

CALORIMETRIC TEST OF PURITY II.
COMPARISON OF DYNAMIC AND STEPWISE MEASURING TECHNIQUE,
OPTIMIZATION OF DATA-PROCESSING

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Dynamic and stepwise purity test techniques were compared, and it was established that in dynamic measurement the sample in many cases can not be considered to be in a state of equilibrium from the thermodynamic aspect.

The problems of the measuring time and the accuracy of the results are discussed for the two-peak method, applicable for the processing of data obtained by the stepwise technique.

It was established that the two-peak method can be improved. By using several peaks, the accuracy of the results and measuring time can be optimized.

A fundamental requirement to be met by the measuring techniques of calorimetric purity tests is to provide for the *thermodynamic equilibrium of the whole sample* during measurement.

With a DSC apparatus the following processes are possible:

A dynamic technique [1-5], in which the sample has to take up the linearly changing temperature of the furnace.

A stepwise technique [6, 7], in which the furnace provides a thermostated environment for the sample between two temperature jumps.

Users of the dynamic technique are of the opinion that in the case of a sample of 2-4 mg and at a heating rate of about 1 degree/min thermodynamic equilibrium of the whole sample is satisfactory approximated. At the same time, it has been recognized that the choosing of the melting range selected for evaluation affects the calculated result considerably [1, 2]. The authors of the papers recommend the use of empirically selected evaluation ranges yielding favourable results for the given system.

We assume that the dependence of the calculated result on the selection of the region to be evaluated arises from the fact that thermodynamic equilibrium over the whole sample can not be approximated in a suitable measure by dynamic techniques.

To prove our assumption, a mathematical model of melting under the conditions of dynamic measurement has been derived, and comparative measurements have been carried out to compare the dynamic and the stepwise techniques from this aspect.

Investigation of non-equilibrium melting

In the mathematical modelling the melting sample was divided into N parts in local equilibrium.

This model is shown in Fig. 1. The temperature of the heating source is T_f , and that of the i -th part of the sample is T_i .

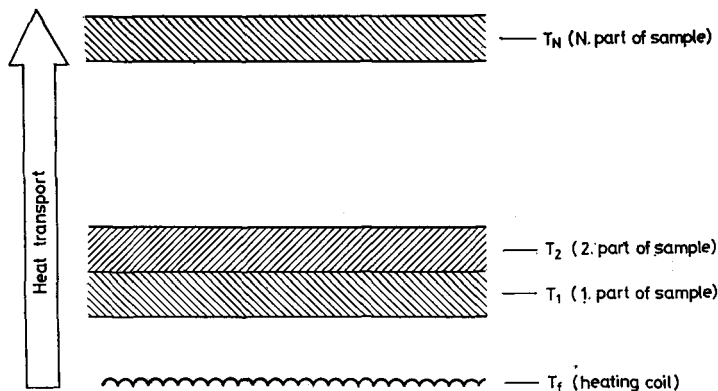


Fig. 1. Separation of the sample into parts in local equilibrium

The heat conduction value between the heating source and the first part of the sample is L_f .

The heat conduction value between the individual parts of the sample is L .

The heat balances are written for the individual parts of the sample:

$$\begin{aligned}
 L_f(T_f - T_1) - L(T_1 - T_2) &= C \frac{dT_1}{dt} + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_1)^2} \frac{dT_1}{dt} \\
 &\vdots \\
 &\vdots \\
 L(T_{i-1} - T_i) - L(T_i - T_{i+1}) &= C \frac{dT_N}{dt} + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_i)^2} \frac{dT_i}{dt} \\
 &\vdots \\
 &\vdots \\
 L(T_{N-1} - T_N) &= C \frac{dT_N}{dt} + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_N)^2} \frac{dT_N}{dt}
 \end{aligned}$$

where

- n is the number of moles in one part of the sample;
- c is the heat capacity of one part of the sample;
- x is the impurity of the sample;
- T_0 is the melting point of the pure main component;
- R is the gas constant.

The left-hand side represents the inlet and outlet heat energy streams, and the right-hand side the heat absorbing processes in the individual parts of the sample.

Transposing the system of equations, and with regard to the linear heating rate applied:

$$\begin{aligned} \frac{dT_1}{dt} &= \frac{1}{C + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_1)^2}} [L_f(T_f - T_1) - L(T_1 - T_2)] \\ &\vdots \\ \frac{dT_i}{dt} &= \frac{1}{C + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_i)^2}} [L(T_{i-1} - 2T_i + T_{i+1})] \\ &\vdots \\ \frac{dT_N}{dt} &= \frac{1}{C + \bar{x}nRT_0^2 \frac{1}{(T_0 - T_N)^2}} [L(T_{N-1} - T_N)] \end{aligned}$$

$$\frac{dT_f}{dt} = a, \text{ where } a \text{ is the heating rate.}$$

This latter differential equation was solved numerically.

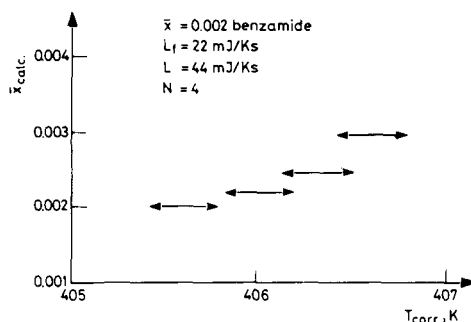


Fig. 2. Effect of the choice of the melting range selected for evaluation on the calculated result in dynamic techniques, according to mathematical modelling

Data on the system phenacetin-benzamide were used for the calculations. The value of L_f was determined by measurement, and that of L by trial. A DSC signal corrected for baseline and a temperature corrected for temperature lag were obtained in the calculations.

The data obtained were evaluated by the method described in our previous paper [8]. The results are shown in Fig. 2. It can be seen from the Figure that the

dependence of the calculated composition on the position of the region selected for evaluation is the same as found experimentally in [1, 2].

This can be taken as a proof of our assumption. Further proof is furnished by the experimental comparison of dynamic and stepwise techniques. From the main

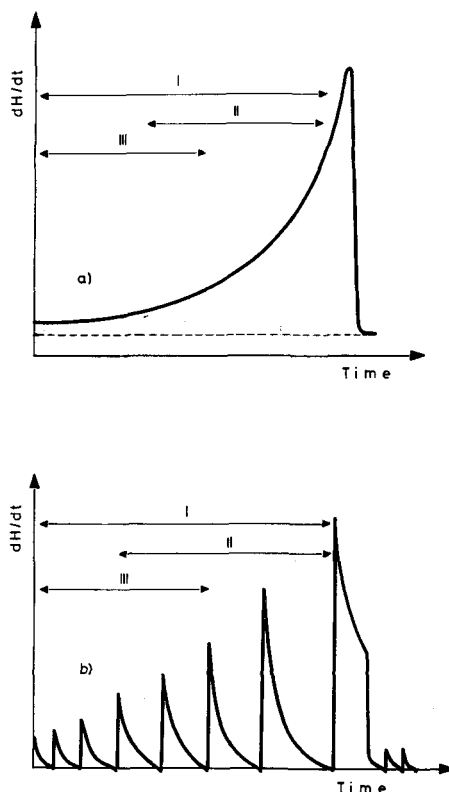


Fig. 3. Location of the sections selected for evaluation of the DSC diagrams obtained by the dynamic (a) and stepwise (b) techniques

component, phenacetin, a mixture containing $x = 0.0019$ mole fraction of benzamide impurity was prepared for the experiments. With samples taken repeatedly from this mixture, the samples were investigated by both techniques.

In the dynamic measurement the following conditions were used:

sample weight	4.2–4.8 mg
heating rate	0.62 K/min

In the stepwise measurement:

sample weight	3.3–3.8 mg
temperature jump	0.2 K

In both cases digital data logging and computerized data-processing were used. The evaluation range was changed as indicated in Fig. 3. The results are shown in Fig. 4.

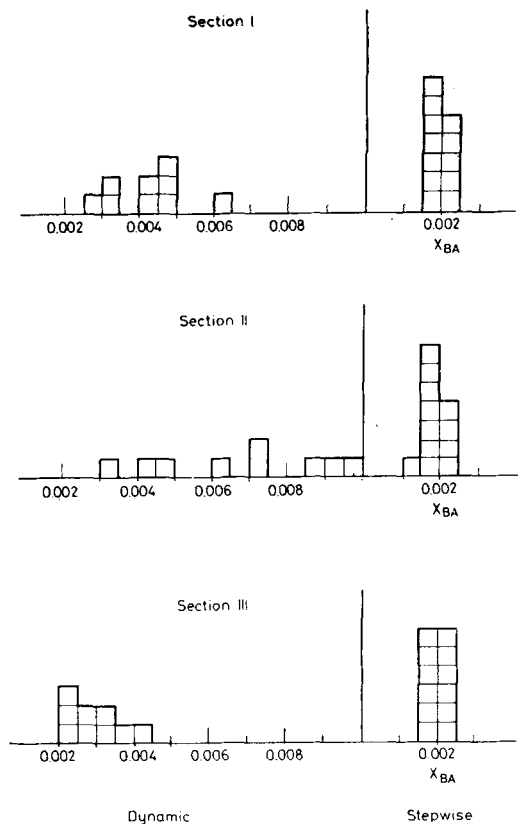


Fig. 4. Histograms of the results obtained by evaluation of the individual sections

To summarize, the investigations showed that the dynamic technique is rather limited for calorimetric purity tests because of the non-equilibrium state of the sample, and proved at the same time that the stepwise technique is a more suitable method, as the equilibrium state of the sample can be approximated in an adequate measure by its use.

Processing of results obtained by stepwise technique

It is well known that with the stepwise technique records of the type shown in Fig. 5 are obtained, where the composition can be calculated from the peak areas and the temperatures relating to them. The practical problem of this procedure is

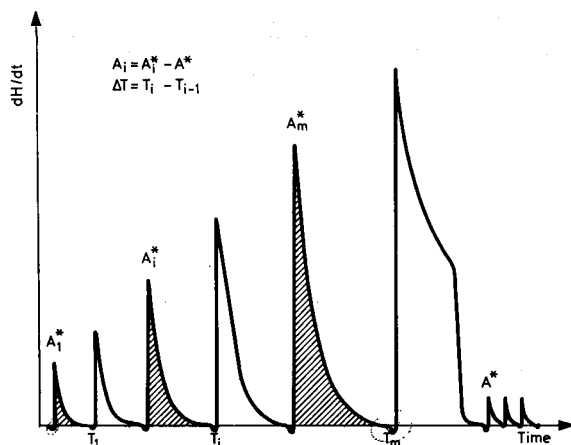


Fig. 5. Data obtained from the DSC records obtained by the stepwise technique

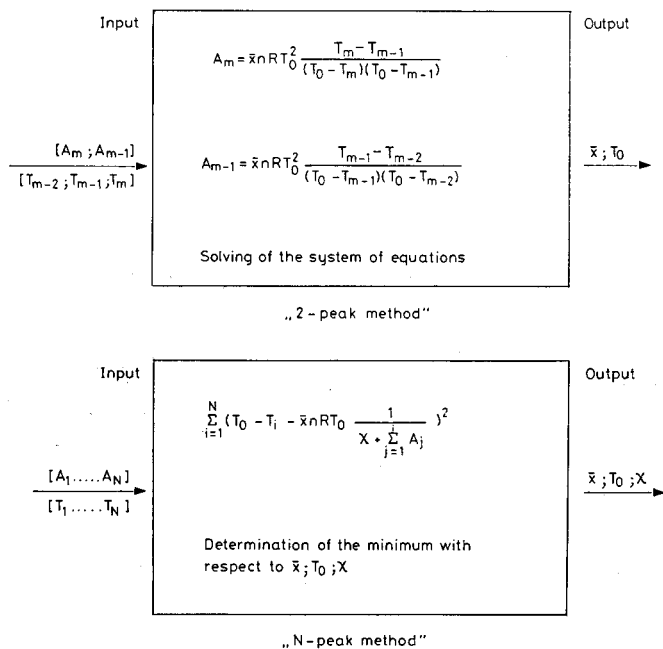


Fig. 6. Course of evaluation of data of DSC records obtained with stepwise techniques by the 2-peak and N -peak methods

the rather long measuring time. Gray [7] dealt with this problem, and introduced the two-peak method. However, in our experience, and as is also understandable from the statistical point of view, in this case the effect of the random error of measurement on the calculated composition increases considerably.

Obviously, two cross requirements should be met simultaneously:

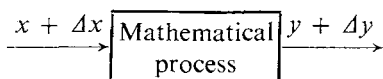
- to measure as few peaks as possible to shorten the measuring time,
- to measure as many peaks as possible to improve the accuracy of the calculated results.

With the method described in our previous paper [8] the data of N peaks can be processed, and by selecting N appropriately, the above two requirements can be satisfied.

The courses of the two kinds of calculations are shown in Fig. 6. Symbols are the same as used earlier. Below, the two data-processing methods will be compared by mathematical simulation and by the processing of the experimental results.

Comparison of the 2-peak and N -peak methods by Monte-Carlo simulation

For the investigations the following data-processing model was taken as basis:



$x + \Delta x$	data measured
x	exact data
Δx	measuring errors
$y + \Delta y$	calculated results
y	exact results
Δy	deviations arising from measuring error.

Our process based on the model was the following:

1. A melting curve (x) characterizable by known parameters (y) was generated
2. The melting curve was perturbed with random errors of normal distribution and of zero expected value ($x + \Delta x$).
3. Data were processed by both methods ($y + \Delta y$).
4. Deviations of the calculated results were determined (Δy).
5. The procedure was repeated 100 times and processed statistically.

From the aspect of the purity test, the impurity \bar{x} is a carrier of useful information. Relevant results are shown in Fig. 7, with indication of the simulation conditions.

An interesting result of simulation is that a lower impurity can be determined with a smaller relative error. This can be achieved in reality only to a given lower limit, because the temperature scale resolution of the experimental apparatus is limited.

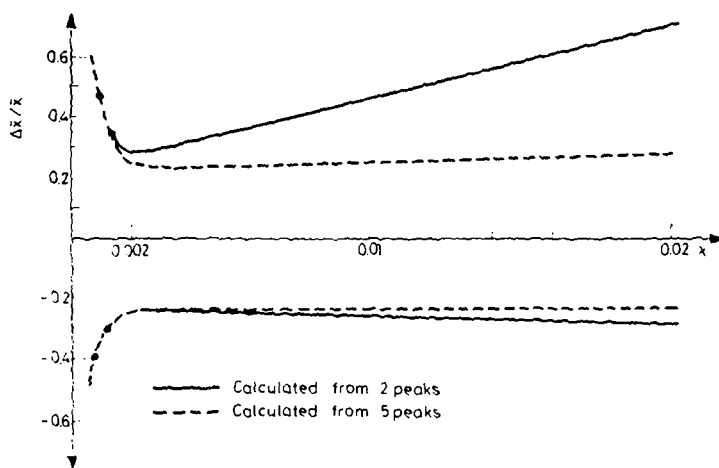


Fig. 7. Confidence limits of results calculated with the 2-peak and N -peak methods at a confidence level of 95% on the basis of Monte-Carlo simulation. Simulation condition 0.2 K temperature jumps. Signal/noise ratio 50

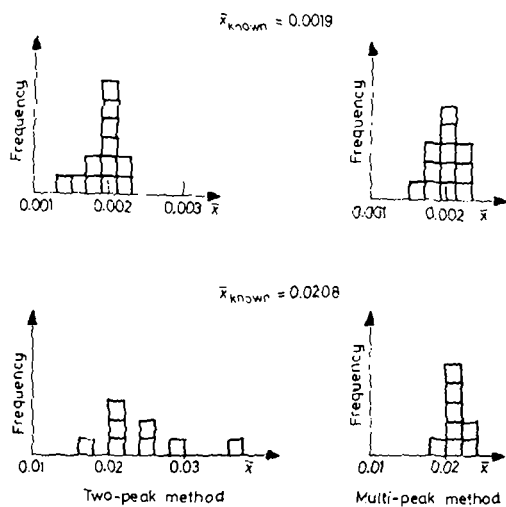


Fig. 8. Histograms of results calculated with the 2-peak and N -peak methods on the basis of the experimental results. Experimental conditions: 0.2 K temperature jumps

Comparison of the 2-peak and *N*-peak methods on the basis of the experimental results

From the main component, phenacetin, mixtures containing $\bar{x} = 0.0019$ and $\bar{x} = 0.0208$ mole fractions of benzamide impurity were prepared. With the repeated taking of samples, several stepwise measurements were carried out.

Measurements were made with a Perkin-Elmer DSC-2 apparatus. Experimental results were collected and evaluated with a computer.

Measuring conditions and results are shown in Fig. 8. The simulation and experimental results reveal that:

1. The measuring time of the two peaks before the last is 15–20 min, depending on the extent of impurity, and the error in the calculated values may be as high as 100%.

2. The measuring time of the six peaks before the last is 30–40 min, depending on the extent of impurity, and the error in the calculated values is about 20%.

Accordingly, $N = 5-6$ is thought to be an optimum value from the aspects of reducing the measuring time and increasing the accuracy of measurement.

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RÉSUMÉ — On a comparé les techniques d'essais de pureté effectués en dynamique et en discontinu. On a établi que lors des mesures dynamiques l'échantillon, dans de nombreux cas, ne peut pas être considéré sous l'aspect thermodynamique comme étant en état d'équilibre.

Les problèmes liés au temps de la mesure et à l'exactitude des résultats ont été discutés pour la méthode à deux pics qui se prête au traitement des données obtenues avec la technique discontinu. On a établi que la méthode à deux pics peut être améliorée. En se servant de plusieurs pics l'exactitude des résultats et la durée des mesures peuvent être optimisées.

ZUSAMMENFASSUNG — Dynamische und stufenweise Techniken der Reinheitsprüfung wurden verglichen und festgestellt, daß bei dynamischen Messungen die Probe in vielen Fällen vom thermodynamischen Aspekt nicht für im Gleichgewichtszustand befindlich betrachtet werden kann.

Die Probleme der Meßzeit und der Genauigkeit der Ergebnisse wurden für die Zwei-Peak-Methode, welche zur Verarbeitung der mit der stufenweisen Technik erhaltenen Daten

geeignet ist, erörtert. Es wurde festgestellt, daß die Zwei-Peak-Methode verbessert werden kann. Durch Anwendung mehrerer Peaks können die Genauigkeit der Ergebnisse und Messzeit optimiert werden.

Резюме — Сопоставлены динамические и ступенчатые методы испытания чистоты веществ. Установлено, что при динамическом измерении образец во многих случаях с термодинамической точки зрения не может считаться в состоянии равновесия. Для двухпикового метода обсуждены проблемы времени измерения и точности результатов, применительно к обработке данных, полученных ступенчатым методом. Установлено, что двухпиковый метод может быть улучшен. Используя несколько пиков, точность результатов и время измерения может быть оптимизировано.