

QUANTITATIVE THERMAL ANALYSIS, III

EFFECT OF EXPERIMENTAL FACTORS IN QUANTITATIVE THERMAL ANALYSIS

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The effect of some experimental factors on quantitative determinations of heat of transformation are discussed. It is shown on the example of solid phase invariant processes that by using the equation derived earlier by the authors, a number of factors, viz. mass, bulk density, thermal conductivity and specific heat of the sample, as well as the position of the junction of the thermocouple, need not be taken into account.

In classical differential thermal analysis, quantitative determination of heat of transformation is performed by comparing the peak areas corresponding to the reference material and to the material being investigated.

The factors which affect the parameters of the DTA curves may be divided formally into external and internal factors, the former determining heat flow conditions from the heating element to the surface of the sample, the latter determining the character of heat flow within the sample.

External factors are basically defined by the design characteristics of the equipment used. These characteristics remain practically unchanged for long periods of operation; therefore external factors can be stabilized to the required degree.

Among internal factors of major importance, including the shape of the sample, the position of the junction of the thermocouple in the sample and the thermophysical properties of the sample, only the shape of the sample and the position of the junction can be fixed, but the thermophysical properties of the sample are always specific for the respective material.

In this paper, an attempt is made to evaluate the effect of some important internal factors, on the one hand on the peak area and on the other hand on the heat of transformation calculated by means of the equation derived earlier [1]

$$q = S \frac{V}{\Delta t} C \quad (1)$$

1. Mass of the sample

In the early development stages of quantitative thermal analysis, a linear relation between the mass of the sample and the peak area was assumed. Some later investigations [2] confirmed the existence of a linear dependence within a defi-

nite mass range. However, at present most authors hold the opinion that in the general case the relation is non-linear [3, 4]. The general relation is shown by the curve ABCD in Fig. 1. An attempt to express this relation in a mathematical form was made by Piloyan [4].

In the range of relatively small masses, the dependence of the peak area on the mass of the sample is described by the line AB which — within experimental error limits — can be considered to be straight and passes through the origin of coordinates.

Section CD is an almost horizontal straight line and reveals practically complete independence of the peak area from the mass of the sample.

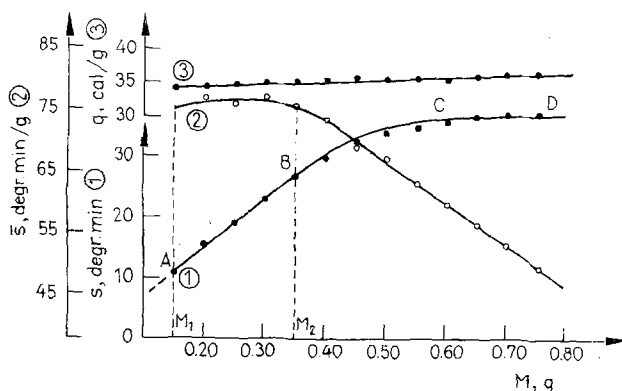


Fig. 1. Peak area and calculated heat of transformation vs. mass of sample

Section BC is a transition between AB and CD where the peak area is still dependent on the mass of the sample but the relation differs substantially from linearity.

Some special features in the technique of measurements are required to determine curve ABCD experimentally since the mass of the sample can be varied both by changing its bulk density and its size.

In our work, we chose to vary the size of the sample to investigate the effect of mass. (The effect of bulk density will be discussed in detail in the next chapter.) Since we use a cylindrical sample, it was simplest to change its height and keep its diameter fixed. Constant diameters are favourable also because in this way it is easiest to meet the requirement that other (external) factors of heat flow remain unchanged.

By varying the height of the sample in the test tube, the question arises of how to locate the junction of the thermocouple in the sample. One might locate the junction either in the centre of the sample or at a constant distance from the upper or lower end of the sample.

Evidently, the first alternative would reflect the dependence of peak area on mass more correctly. However, experimental technique and equipment design

call for a choice of the second alternative. In our equipment [5], the junction of the thermocouple is fixed at a constant distance from the lower end of the sample while the height of the sample can be varied. To ensure — as far as possible — constant bulk density, the samples are lightly compressed under constant pressure.

In principle, great variety in design and experimental technique is feasible for investigating the dependence of the peak area on the mass of the sample, each of these solutions having unquestionable advantages. In this respect, the investigations of Sementovsky [6, 7] are certainly of great interest.

In Fig. 1, the experimentally obtained relation between the peak area and the mass of the sample (curve 1), and that between the specific peak area and the mass of the sample (curve 2) are presented for the polymorphous transformation of potassium perchlorate.

The perception that the mass of the sample must be taken into account, or rather — to be more exact — that it must be considered within a certain mass range has led to the following statement: "Since the peak area corresponding to a phase transformation increases with the mass of the sample only to a certain limit and then remains unchanged, a maximum mass T_{\max} has been determined and samples with masses much below this limit were used in the experiments. Owing to this procedure, true values for the peak areas corresponding to the actually employed sample could be obtained" [3].

As a consequence, however, sample masses used in our equipment have to be limited strictly to the range M_1 — M_2 in Fig. 1. If greater masses were used, non-linear dependence might result. In the case of smaller samples, other difficulties would arise, connected with effects due to other factors, namely the position of the junction in the material, size reduction of the peak area, errors in weighing, etc.

Table 1

Dependence of peak area and calculated heat of transformation on the mass of the sample

No.	M g	S degr. min.	V degr./min.	Δt degr.	\bar{S} degr. min/g	q cal/g	Δq %
1	0.150	10.98	4.88	0.408	73.2	33.4	-4.01
2	0.200	15.41	4.94	0.576	77.0	33.6	-3.45
3	0.250	19.00	5.73	0.818	75.9	33.9	-2.43
4	0.300	23.12	5.08	0.870	77.1	34.3	-1.44
5	0.350	26.45	4.74	0.916	75.6	34.3	-1.44
6	0.400	29.80	5.61	1.202	73.2	34.7	-0.29
7	0.450	31.13	5.52	1.245	69.2	35.0	+0.58
8	0.500	33.62	5.43	1.300	67.2	35.1	+0.86
9	0.550	34.61	5.37	1.335	62.9	35.3	+1.44
10	0.600	35.80	5.25	1.368	59.7	34.9	+0.29
11	0.650	36.55	5.19	1.352	56.3	35.6	+2.30
12	0.700	37.06	5.24	1.369	53.0	36.0	+3.45
13	0.750	36.97	4.61	1.200	49.3	36.0	+3.45

Experimental data presented in Table 1 for calculating the heat of transformation by means of Eq. (1) give an answer to the question of whether the mass of the sample need be taken into account in the calculation.

Both Table 1 and curve 3 in Fig. 1 show that the calculated values of heat of transformation are fairly constant within the total range of sample masses. Since an error of the order of 10% is generally accepted in quantitative thermal analysis [8], it may be concluded that the derived equation yields values for heat of transformation which — within the limits of experimental error — are independent of the mass of the sample. We wish to add that the slight systematic increase of the calculated values with increasing mass is due, in our opinion, to heat flow along the wires of the thermocouple.

Since the mass of the sample is not involved directly in the equation for calculating the heat of transformation and practically does not affect its results, in principle weighing of the sample for quantitative determinations is not compulsory. This circumstance opens up wide potentialities for developing thermal analysis from a qualitative method into a quantitative one, particularly in cases where — owing to design considerations — weighing is either impossible or connected with serious relative errors [9].

With the design used in our work [5] allowing the use of greatly differing sample masses (from 0.15 to 0.75 g), it is preferable to weigh the sample, not because mass would affect experimental results but solely because the use of identical weights of different materials permits a visual comparison of the thermograms. In addition, the selection of a particular sample weight is often motivated by indirect reasons such as the sensitivity of recording instruments (in the case of very low weights), the superposition of effects (in the case of high weights), etc.

2. Bulk density of the sample

The relation between peak area and bulk density is closely connected with the relation between peak area and mass of the sample discussed in the previous chapter.

In thermal analysis, the material being investigated is usually a powder capable of substantial increases of density through the application of relatively low pressures. Thus, e.g., finely ground sodium sulphate is capable of increasing its bulk density by a factor of more than 2.5 under low pressures. For this reason, varying quantities of the material being investigated may be contained in one and the same test tube or crucible even if the volumes and shapes of the samples are identical.

This raises the question of whether the result of quantitative determinations (in our case the determination of heat of transformation) is affected by changes of the bulk density and of how this effect can be taken into account.

Most authors, discussing factors which affect the coefficient of heat transfer directly or indirectly, point out that peak area depends on the bulk density of the

material. However, we could not detect any paper dedicated to the particular problem of how this relation should be taken into account in thermal analysis.

In investigations of the relation between peak area and bulk density, it is imperative to ensure maximum stability of all other experimental conditions.

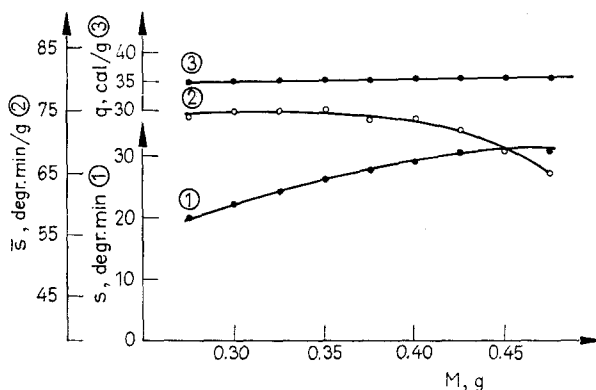


Fig. 2. Peak area and calculated heat of transformation vs. density of the sample

The data for potassium perchlorate presented in Table 2 and Fig. 2 were obtained in experiments where the volume and shape of the sample, the position of the junction, and all other experimental conditions were strictly identical. The carefully ground material was weighed in all experiments into one and the same test tube and compressed by means of a metal rod which was immersed into the test tube to a fixed length. In this manner, constant volume and shape of the sample were ensured. (In Fig. 2, the abscissa does not represent bulk density but

Table 2

Dependence of peak area and calculated heat of transformation on the density of the sample

No.	M g	S degr. min	\bar{V} degr./ min	Δt degr.	\bar{S} degr. min/g	cal/g	ΔS %	Δq %	γ g/cm ³
	1	2	3	4	5	6	7	8	9
1	0.275	20.35	4.87	0.725	74.0	34.7	+2.2	-1.14	0.42
2	0.300	22.45	5.52	0.905	74.8	34.8	+3.3	-0.85	0.46
3	0.325	24.37	4.95	0.875	75.0	35.0	+3.6	-0.29	0.50
4	0.350	26.27	5.08	0.970	75.1	35.1	+3.7	-0.00	0.54
5	0.375	27.62	5.18	1.040	73.7	35.0	+1.8	-0.29	0.58
6	0.400	29.30	5.15	1.090	73.8	35.1	+1.2	0.00	0.62
7	0.425	30.61	5.12	1.128	72.0	35.3	-0.5	+0.57	0.66
8	0.450	31.00	5.52	1.230	68.8	35.3	-5.0	+0.57	0.70
9	0.475	30.88	4.73	1.048	65.0	35.4	-10.3	+0.85	0.74

weight of the sample. Under the condition that the volume of the sample is constant, bulk density is proportional to the weight of the sample which can be determined very accurately. In column 9 of Table 2, approximate values of the corresponding densities are listed.)

The relation between peak area and bulk density is shown in Fig. 2 (curve 1) and Table 2. The general character of this relation is made particularly clear through curve 2 in Fig. 2 (specific peak area vs. bulk density), showing that peak area decreases with increasing bulk density. A 50% change in bulk density leads to a peak area change of approximately 7% in the case of potassium perchlorate. This value is almost one order of magnitude higher than the potential error of measurement.

These results raise the question of whether it is possible in some way to take into account the dependence of peak area on bulk density and perform a corresponding correction of the results in the case when heat of transformation is determined by a simple comparison of the peak areas.

In our opinion, there is no point in constructing some sort of calibration graph or introducing a correction for the dependence of peak area on density. The density values of various materials are so different (e.g. the densities of AgI and NH_4Cl differ by a factor of 2.5) that it is sometimes quite impossible to compare the values for the reference material and the material being investigated. In such cases, no unequivocal criterion exists by which the density of the sample and the reference material, respectively, could be identified.

Thus, if heat of transformation is determined quantitatively by a simple comparison of the peak areas, the respective densities of the material being investigated and of the reference material are of major importance. In practice, it is obviously impossible to correct the results by taking the actual density in account. (If a change of thermal conductivity is the reason for the change of peak area, corrections might be based on calculations of thermal conductivity, or else special techniques might be applied to eliminate the effect of this factor. In the opinion of several authors [10—12], the latter can be performed e.g. by placing a thermosensing element behind the sample. The discussion of such special techniques is beyond the scope of the present paper.)

However, if the heat of transformation is determined by calculation using Eq. (1), the position is totally different. Curve 3 in Fig. 2 represents heat of transformation values calculated by means of Eq. (1) vs. bulk density of the sample. This curve, as well as the data presented in Table 2 (column 8) show that calculated values of heat of transformation are practically independent of the density. Mathematically this independence can be explained in the following way. Variations of bulk density (and correspondingly of mass) result in changes of S . However, the values of Δt change in the same degree and in the same direction. Thus, the ratio $S/\Delta t$ remains unchanged not only in the case of mass changes (as shown in the previous chapter) but also in the case of density changes.

The errors due to density variations are listed in Table 2, column 7 (for values obtained by a comparison of peak areas) and column 8 (for values obtained by

calculation using Eq. (1)). As in the case of the data in Table 1, the slight systematic increase of the calculated values with increasing bulk density is due, in our opinion, to the heat flow along the wires of the thermocouple.

3. Thermophysical properties of the sample (specific heat and thermal conductivity)

The effect of the thermal conductivity of the sample on the quantitative characteristics of the DTA curve is one of the most important questions in thermal analysis and has received due attention both theoretically and experimentally [6, 13].

However, the effect of specific heat on the quantitative characteristics of the DTA curve, primarily on the peak area, can scarcely be considered as a fully elucidated problem [6]. This problem is also of "formal" interest in view of a fact which seems paradoxical at first sight: on the one hand, the material does not change its temperature at the moment of transition and therefore its specific heat cannot affect the peak area. On the other hand, the specific heat is involved directly in the equation for calculating the heat of transformation.

Let us try to establish the effect of specific heat on peak area from the purely mathematical side. For this purpose, the design parameters of the experiment must be defined more exactly. Let us assume a cylindrical sample with radius R and a position of the junction of the thermocouple strictly on the axis of the cylinder. Let us now introduce the following substitutions into Eq. (1) [14, 15]:

$$\Delta t = \frac{VR^2}{\Gamma a} \quad \text{and} \quad a = \frac{\lambda}{C\gamma}$$

and then write Eq. (1) expressed for S :

$$S = q \frac{\gamma R^2}{\lambda \Gamma} \quad (2)$$

showing that the peak area is directly proportional to the heat of transformation q , to the second power of the radius R and to the bulk density γ of the sample, and inversely proportional to the thermal conductivity λ . (The shape coefficient Γ is a constant.)

Eq. (2) reveals that neither the peak area nor the calculated heat of transformation is affected by the specific heat of the sample since the latter does not occur explicitly in the equation and does not affect any of the quantities involved.

Thus, both physical and mathematical considerations lead to the result that the specific heat of the sample does not affect the peak area and the heat of transformation. Specific heat is solely involved in one of the characteristics of the DTA curve, viz. Δt which appears in the original form of Eq. (1). The same is obviously valid for the rate of heating.

However, it should be mentioned that the specific heat of the sample, or, strictly speaking, the difference between the specific heat of the initial and the final phase,

Table 3

Dependence of peak area and calculated heat of transformation on thermal

No.	Diluent	S degr. min	V degr./min	Δt degr.	C cal/g · degr.
	1	2	3	4	5
1	Al	9.68	8.68	0.962	0.2500
2	K ₂ SO ₄	10.96	5.42	0.950	0.2462
3	NaCl	11.23	5.74	0.997	0.2433
4	Al ₂ O ₃	11.29	5.88	1.054	0.2528
5	Na ₂ SO ₄	12.00	5.32	1.060	0.2645
6	KClO ₄	12.09	6.16	1.183	0.2540
7	KCl	12.24	5.52	0.900	0.2152
8	CuO	12.52	5.95	0.920	0.2037
9	SiO ₂	12.60	5.95	1.185	0.2520
10	Fe ₂ O ₃	12.68	5.85	1.100	0.2291

may necessitate some corrections of the results. Theoretically, this may be explained by the fact that the temperature distribution in the mass of the sample will not be identical before and after the phase transformation even if the rate of heating is constant and strictly quasi-steady conditions are observed. If the heat content is calculated on the basis of the mean integral temperature in the mass of the sample, then, for samples heated with a constant rate of heating and differing solely in respect to specific heat, their heat content will differ even if the temperature in the centre of the samples is identical. However, in practice a consideration of the difference between the specific heat of the initial and final phase is not required since preliminary calculations have shown that the effect caused by this difference is negligible.

Unfortunately, a direct experimental confirmation of the independence of the peak area and of the calculated heat of transformation of specific heat is connected with great difficulties since it is practically impossible to prepare even two samples which differ exclusively in respect to specific heat.

Literature data on the effect of thermal conductivity on peak area and other quantitative characteristics of the thermograms reveal that the higher the thermal conductivity, the lower the peak area and the deviation of the differential curve from the zero line [3, 13]. These findings were also confirmed mathematically [8].

The effect of thermal conductivity on peak area and calculated heat of transformation can be investigated experimentally by comparing the DTA curves of mixtures of a thermoactive material with various diluents (Table 3).

Depending on the type of diluent, the peak area corresponding to one and the same value of heat of transformation does not remain unchanged. The differences in the peak area may even exceed 20%. All data presented in Table 3 refer to mix-

conductivity and specific heat of the sample

(λ) $VC/\Delta t$	Order in respect to			q cal/g	Δq %	ΔS %
	λ	S	C			
6	7	8	9	10	11	12
157.5	1	1	6	15.26	-3.5	-17.5
140.2	2	2	5	15.37	-2.8	-6.6
140.2	3	3	4	15.75	-0.4	-4.3
142.5	4	4	8	15.92	+0.7	-3.8
133.0	5	5	10	15.95	+0.8	+2.3
132.1	6	6	9	15.98	+1.1	+3.1
131.8	7	7	2	16.12	+1.9	+4.3
131.5	8	8	1	16.48	+4.2	+6.7
125.8	9	9	7	15.88	+0.3	+7.4
121.8	10	10	9	15.45	-2.3	+8.1

tures of the thermoactive material $KClO_4$ and the respective diluent in ratios of 1 : 1 and constant volumes, shapes and masses of the samples.

The calculated values of $VC/\Delta t$ which are directly proportional to the thermal conductivity of the investigated mixtures are listed in column 6 of Table 3. The proportionality follows from the mathematical analysis of the equation $\Delta t = VR^2/\Gamma a$. Since $a = \lambda/C\gamma$, $\Delta t = VR^2C\gamma/\Gamma\lambda$ or $\lambda = \frac{R^2\gamma}{\Gamma} \cdot \frac{VC}{\Delta t}$. In our case $R^2\gamma/\Gamma = K = \text{constant}$, therefore $\lambda = K \cdot VC/\Delta t$.

In column 7, the serial numbers of the investigated mixtures are arranged in the order of decreasing thermal conductivities. It may be seen that their order is identical to the order of increasing peak areas (column 8). This, in our opinion, is a further proof of the fact that the peak area is inversely proportional to the thermal conductivity of the sample ([13], Eq. 2).

The data presented in Table 3 also support the statement that the peak area is independent of the specific heat of the sample since the order of the mixtures in respect to peak area is not in conformity with the order in respect to specific heat (columns 8 and 9).

Owing to the substantial effect of thermal conductivity on peak area, the determination of heat of transformation by a simple comparison of the peak areas, with no corrections for thermal conductivity, may result in errors of more than 10% (column 12 in Table 3).

Among others, Berg and Borisova [3] made an attempt to correct the results obtained by classical thermal analysis by taking thermal conductivity into account. Their work was based on the same principle of correlation which was applied in the present paper, namely the division of S by Δt . In this aspect, the application of Eq. (1) may be looked upon as a further development of the method adopted in [3].

The data in columns 10 and 11 of Table 3 reveal that by applying Eq. (1), it becomes possible to determine heat of transformation without using any special correction for thermal conductivity. The errors listed in column 11 are quite high but still acceptable and fully random. In addition, the possibility cannot be excluded that these errors are mainly due to inadequate accuracy (in the order of 3%) of literature data for specific heat, and also in some cases (e.g. in the case of aluminium) to chemical impurities of the diluent.

4. Position of the junction of the thermocouple in the sample








All literature data show that the position of the junction of the thermocouple affects peak area substantially. For this reason, one of the main requirements if quantitative determinations are performed by the comparison of peak areas is that strictly identical positions of the junction are observed. This is usually checked by taking repeated curves of the control material.

In Tables 4 and 5, data of the thermal analysis of sodium sulphate with various positions of the junction are listed. The position is shown only schematically in the tables since actual measurements of the distance along the radius and height, respectively, are connected with such serious errors that they have no practical value. (It should be remembered that — in view of design considerations — the inner diameter of the test tube in our experimental work cannot exceed 8 mm.)

The data in Tables 4 and 5 reveal that varying positions of the junction do not affect the heat of transformation calculated by means of Eq. (1).

Table 4






Dependence of peak area and calculated heat of transformation on the position of the junction along the axis of the sample

							
	1	2	3	4	5	6	7
S	3.64	9.33	10.62	12.32	14.31	14.05	13.37
V	7.86	6.78	7.27	7.00	5.01	6.93	4.78
Δt	0.648	1.345	1.570	1.750	1.430	1.911	1.271
q	12.12	12.95	13.41	13.55	13.78	13.83	13.80
Δq	—	-5.9%	-2.2%	-1.7%	0.0%	+0.4%	+0.1%
ΔS	—	-34.8%	-25.8%	-13.9%	0.0%	-1.8%	-6.6%

Note: the error percentages refer to the position usually recommended in the literature (column 5).

Table 5

Dependence of peak area and calculated heat of transformation on the position of the junction along the radius of the sample

Position of the junction	S degr. min	V degr./min	Δt degr.	q cal/g	Δq %	ΔS %
	14.31	5.01	1.430	13.78	0.00	0.00
	13.41	7.34	1.942	13.93	+1.1	-6.3
	10.83	7.12	1.536	13.81	+0.2	-24.0
	9.94	6.93	1.360	13.91	+0.9	-30.5
	7.18	3.48	0.56	12.27	—	—

Note: the error percentages refer to the position usually recommended in the literature (line 1).

In conclusion, it can be stated that calculated values of heat of transformation are independent — within the limits of experimental error — of the mass, bulk density, specific heat and thermal conductivity of the sample as well as of the position of the junction of the thermocouple. No corrections of the equation derived in [1] are needed in connection with variations of these characteristics.

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RÉSUMÉ — On a discuté l'influence de divers facteurs expérimentaux sur la détermination quantitative de la chaleur de transformation. On a montré sur l'exemple des processus invariants en phase solide et en utilisant une équation déduite précédemment par les auteurs, que l'on ne doit pas prendre en considération des facteurs comme masse, densité apparent, conductivité thermique et la chaleur spécifique de la matière examinée, en outre la position de la sonde du thermocouple.

ZUSAMMENFASSUNG — Der Einfluß verschiedener experimentaler Faktoren auf die quantitative Bestimmung der Umwandlungswärme wurde besprochen. Am Beispiel von invarianten Vorgängen in fester Phase wurde gezeigt, daß bei Anwendung einer von den Verfassern früher abgeleiteten Gleichung gewisse Faktoren, wie Masse, Schüttgewicht, thermische Leitfähigkeit und spezifische Wärme der Probe, weiterhin Lage der Verkoppelung des Thermoelements nicht zu berücksichtigen sind.

Резюме — В статье анализируется влияние некоторых факторов эксперимента на результаты количественных определений теплот фазовых превращений. Статья является продолжением двух ранее опубликованных работ. Экспериментально показывается на примере твердофазных инвариантных процессов, что в случае пользования расчетными уравнениями, описанными авторами ранее, отпадает необходимость специального учета многих факторов эксперимента; в частности: массы образца, плотности, теплопроводности, теплоемкости образца и положения спая термопары в образце.