

Dedicated to Professor Slade St. John Warne on the occasion of his 60th birthday

EVALUATION OF THERMAL ANALYSIS EXPERIMENTAL DATA

II. Optimal conditions for evolved gas analysis of thermal decomposition of solids

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The influence of various factors on EGA and TG/DTG results of thermal decomposition of solids is analyzed. Following factors have been considered: the flow rate of the gas medium in the dynamic measurements, the diffusion resistance of the solid sample for gaseous products, the shape of samples, the grain size distribution of the disperse samples.

The ways how to determine optimum values of the parameter have been discussed. The use of THERMOKIN software package is recommended for this purpose.

Keywords: EGA, experimental conditions, TG-DTG

Introduction

Evolved gas analysis has been extensively used by a number of authors in the investigation of thermal decomposition of solids. S. St. J. Warne and co-authors [1] successfully used this method in the investigation of kinetics and mechanism of thermal decomposition of minerals, as well as for the identification of organic and inorganic components contained by the coal and oil shales, and other minerals.

It was recognized by many authors using thermal analysis that the experimental conditions may considerably influence results of thermal analysis methods, such as EGA, TG. Optimal experimental conditions should be determined for the

respective measurements to ensure that results of the thermoanalytical measurements reflect the "true" curves. The distortion of the thermoanalytical EGA curves caused by the mixing effect of gas detector shall be taken into account and reasonable minimized.

In this paper the influence of various factors on the EGA and TG/DTG experimental results will be analysed using computer modelling approach. Following factors are considered:

- (i) flow rate of the gas medium in the dynamic EGA equipment,
- (ii) diffusion resistance of the solid for gaseous products of thermal decomposition,
- (iii) grain size distribution of the dispersed solid sample.

The ways for selection of the optimal conditions for EGA and TG/DTG measurements will be discussed, based on the use of THERMOKIN software package which was described in the previous paper of this series [2].

In the computer modelling of EGA curves following equation is considered for the gas flow rate $J(t)$

$$J(t) = k_0 \cdot \alpha_0 \cdot \exp(-E/RT) \cdot \exp(\tau) \quad (1)$$

where

$$\tau = \frac{k_0 E}{\beta R} \left[-\frac{\exp(z)}{z} + E_i(z) \right] \text{ for the limits } \begin{cases} z = -E/RT \\ z = -E/RT_0 \end{cases}$$

and $E_i(z) = \int_{-\infty}^z \frac{\exp(t)}{t} dt$ integral-exponential function; k_0 is pre-exponential factor,

α_0 is initial fraction of reagent, R is the gas constant, β is the heating rate, T_0 is the temperature of the onset of sample heating, T is the current temperature.

Effect of dynamic gas medium flow rate

It is known that the flow rate of the dynamic gas medium may affect the experimental results of EGA and TG measurements. The effect may be caused by the mixing effect or inertia of the detector (katharometer, mass-spectrometer). The inertia of the detector is defined by the ratio $Z = v/\theta$ where v is the volume of the detector, θ is the flow rate of the gas medium (or rate of pumping-out for a MS-detector).

For a detector with constant volume we can expect that if the flow rate of the gas medium increases, the inertia of the detector decreases, however the sensitivity of the EGA detector decreases as well. That is why the optimal flow rate

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should be determined, providing a compromise between the sensitivity and the inertia of the gas detector.

The affected EGA peaks by the influence of the flow-rate of the gas medium, flowing over the sample during its thermal decomposition, are demonstrated in Fig. 1. In the computer modelling the first order reaction was used as thermal decomposition reaction mechanism, supposing the absence of the diffusion resistance of the solid sample towards the released gas products.

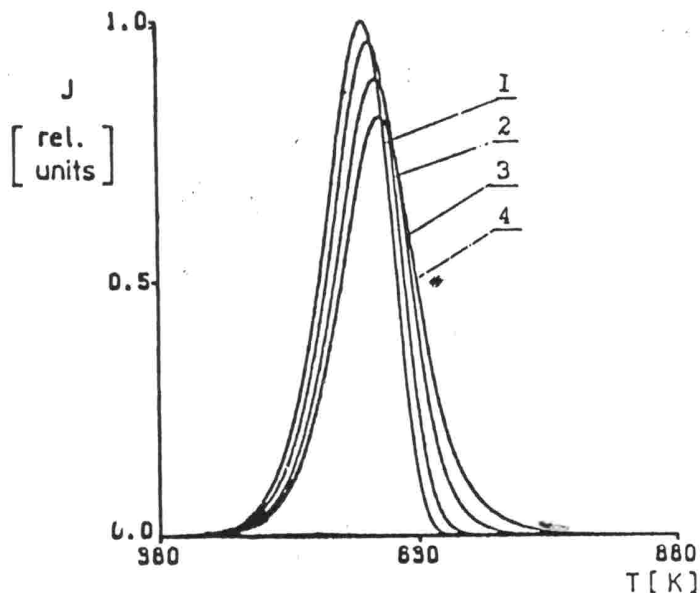


Fig. 1 Demonstration of the effect of gas medium flow rate on the shape of EGA peak. The flow rate variation is expressed by the parameter $Z=v/\theta$, where v is the volume of the detection chamber and θ is the flow rate or pumping-out rate of the gas. Curve 1 corresponds to $z \rightarrow 0$, an idealized case of the detection chamber volume $v \rightarrow 0$, curves 2-4 correspond to $z = 0.5, 0.25$ and 0.167 resp.

It follows from Fig. 1 that the EGA peaks broaden and are displaced towards higher temperatures when the carrier gas flow rate decreases. The main effect on the EGA curve was observed at the descending part of the peak. Performing the EGA measurements at different flow rates θ one should find in optimal value θ_{opt} . The method of the functional scales described in [2] can be used for the determination of the interval, where the distortion of the EGA curve takes place (Fig. 2). Using the functional scale, the EGA peaks are transformed into straight lines. Using the THERMOKIN software package [2] the linearization of the EGA curves can be obtained. The intervals in which distortions of the EGA curves take

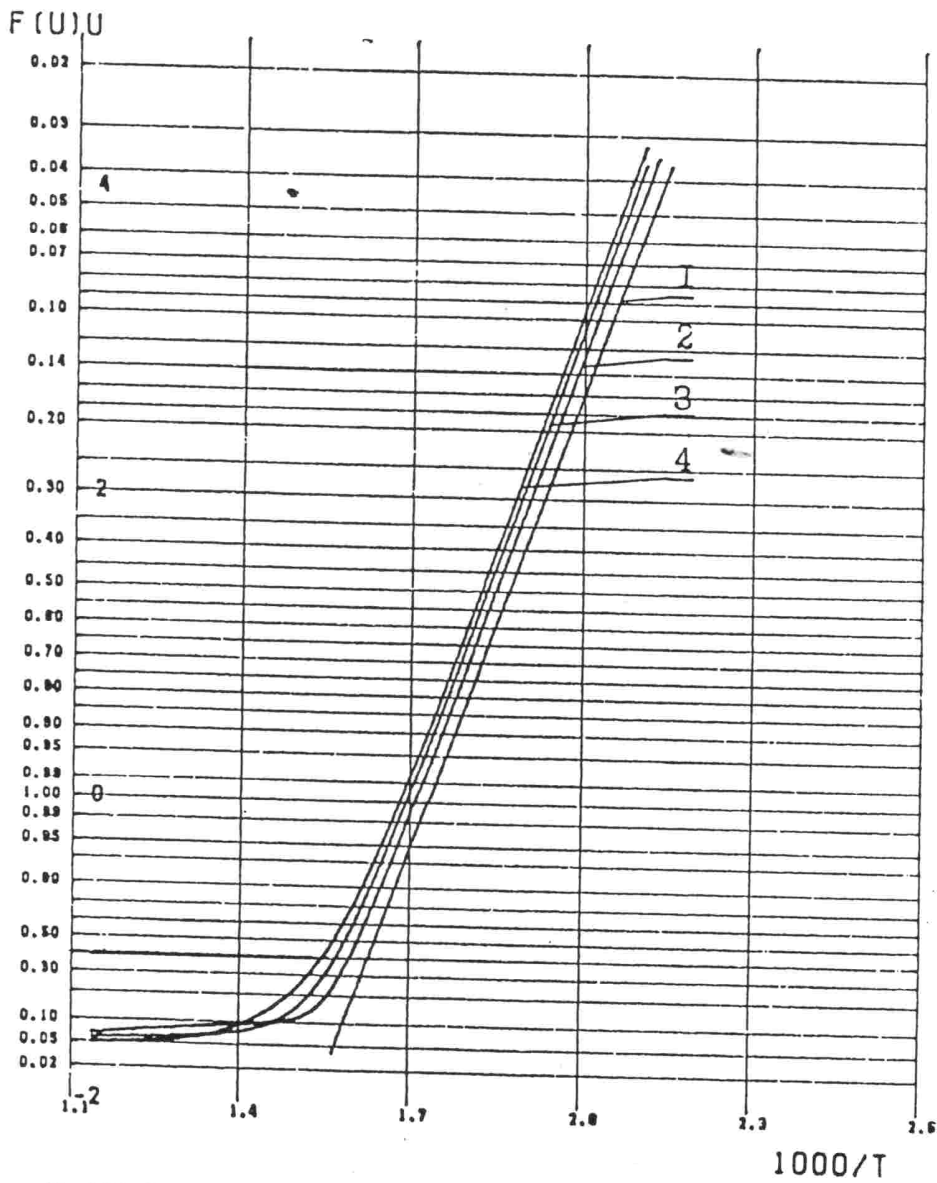


Fig. 2 The linearized EGA peaks demonstrated in Fig. 1, showing how the flow rate of the gas medium in the dynamic thermoanalytical equipment can affect the shape of the EGA peak. (The notation of the curves 1-4 is the same as in Fig. 1.) The symbols on the ordinates are described in the text

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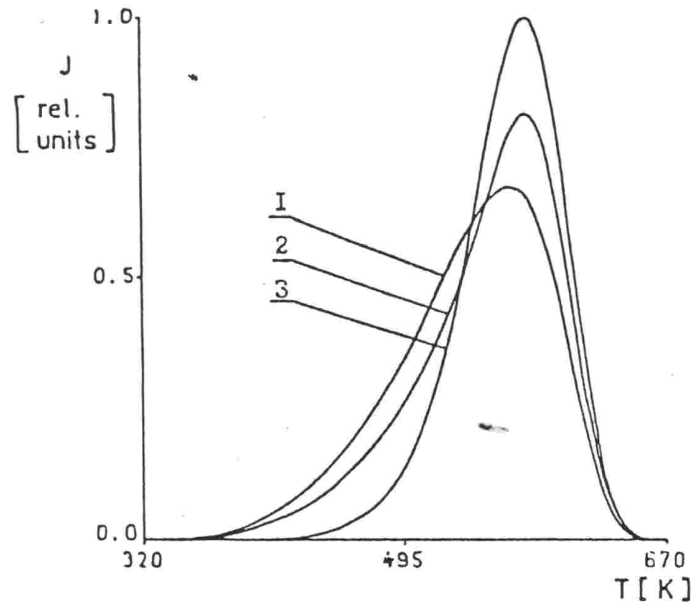


Fig. 3 Demonstration the EGA peaks caused by varying diffusion resistance for the released gases and various sample shape. Curve 1: effect of gas diffusion resistance supposed; spherical sample. Curve 2: effect of gas diffusion resistance supposed; sample in the form of a plate. Curve 3: no effect of gas diffusion resistance supposed, for samples both in the form plate and sphere the curves are identical

In Fig. 4 the EGA peaks are demonstrated in the linearized form, achieved by means of the functional scale method [2].

The effect of the gas diffusion resistance has been observed only at low temperature part of the EGA peaks, being different for samples in the form of sphere or plate. Using the linearized EGA curves in functional scales, the linearity of the curves has been used as the criterion for the absence of the gas diffusion effect. The use of THERMOKIN software [2] package enabled us to assess the gas diffusion resistance effect on the EGA curves. In this way the temperature intervals have been determined, where the effect of the gas diffusion resistance and the sample shape on the EGA curves can be neglected.

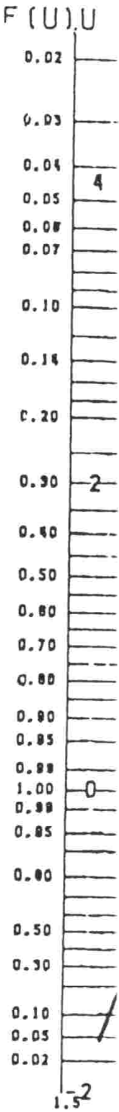


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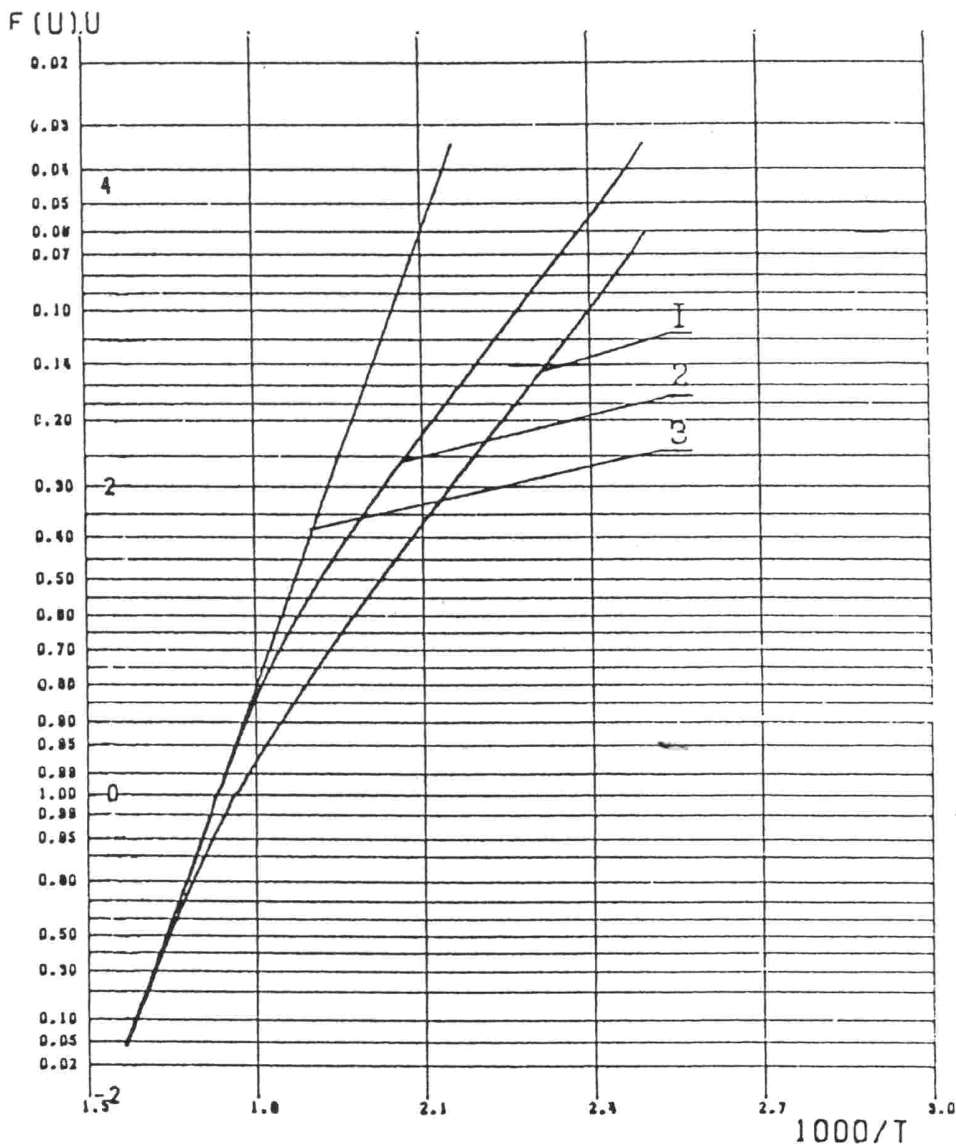


Fig. 4 The linearized EGA peaks demonstrated in Fig. 3, showing how the EGA curves can be affected by the sample shape and gas diffusion resistance: curves 1 and 2 correspond to cases of sample forms sphere and plate, resp., supposing the gas diffusion resistance; curve 3 corresponds to the cases when no gas diffusion resistance is supposed it is identical for samples both in the form plate and sphere

Effect of the grain size distribution

The analysis of different mechanisms of solid-phase reaction showed that in a number of cases one should expect a strong effect of grain size distribution on the EGA curve. We shall demonstrate this statement on a decomposition of solids supposing of contracting sphere reaction mechanism [3].

Let us consider the thermal decomposition reaction which starts on the surface of a grain and assume that the grain surface is rapidly covered by the layer of newly produced phase, and that subsequently there is a continuous increase of the product layer. If the gas release rate is limited by a solid state reaction, the integral equation of the reaction is

$$1 - \sqrt[3]{1-\alpha} = K_K \tau \quad (4)$$

If the rate is limited only by diffusion through the product layer, then

$$(1 - \sqrt[3]{1-\alpha})^2 = K_D \tau \quad (5)$$

Processes in the powdered systems occur as a rule in the transient region where the rates of diffusion and the chemical reaction itself are compatible and consequently neither kinetics nor diffusion model are applicable in the pure forms. To analyse the experimental data in this case the following equation is used:

$$\frac{1 - \sqrt[3]{1-\alpha}}{K_K} + \frac{(1 - \sqrt[3]{1-\alpha})^2}{K_D} = \tau \quad (6)$$

These expressions do not take into account the size distribution of grains. Let us characterize the dispersity of a sample by introducing the granulometric function:

$$f(a_0) = \frac{1}{M_0} \cdot \frac{dM_{a_0}}{da_0} \quad (7)$$

where M_0 is the general mass of a sample, dM_{a_0} is the mass of grains the sizes of which a_0 are between $a_0 + \frac{da_0}{2}$, $a_0 - \frac{da_0}{2}$, then

$$1 - \alpha = \int_x^{a_m} (-A_{a_0} y^3 + B_{a_0} y^2 - C_{a_0} y + 1) f(a_0) da_0$$

$$\text{where } A_{a_0} = \frac{1}{1 + (\lambda_{a_0} + \mu_{a_0}) + \lambda_{a_0} \mu_{a_0}}; \quad B_{a_0} = \frac{3 + (\lambda_{a_0} + \mu_{a_0})}{1 + (\lambda_{a_0} + \mu_{a_0}) + \lambda_{a_0} \mu_{a_0}} \quad (8)$$

$$C_{a_0} = \frac{3 + 2(\lambda_{a_0} + \mu_{a_0}) + \lambda_{a_0} \cdot \mu_{a_0}}{1 + (\lambda_{a_0} + \mu_{a_0}) + \lambda_{a_0} \cdot \mu_{a_0}}; \quad x \text{ is the product layer depth;}$$

$$y = x/a_0 = \sqrt{\theta^2/4 + (1+\theta)\tau} - \theta/2; \quad \theta = 2D/(a_0 k_1);$$

D is the diffusion coefficient; a_0 is the minimum size of the grain, k_1 is the reaction rate constant on the surface particle; $\tau = t/t_{max}$ is the reduced time. If the diffusion resistance increases, $\theta \rightarrow 0$.

The particles may be characterized by three parameters a , b , c , so that their volume is $V = \varphi abc$, where φ is the grain shape factor (for rectangular parallelepiped $\varphi = 8$). a_0 is the least size parameter, $b_0 = a_0 + \lambda_{a_0}$; $c_0 = a_0 + \mu_{a_0}$, where λ_{a_0} and μ_{a_0} are the parameters characterizing relationships between the sizes of a grain.

At omnilateral development of the reaction zone $\lambda = \mu = \infty$:

$$1 - \alpha = \int_x^{a_m} (1 - y) f(a_0) da_0 \quad (9)$$

At two-lateral development of the reaction zone $\lambda = 0$; $\mu = \infty$:

$$1 - \alpha = \int_x^{a_m} (1 - y)^2 f(a_0) da_0 \quad (10)$$

At three-lateral development of the reaction zone:

$$1 - \alpha = \int_x^{a_m} (1 - y)^3 f(a_0) da_0 \quad (11)$$

Using the relationships given above we have made the computer modelling of EGA curves and TG/DTG curves for different types of grain size distributions, namely one sized grains, normal statistical distribution of grain size, polysized distribution with equal realistics, and two sized grains.

Figure 5 shown as an example the integral (TG) and differential (DTG, EGA) curves for the case of linear heating and contracting sphere kinetics calculated for different functions of the size distribution of grains. It can be seen that for omnimodal distribution (curves 1) the differential curves are represented by a single peak, the position and shape of which essentially depend on the form of initial size distribution of grains.

For the case of the bimodal distribution the DTG (or EGA) curves are represented by not a fully resolved double peak. The presence of such peaks on the ex-

perimental curves could be misleadingly interpreted like the occurrence in a sample of two chemical reactions with different values of the activation energy.

Consequently, we can recommend preliminary measurement by the EGA and/or TG/DTG in order to find optimum grain size distribution for investigation of thermal decomposition of powdered solids.

The preliminary experiments with powders of different types of size distributions of grains should enable the investigator an optimal type of the distribution

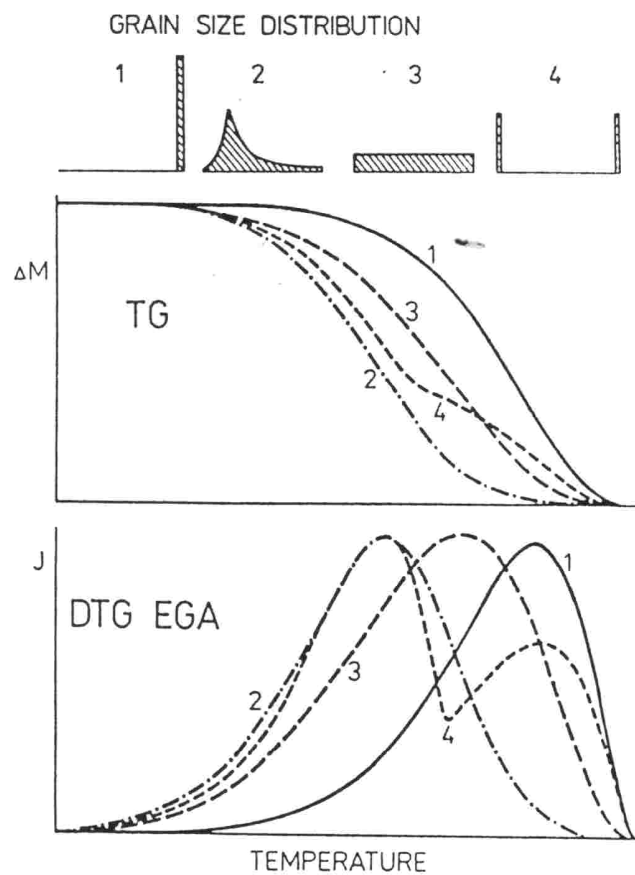


Fig. 5 Computer modelling of TG/DTG and EGA curves for thermal decomposition of disperse solids of four types of initial grain size distribution. a – grain size distribution scheme: 1 – one sized grains, 2 – normal statistical distribution, 3 – widely polysized distribution with equal statistics, 4 – two sized grains. b – thermogravimetric model curves corresponding to the grain size distributions (types 1 to 4), c – evolved gas analysis and/or DTG model curves corresponding to the grain size distributions (types 1 to 4)

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Conclusions

The influence of the initial grain size distribution on the shape of the TG curve and the final weight residue is considered. The optimum conditions for the MOKIN program are determined.

References

- 1 S. St. J. V.
- 2 I. N. Beck
- 3 N. N. O. University

Zusammenfassung
Ergebnisse der Computermodellierung der TG/DTG und EGA Kurven für die thermische Zersetzung von dispergierten Feststoffen mit vier verschiedenen Arten der anfänglichen Korngrößenverteilung. Die Faktoren der Diffusionskinetik und des Beitrags der Kinetik werden untersucht. Es werden optimale Bedingungen für das MOKIN-Programm festgestellt. Für die

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$f(a_0)$ and estimating an error made in the calculated parameters of the solid-phase reaction by polydispersity of the powdered sample under investigation.

The THERMOKIN software package contains the program which provided automatic choice of the optimal conditions. The package includes special programs for control, planning and optimization of the thermal experiment based on the methods of mathematical (statistical) planning of experiment, analysis and artificial intelligence.

Conclusion

The influence of characteristics of solids and measuring conditions on the EGA curves measured during thermal decomposition of solids was analyzed. The shape of sample, grain size distribution, the gas diffusion resistance in the sample and the flow rate of the gaseous media in the dynamic measuring system were considered. These factors should be taken into consideration when of the optimum conditions for EGA and TG measurements be determined. The THERMOKIN software package can be recommended for the assessment of the optimum conditions.

References

- 1 S. St. J. Wame, A. J. Bloodworth and D. J. Morgan, *Thermochim. Acta*, 93 (1985) 745.
- 2 I. N. Beckman, A. V. Zheleznov and V. Balek, *J. Thermal Anal.*, 37 (1991) 1479.
- 3 N. N. Oleynikov, in: *Principles of cryogenic technology* (Ed: Ju. D. Tretyakov), Moscow University Publ. House 1987, p. 70.

Zusammenfassung — Es wird der Einfluß verschiedener Faktoren auf die EGA- und TG/DTG-Ergebnisse der thermischen Zersetzung von Feststoffen untersucht. Dabei wurden folgende Faktoren berücksichtigt: der Durchsatzstrom des Gasmediums bei einer dynamischen Messung, der Diffusionswiderstand fester Proben gegenüber gasförmigen Produkten, die Probenform sowie der Beitrag der Korngröße von dispersen Proben.

Es werden Wege besprochen, wie die optimalen Werte für diese Parameter gefunden werden können. Für diesen Zweck wird die Anwendung des THERMOKIN Software-Paketes empfohlen.