that of the sample studied. It is necessary to keep the same geometric pat-

tern for the sample studied in these circumstances because changes in the pattern, e.g. from the shape of a calotte, to the semi-ball shape of the flask, influence to a large extent the area of the DTA peak obtained [17].

Figure 1 shows the relationship between the area of the DTA peak and the sample mass for the smallest fractions of samples of $MgCO_3$, $CaCO_3$ and $CdCO_3$. From this figure, it may be seen that with the increase in sample mass, the area of the DTA peak increases linearly up to a certain mass, and that further increase in mass does not cause curvature of the straight line $S = f(m)$ as stated by Berg and Egunov [2], but gives another straight line with a much smaller slope.

For the straight lines in Fig. 1, it may be possible to approximate the end portion to a curved hyperbolic relationship, but as far as the results in Fig. 2, which refer to $MgCO_3$ and $CaCO_3$ samples with average particle diameters of 275 μm, are concerned, it is obvious that this is not possible. Therefore, for a cylindrical sample, the relationship $S = f(m)$ is linear over the whole range of sample mass investigated, apart from a break point at a certain sample mass. This limiting sample mass is also the maximum sample mass to which investigations may go in quantitative DTA for a given sample particle size because over this mass the same calibration constant gK_s is not valid [16]. Above this limiting mass, when there is a break point on the straight line $S = f(m)$, the area of the DTA peak is influenced mostly by the geometric parameter, g.

In these experiments, all the samples were in the shape of a cylinder, thus keeping the same geometry at all times. The change in slope of the straight line $S = f(m)$ may be considered to be due to changing conditions of thermal conductivity per sample height, i.e. to the change of vertical temperature gradient with the increase of sample mass.
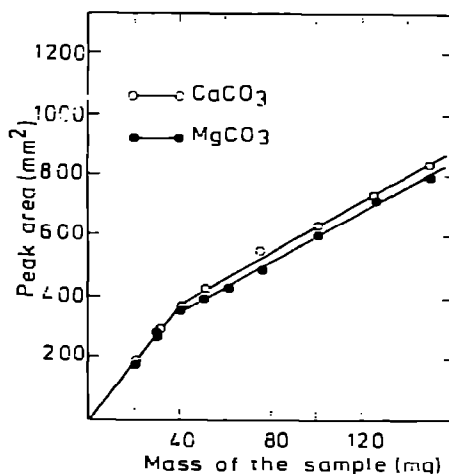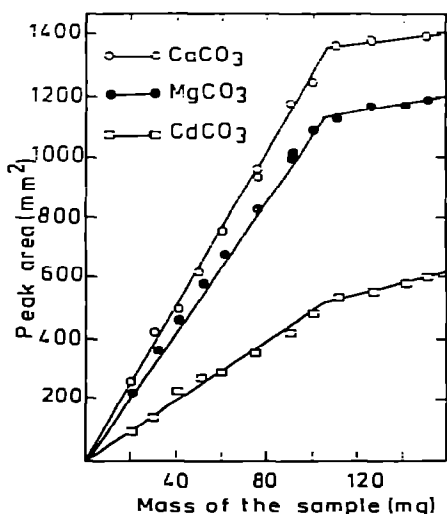

Fig. 1. Relationship of the area of the DTA peak with sample mass. Average particle diameter of samples: $CaCO_3$, 18 μm; $MgCO_3$, 20 μm; $CdCO_3$, 8 μm.

Fig. 2. Relationship of the area of the DTA peak with sample mass. Average particle diameter of sample 275 μm.

It was observed, based on the results presented above, that for different particle sizes of the same sample, apart from different slopes of the straight line $S = f(m)$ up to the break point, because of differences in the thermal conductivity coefficient, the limit up to which linear increase in the area of the DTA peak with the increase of sample mass is valid also changes.

Figure 3 shows the relationship $S = f(m)$ for two samples of magnesite of approximately equal particle size (average particle diameter of the samples 177.5 and 229 μm), as well as of a 50 : 50 mixture. It may be seen that the initial part of the curve for all three cases approximates to a straight line (because the coefficients of thermal conductivity for all three samples are approximately equal), and that the break point shifts towards smaller sample masses with increase in mean particle diameter. These results also show that the influence of the constant g on the break point of the straight line $S = f(m)$ is more pronounced than that of the constant K_s on its slope.

If, based on all the results for a specific maximum sample mass up to which the initial relationship $S = f(m)$ is valid for different sample particle sizes, the relationship between such determined maximum masses and the average particle diameters to which the maximum masses refer is drawn, a straight line is obtained and is shown in Fig. 4.

From Fig. 4 it may be seen that results obtained for a narrow range of particle sizes of $MgCO_3$, $CaCO_3$ and $CdCO_3$ as well as polydispersed samples of $MgCO_3$ are subjected to the same relationship. It should be expected that this relationship is also valid for other powdered substances if the investigations were carried out on the same equipment. The straight line shown in
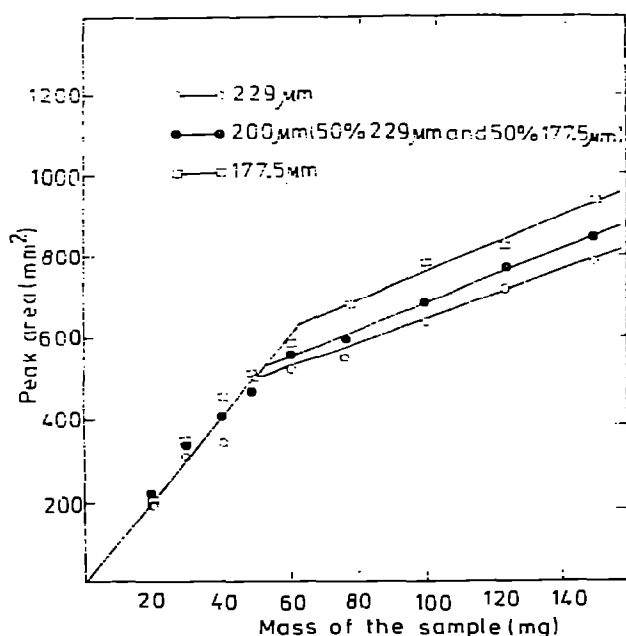

Fig. 3. Relationship of the area of the DTA peak with sample mass of the magnesite.
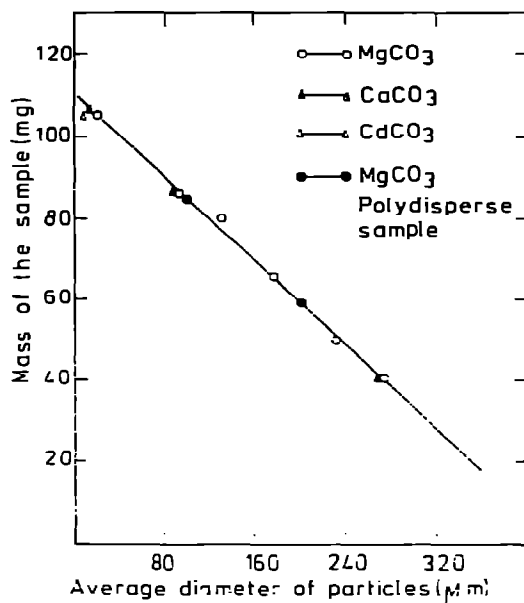
Fig. 4. Relationship of maximum sample mass, up to the point where the initial linear increase of the area of the DTA peak with the increase in sample mass is valid, as a function of the average particle diameter.
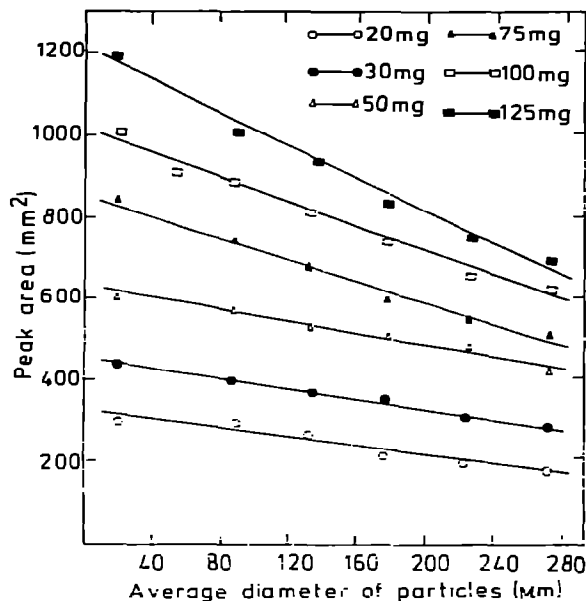
Fig. 5. Relationship of the area of the DTA peak with the average particle diameter of magnesite for different sample masses.

Fig. 4 may be analytically defined by

$$m_{max} = 142.66\text{-}0.4605\ d_{ave} \tag{2}$$

where m_{max} is the maximum mass up to which the area of the peak increases linearly (mg) and d_{ave} is the average particle diameter of the sample (μm).

Equation (2) provides for the possibility that, based upon the average particle diameter of the sample (which may be determined from the particle size distribution), the limiting mass of the sample up to which the initial linear increase of the area of the peak with the increase in mass is valid, can be determined, i.e. the limiting sample mass up to which one may go in quantitative DTA on this equipment. For any other equipment, where the sample geometry is different from the one used in this article, it is necessary to define this relationship experimentally in a similar way. All minerals, transformations of which belong to the group of processes of the same type ($A_s = B_s + C_g$), are subjected to this relationship. This limit also represents the limiting sample mass for the given equipment up to which the geometric factor, g, has no influence upon the calibration constant gK_s.

If we represent graphically the DTA peak area as a function of the average particle diameter of the sample for different masses, Figs. 5 and 6 for MgCO$_3$ and CaCO$_3$, respectively, it may be seen that, as the average diameter of the sample increases, the area of the DTA peak decreases, this decrease being more prominent for larger masses in both cases.

With the smallest sample masses in Figs. 5 and 6, decrease in the area of the peak with the increase in average particle diameter is a result of the
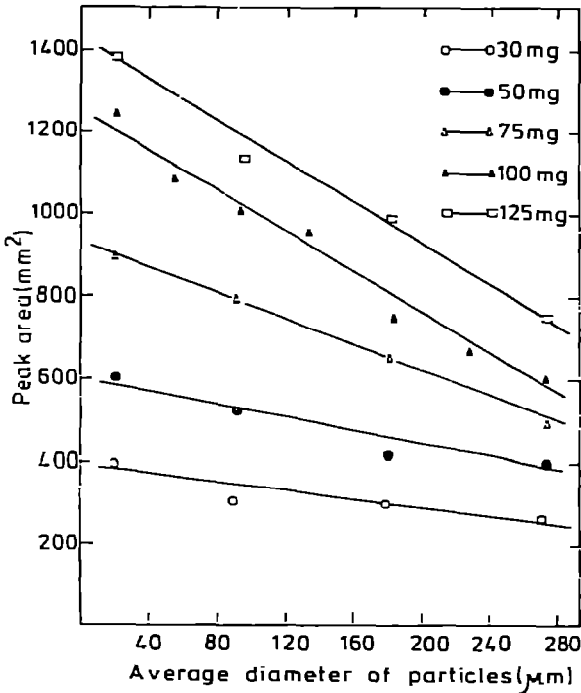
Fig. 6. Relationship of the area of the DTA peak with the average particle diameter of calcite for different sample masses.

increase in the thermal conductivity coefficient of the sample, and thus in the constant gK_s [16]. In this case, the increase in the constant gK_s is related to the increase in the constant K_s, while it may be considered that the constant g has no influence. With further increases in sample mass, the slopes of the straight lines in Figs. 5 and 6 increase because, for a larger sample mass, the increase in the constant gK_s is influenced by the geometric factor, g. Therefore, for these slopes, in every case, the change in the thermal conductivity coefficient makes the same contribution, and the contribution of the geometric factor, for different sample masses, is different.

If we represent the slopes of the straight lines in Figs. 5 and 6 by tan α, the area of the peak in cm^2 and the average particle diameter in cm, the dimensions of the slope would be

$$\tan \alpha (=) \frac{cm^2}{cm} (=) cm \qquad (3)$$

which corresponds to the dimensions of the geometric factor g. Based on this analysis, one may write

$$\tan \alpha \propto g \qquad (4)$$

Figure 7 shows tan α as a function of the sample mass based upon the results in Figs. 5 and 6. It may be seen that, in both cases, tan α maintains a constant value up to the sample mass of about 40 mg and that after this mass, it increases linearly. This is in accordance with the results in Fig. 4 where it may be seen that in the range of sample particle size studied, the
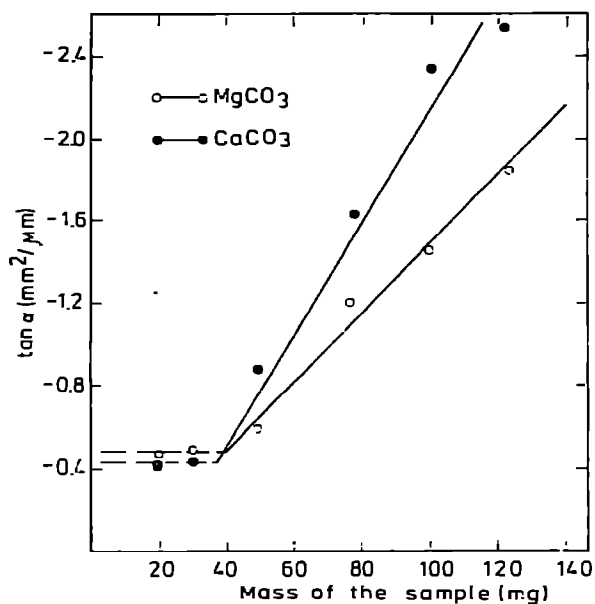
Fig. 7. Relationship of tan α with the sample mass.

lowest mass up to which the linear relationship $S = f(m)$ is maintained is about 40 mg for the sample with an average particle diameter of 275 μm. With a further increase in the sample mass (taking into consideration the largest sized sample), the geometric factor, g, increases linearly. This increase depends upon the porosity of the sample studied, which is always significant in powdered materials.

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