

## **THERMAL ANALYSIS OF POWDERED ALUMINA MATERIALS**

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### **Abstract**

How a DSC result is influenced by the particle size distribution of a powder sample is shown, and a simple and optimal method to be included in a routine DSC analysis (e.g., purity determination) to improve the reliability of the analysis is proposed. In case of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powder, most reliable heat capacity data can be obtained by preparing a powder with a self-similar particle size distribution with a distribution constant of 0.7, and by compressing it under a pressure of 1.5 MPa for a duration of 5 min or longer.

**Keywords:** distribution constant, DSC, powder compact, Rosin-Rammler particle size distribution, thermal resistance

### **Introduction**

Pharmaceuticals and industrial raw materials are often provided in the form of a powder. The determination of the absolute purity of materials by differential scanning calorimetry (DSC) is a well known technique in the pharmaceutical and chemical industries since the development of the DSC in the early 1960s [1].

Although dynamic purity determination has been shown to be a rapid and accurate technique, it is also known that the results are influenced by the heat conductivity of the sample, packing state of the powder sample in the sample pan, shape of the particles constituting the powder, etc. Furthermore, thermal resistances between the particles increase with increasing sample size. The technique itself requires operating at a moderate to low scanning rate on a sample of small size and correcting for thermal resistance between the sample and the sample pan. However, too slow a scanning rate or too small a sample size reduces the signal. This leads to an increase in S/N ratio as to impair the precision of the measurement.

Numerous methods for determining the heat conductivity of a sample in the form of a powder compact by means of DSC have been proposed to the early 1980's [2, 3]. The thermal conductivity of porous compacts are also considered both theoretically and phenomenologically [4, 5].

The present work shows how a DSC result is influenced by the particle size distribution of a powder sample, which assumably influences thermal resistance within

the powder sample packed inside a pan, and proposes a simple and optimal method to be included in a routine DSC analysis (e.g., purity determination) to improve the reliability of the analysis.

## Experimental

### *Preparation of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> samples differing in particle size distribution*

Samples differing in particle size distribution were prepared. Aluminum oxide suitable for chromatographic adsorption (Merck 1097) was used as the starting material. This was selected because it is prepared from carefully screened aluminum hydroxide having no self-similar particle size distribution [6](all particles through 150 mesh, 40% on 200 mesh, 40% on 325 mesh).

After thoroughly converting the starting material into thermally inert  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by heating it at 1100°C for 24 h, the material was mechanically size-reduced and classified using Tyler sieves to obtain five samples differing in particle size distribution (No. 1: -325 mesh, No. 2: -200 to +325 mesh, No. 3 and No. 4: -100 mesh, and No. 5: non-classified  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> without size reduction). Samples No. 3 and No. 4 were taken at different stages of grinding to see the differences in particle size distribution depending on grinding duration, but as is described hereinafter, no significant difference was observed between them.

Particle size distribution of each of the samples was obtained using SALD-1100 laser diffraction particle size analyzer (manufactured by Shimadzu Corporation) for a particle size range of from 1 to 150  $\mu$ m. The powder samples were dispersed in water using sodium metaphosphate as a dispersant.

### *DSC of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> samples differing in particle size distribution*

DSC was performed on about 20 mg portions of the sample and by using a 19.54 mg weight sapphire pellet as the reference material, both charged in aluminum sample pans (ca. 13 mg in weight) mounted on a sample holder of a heat-flux DSC 200 operated by SSC 5040 TA station manufactured by Seiko Instruments Inc.

Repeatability of DSC signals was checked by scanning three times over a given temperature range (200 to 400°C) at a heating rate of 15°C min<sup>-1</sup> (the sample was

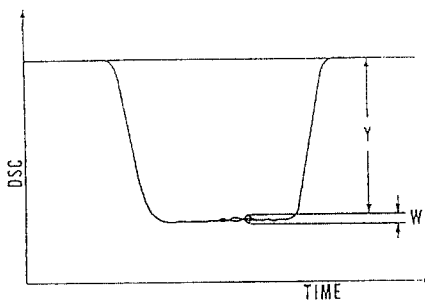


Fig. 1 Schematic drawing explaining how to determine repeatability

held for 10 min at the starting temperature 200°C and at the programmed upper temperature limit 400°C). Repeatability is expressed by

$$\text{Repeatability (\%)} = W/Y \times 100$$

where  $W$  is the maximum deviation for three superposed DSC curves and  $Y$  is the shift of the signal from the baseline at the maximum deviation (Fig. 1). The results are given in Table 1.

**Table 1** Repeatability for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders differing in particle size distribution

Sample No.	Repeatability/%
1 (-325 mesh)	0.74
2 (-200 to +325 mesh)	0.76
4 (-100 mesh)	0.73
5 (Non-classified)	0.76

Specific heat capacity of the samples were obtained according to an established method [7] by scanning over a temperature range of from 200 to 400°C at a heating rate of 15 or 10°C min<sup>-1</sup>. Samples (ca. 20 mg) were weighed by using a Mettler H20T semi-micro balance. The powder samples were each packed in the pan manually by lightly pressing a flat and smoothed head of a glass rod against the sample. The data thus obtained were analyzed and specific heat capacity was calculated using DSCSUB and DSCCP programs supplied in SSC5200 Ver.4.30 Thermal Analysis software package.

### *Effect of the duration of applying pressure to samples*

The duration of applying pressure to the sample was varied (5 min and 30 min) to see how the duration of compaction influences the results. The same pressure of 1.5 MPa was applied manually by placing the sample in a pan mounted on a scale, and pressing it with a 0.5 cm diameter glass rod having a flat and smooth end in such a manner that the scale indicates 5 kgf.

## **Results and discussion**

### *Particle size distribution of the samples*

The results are plotted on a Rosin-Rammler diagram which is shown in Fig. 2. The plots for sample No. 3 is omitted because it is substantially the same as that of sample No. 4. Thus, No. 3 is excluded from the discussion hereinafter.

All the powder samples obey the Rosin-Rammler distribution function or Over-size distribution  $R$  which is expressed by:

$$R(x) = 100 \exp\{-(x/x_e)^N\}$$

where  $x$  is the particle size,  $xe$  is the absolute size constant, and  $N$  is the distribution constant. The parameters  $xe$  and  $N$  for the samples are:  $xe=9.9\ \mu\text{m}$  and  $N=0.7$  for No. 1;  $xe=20.5\ \mu\text{m}$  and  $N=0.7$  for No.2;  $xe=38\ \mu\text{m}$  and  $N=1.2$  for No. 4; and  $xe=65\ \mu\text{m}$  and  $N=1.8$  for No. 5. It can be seen that samples differing in particle size distribution are obtained, but that Nos 1 and 2 are similar. That is, the plots for No. 2 is parallel shifted to the larger particle size side with respect to those for No. 1. In general, it is known that powder samples obtained by mechanical size reduction in a closed system and containing smaller particles at a larger fraction tend to yield  $N$  values not larger than 1.0. Theoretically, a bulk reduced to a group consisting of smaller particles yield a self-similar particle size distribution [8]. It can be naturally understood that, although not consolidated, the pieces which constituted a bulk may rearrange themselves into the original bulk. It is also well accepted that smaller particles are capable of forming a denser packed state.

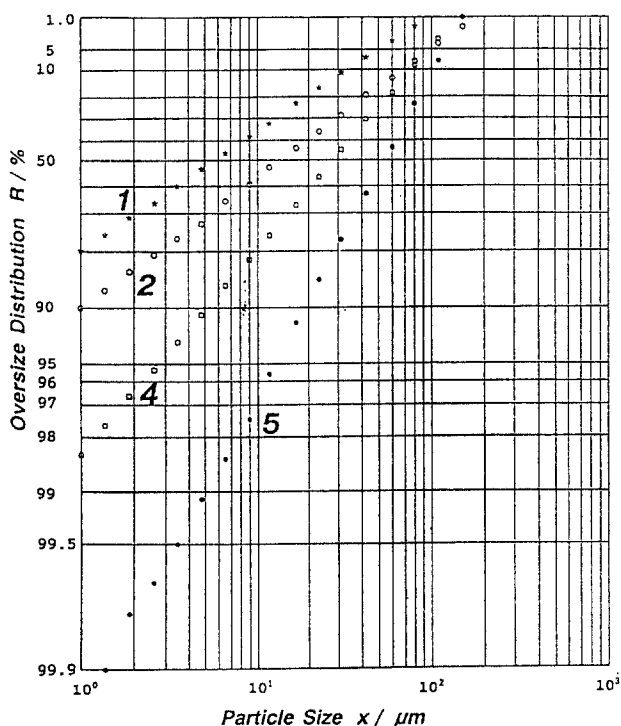


Fig. 2 Particle size distribution of  $\alpha\text{-Al}_2\text{O}_3$  powders plotted on Rosin-Rammler coordinate paper. The exponent  $N$  on the Rosin-Rammler particle size distribution function is 0.7 for samples No. 1 and No. 2; 1.2 for sample No. 4; and 1.8 for sample No. 5

### DSC results

No significant difference is observed among the repeatability of DSC signals for the samples (Table 1).

The specific heat capacity for the samples is given in Table 2 together with a literature value [9]. Percentage deviation (relative error %) of the observed values is calculated, and is plotted in Fig. 3.

The specific heat capacity for samples differing in duration of compaction are given in Table 3 and in Fig. 4. There is no significant difference between the two observed values.

Referring to DSC results shown in Fig. 3, it can be seen that the results are roughly classified into two groups. The first group yields specific heat capacity val-

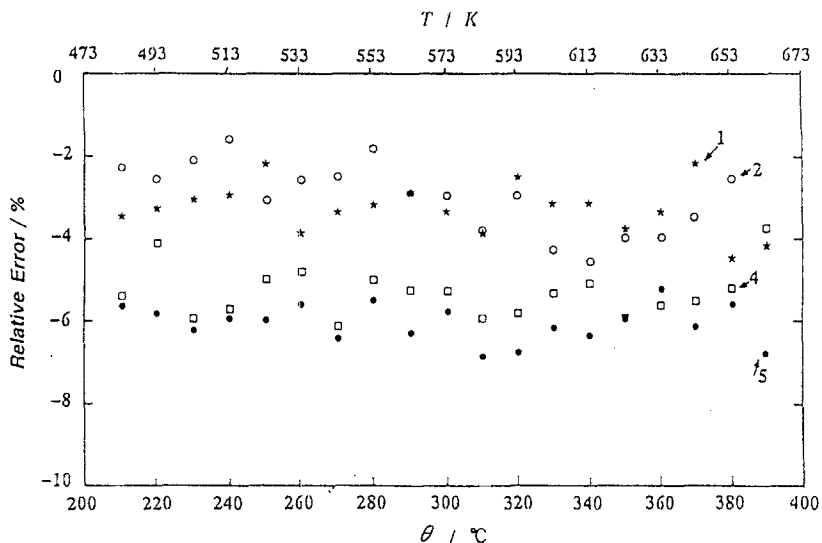


Fig. 3 Specific heat capacity  $C_p$  for  $\alpha\text{-Al}_2\text{O}_3$  powder sample Nos 1, 2, 4, and 5, expressed by relative error with respect to literature value

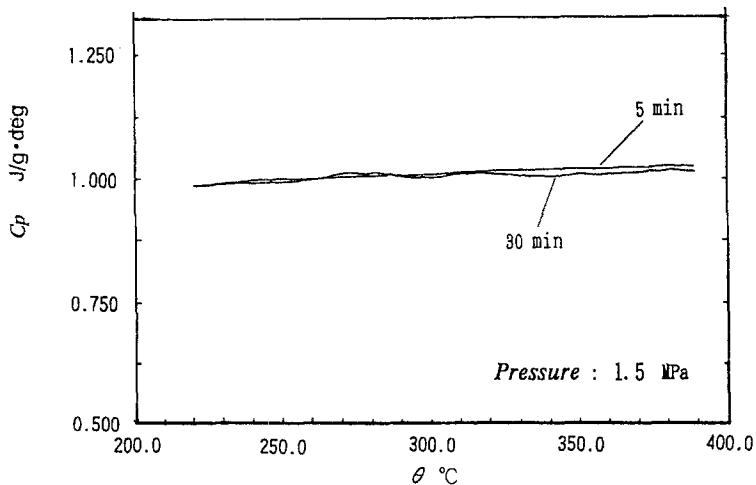


Fig. 4 Specific heat capacity  $C_p$  for  $\alpha\text{-Al}_2\text{O}_3$  powder sample ( $\sim 325$  mesh) pressed under 1.5 MPa for 5 and 30 min

Table 2 Specific heat capacity  $C_p$  for  $\alpha$ - $Al_2O_3$  powder samples (in air)

$T/^\circ C$	$C_p/J(g^\circ C)^{-1}$		$C_p/J(g^\circ C)^{-1}$		$C_p/J(g^\circ C)^{-1}$		$C_p/J(g^\circ C)^{-1}$	
	Literature	-325 mesh	-200 to +325 mesh	-100 mesh	Non-classified	Error/%	Error/%	Error/%
210	1.025	0.990	1.002	0.971	0.968	-3.5	-2.3	-5.4
220	1.034	1.000	1.007	0.992	0.974	-3.3	-2.6	-4.1
230	1.042	1.010	1.020	0.981	0.977	-3.1	-2.1	-5.9
240	1.049	1.019	1.033	0.990	0.987	-3.0	-1.6	-5.7
250	1.056	1.034	1.024	1.004	0.993	-2.2	-3.1	-5.0
260	1.063	1.022	1.036	1.013	1.003	-3.9	-2.6	-4.8
270	1.070	1.035	1.044	1.005	1.001	-3.4	-2.5	-6.1
280	1.076	1.042	1.058	1.023	1.017	-3.2	-1.8	-5.0
290	1.083	1.052	1.051	1.027	1.015	-2.9	-3.0	-5.2
300	1.089	1.052	1.056	1.031	1.026	-3.4	-3.0	-5.3
310	1.094	1.052	1.053	1.030	1.018	-3.9	-3.8	-5.9
320	1.100	1.071	1.067	1.036	1.025	-2.6	-3.0	-5.8
330	1.105	1.071	1.058	1.047	1.037	-3.2	-4.3	-5.3
340	1.110	1.075	1.059	1.054	1.036	-3.2	-4.6	-5.1
350	1.115	1.074	1.071	1.050	1.049	-3.8	-4.0	-5.9
360	1.120	1.082	1.075	1.057	1.059	-3.4	-4.0	-5.6
370	1.124	1.100	1.085	1.063	1.055	-2.2	-3.5	-5.5
380	1.129	1.078	1.100	1.071	1.066	-4.5	-2.6	-5.2
390	1.133	1.086	1.090	1.092	1.056	-4.5	-3.8	-3.7

**Table 3** Specific heat capacity  $C_p$  for  $\alpha\text{-Al}_2\text{O}_3$  powder samples (-325 mesh) pressed under 1.5 MPa for 5 and 30 min

$T/^\circ\text{C}$	5 min press -325 mesh	$T/^\circ\text{C}$	30 min press -325 mesh
220.17	0.984	220.15	0.987
230.17	0.989	230.15	0.989
240.17	0.992	240.15	0.997
250.17	0.994	250.15	0.999
260.17	0.999	260.15	0.997
270.17	1.004	270.15	1.010
280.17	1.007	280.15	1.010
290.17	1.008	290.15	1.000
300.17	1.011	300.15	1.001
310.17	1.014	310.15	1.008
320.17	1.016	320.15	1.009
330.17	1.018	330.15	1.004
340.17	1.019	340.15	1.003
350.17	1.020	350.15	1.007
360.17	1.021	360.15	1.008
370.17	1.023	370.15	1.011
380.17	1.023	380.15	1.015
390.17	1.026	390.15	1.012

ues falling closer to the literature values within a relative error of about 2 to 4%. The other group yields values deviated from the literature values by more than 5%. As a matter of fact, there is a problem of which literature to select as a standard, because, for example, the data cited hereinbefore differ from those of Ditmars *et al.* [10]. However, in the temperature range of from 200 to 400°C, the difference is negligible (less than 0.2%). The difference between the two groups is, far greater than 0.2%. The reason for this cannot be fully explained, but the greater deviation from literature values for the latter group is assumably attributed to a larger thermal lag. Since the heat flow through compacts is determined by the pore sizes and the contact areas between the neighboring particles, it may be safely said that packed structures consisting of coarser particles have smaller contact areas and hence form larger pores.

According to the percolation theory [11], electrical conductivity  $\sigma$  in heterogeneous media can be expressed by:

$$\sigma \propto (f' - f'c)^t$$

where  $f'$  and  $f'c$  are the volume fraction and critical volume fraction of the conducting component, and  $t$  is the exponent. The equation above should also apply to ther-

mal conductivity, and considering that  $f'c$  is a value of about 0.3 and that  $t$  is in a range of from about 2 to 3, it is readily understood that the thermal conductivity changes considerably with the change in porosity expressed by  $1-f'$  in case of a system consisting of a single conducting medium and an insulator (air).

Referring to Fig. 4, under a packing pressure of 1.5 MPa, there is no difference between the samples. This pressure was selected because it can be readily applied manually in laboratory experiments without using any particular equipment. However, it is known that measured conductivity changes abruptly upon attaining a certain value (e.g., about 3.5 MPa for pentaerythritol tetraacetate and about 100 MPa for tar granulated carbon [12]). The change is attributed to the change in the structure of the compacts, and so long as packed particles are considered, this need not to be taken into account.

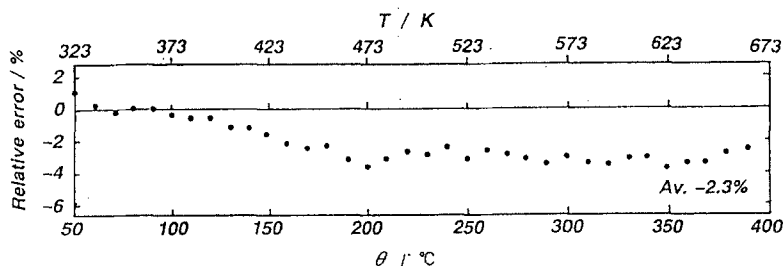


Fig. 5 Specific heat capacity  $C_p$  for  $\alpha$ - $\text{Al}_2\text{O}_3$  powder sample (-200 to +325 mesh) obtained under optimal conditions, expressed by relative error. Sample mass 19.98 mg; Al pan 13.98 mg; heating rate  $10^\circ\text{C min}^{-1}$

Thus, optimal conditions for performing DSC on packed particles are determined. As is shown hereinbefore, the influence of thermal lag or porosity can be minimized by using a powder having a self-similar particle size distribution with a distribution constant of 0.7 (assumably less than 1.0), and by compressing the powder sample uniaxially (i.e., by applying pressure downward from the upper surface of the sample) at a pressure of 1.5 MPa. Thus, the result for sample No. 2 (-200 to +325 mesh), which was obtained by using 19.98 mg of sample and at a heating rate of  $10^\circ\text{C min}^{-1}$ , is shown in Table 4 and in Fig. 5 expressed by percentage deviation.

Table 4 Specific heat capacity  $C_p$  of  $\alpha$ -alumina sample (in air)

Temperature/ $^\circ\text{C}$	$C_p/\text{J (g }^\circ\text{C)}^{-1}$		Error/%
	Literature	-200 to +325 mech	
50	0.823	0.832	1.1
60	0.841	0.843	0.2
70	0.858	0.855	-0.3
80	0.874	0.874	0.0
90	0.890	0.890	0.0
100	0.904	0.901	-0.4
110	0.918	0.913	-0.6



Table 4 Continued

Temperature/°C	$C_p/J (g\ ^\circ C)^{-1}$		Error/%
	Literature	-200 to +325 mech	
120	0.932	0.926	-0.6
130	0.944	0.933	-1.2
140	0.956	0.945	-1.2
150	0.968	0.951	-1.7
160	0.979	0.957	-2.2
170	0.989	0.964	-2.5
180	0.999	0.975	-2.4
190	1.008	0.975	-3.3
200	1.017	0.981	-3.6
210	1.026	0.991	-3.4
220	1.034	0.995	-3.8
230	1.042	0.997	-4.3
210	1.025	0.990	-3.5
220	1.034	1.000	-3.3
230	1.042	1.010	-3.1
240	1.049	1.019	-3.0
250	1.056	1.034	-2.2
260	1.063	1.022	-3.9
270	1.070	1.035	-3.4
280	1.076	1.042	-3.2
290	1.083	1.052	-2.9
300	1.089	1.052	-3.4
310	1.094	1.052	-3.9
320	1.100	1.071	-2.6
330	1.105	1.071	-3.2
340	1.110	1.075	-3.2
350	1.115	1.074	-3.8
360	1.120	1.082	-3.4
370	1.124	1.100	-2.2
380	1.129	1.078	-4.5
390	1.133	1.086	-4.5

Sample mass: 19.98 mg

Mass of Al pan: 13.98 mg

Heating rate: 10°C min<sup>-1</sup>

## Conclusion

DSC measurements of packed particles are greatly influenced by the porosity of the compact which is closely related with thermal resistance of the sample itself. This should be considered in routine measurements, and, by once determining optimal conditions, samples deviating from the specified conditions for sample preparation can be easily distinguished. In other words, although the method does not provide absolute values, it is effective when used in a routine quality control of packed structures or prior to a run for purity determination.

In case of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder, most reliable heat capacity data can be obtained by preparing a powder with a self-similar particle size distribution with a distribution constant of 0.7, and by compressing it under a pressure of 1.5 MPa for a duration of 5 min or longer.

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