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Thermal Degradation of Polymers. V. Derivation of Thermogravimetric and Kinetic Data from Mass Spectrometric Thermal Analysis*

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Summary

Derivation of kinetic and thermogravimetric data from mass spectrometric thermal analyses of polytetrafluoroethylene and silicone resins has been achieved using a new method of data treatment applicable to the entire temperature range in which degradation occurs even at relatively high heating rates (66 to 118°C/min). For heating rates to 300°C/min, the method of Ozawa relating activation energy to the slope of a graph of log (heating rate) vs. reciprocal temperature of the MTA maximum was employed to estimate an activation energy for polytetrafluoroethylene. Both methods give data in satisfactory agreement with results obtained by other methods.

Previously reported applications of mass spectrometric thermal analysis (MTA) to derivation of kinetic data have relied on the use of the initial, low-temperature portion of the MTA curve to provide a linear Arrhenius plot, before the amount of polymer changes significantly [1-4]. This paper describes a new method of data treatment which provides a kinetic analysis over the entire degradation range, as well as yielding a thermogravimetric analysis. The ion current vs. time trace provided by the mass spectrometer was divided into uniform time intervals, Δt, (usually 1 or 6 sec). Assuming the mass

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spectrometer output to be linear at the settings employed, it was then necessary to consider peak height proportional to the rate of weight loss, dw/dt, and, consequently, proportional to the weight loss, Δw, over each time interval, Δt. Correlation of this data with sample thermocouple data permitted derivation of degradation kinetics of a test material. Several assumptions were necessary:

1. Degradation was first order (i.e., $dw/dt = -Kw$ at a given temperature).
2. The ratio of each individual degradation product to total degradation products remained constant over the entire degradation region (so that ion current was related to mass by a constant factor).
3. Pumping of volatiles from the furnace tube, where they originated, to the ionization region of the mass spectrometer was instantaneous and complete (so that ion current accurately correlated with mass changes of the sample).

The frequently used kinetic parameter of active residual weight fraction was related to measured heights, H, on the ion current vs. time curve in the following manner. At time = x,

$$\frac{w_x - w_r}{w_0 - w_r} = \frac{\sum_{t=x}^{\infty} H}{\sum_{t=o}^{\infty} H}$$

Similarly, over each brief time interval Δt,

$$\left(\frac{\Delta w}{\Delta t}\right)_x \approx \frac{dw}{dt}_x \approx H_x \frac{w_0 - w_r}{\sum_{t=o}^{\infty} H}$$

from which

$$H_x = \left(\frac{dw}{dt}\right)_x \frac{\sum_{t=o}^{\infty} H}{w_0 - w_r}$$

Thus one may determine

$$\frac{H_x}{\sum_{t=x}^{\infty} H / \sum_{t=o}^{\infty} H} = \frac{(dw/dt)_x}{(w_x - w_r)/(w_0 - w_r)} \; \frac{\sum_{t=o}^{\infty} H}{w_0 - w_r}$$

Since the first-order rate constant, K, is defined as $(-dw/dt)/w - w_r$, the above quantity is equivalent to K × $\sum_{t=0}^{\infty} H$. Since uniform time intervals were used, H is proportional to area of the increment, so that this method actually relates the area under the MTA curve above a given temperature to the total area under the curve, just as a thermogravimetric analysis relates residual weight fraction to total weight loss. A plot of the logarithm of this quantity vs. reciprocal absolute temperature should give a straight line whose slope is indicative of the activation energy. No knowledge of initial sample weight (w_0), mass spectrometer sensitivity settings, or non volatile sample residue (w_r) is necessary.

The method was applied to polytetrafluoroethylene and a silicone resin, chosen because they represent extreme alternative decomposition modes. The former degrades to tetrafluoroethylene in 94% or greater yield [5], leaving no residue. The latter gives a mixture of at least 40 products, and leaves a 15–20% residue of silica [6].

The activation parameters for polytetrafluoroethylene derived from MTA are in good agreement with those reported previously using gravimetric [7] and manometric [5] techniques, as shown in Table 1. A reasonably linear Arrhenius plot was obtained over a range from 1 to 96% decomposition, establishing the validity of the assumptions underlying this method for polymers having a simple degradation mode. For the silicone resin,* comparison of the MTA

TABLE 1. Polymer Kinetic Data

Resin	Preexponential factor A, min^{-1}	Activation energy Ea, kcal	Method	Ref.
Polytetrafluoroethylene	2×10^{20}	79 ± 3	MTA	—
	5×10^{18}	80.5	Isothermal TGA	[7]
Silicone	3×10^{19}	83	Manometric	[5]
	7×10^{5}	20	MTA	—
	1×10^{12}	43.5	TGA	[3]
	—	23	Stress relaxation	[8]
	—	19	MTA	[3]

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*General Electric 655, a methyl phenyl vinyl silicone.

with other methods is difficult. The degradation of this resin is strongly dependent on pressure and geometry of the pyrolysis vessel [6]. Therefore, the difference between the activation energy of 20 kcal determined by this method from an Arrhenius plot (Fig. 3) linear between 0.4 and 98% decomposition and that of 43 kcal determined thermogravimetrically under atmospheric pressure may not be significant. It is of interest that an activation energy of 23 kcal for chain scission in a methyl siloxane polymer has been reported [8]. An activation energy of 19 kcal was derived from individual activation energies for formation of each major pyrolysis product. This latter value agrees well with that determined in this investigation. The gross simplification involved in substituting total ion current for a detailed product kinetic analysis apparently made little difference in the results.

An alternative method for treating MTA data was suggested by the work of Ozawa [9]. In a thermal analysis, the temperature at which any given percentage of decomposition occurs is dependent on heating rate. It has been shown [10] that the maximum rate of decomposition in a first-order reaction should occur at 1/e, or 36.8% weight fraction. Thus, for any series of MTA data, the temperatures in which maximum decomposition rate occurs can be determined readily by inspection and, when properly plotted against heating rate, should give a straight line which is a function of activation energy, according to the equation

$$d(\log \dot{T})/d(1/T_{max}) = 0.457Ea/R$$

To determine kinetics of polytetrafluoroethylene degradation at higher heating rates, such a plot was prepared (Fig. 4). Because of data scatter and the possibility that the sample temperature rise lagged behind that of the thermocouple at the highest heating rates, it is not clear whether the change in slope is real. It would appear that up to heating rates of 300°C/min, a straight line with a slope corresponding to an activation energy of 83 kcal adequately represents the data. For comparison, a similar plot based on differential thermal analysis endotherm maxima taken at lower heating rates is given. Its slope corresponds to an activation energy of 103 kcal. Because the DTA endotherm peak does not occur at a constant residual weight fraction, this value must be regarded as an approximation, at best.

MTA Apparatus

The temperature controller and general design have been described previously [3]. The furnace was modified slightly. The outer stainless-steel jacket was removed, so that a tantalum furnace tube and quartz insulator were supported by the heating filament. The path of the reference and control thermocouple wires was then shortened and straightened, simplifying furnace maintenance.

MTA of Resins

A small sample weighing approximately 3 mg was placed in the tantalum tube. A wire screen was placed in the tube to prevent expulsion of the sample by gases generated from its decomposition. Heating was conducted at a linear rate, while ion current was monitored (118°C/min, m/e 31 for polytetrafluoroethylene; 66°C/min, total ion current for silicone) and recorded on an oscillograph. A simultaneous record of thermocouple voltage was made, with simultaneous timing marks on both charts immediately before and after the degradation being used to correlate times. Thermograms (Fig. 1 and 2)

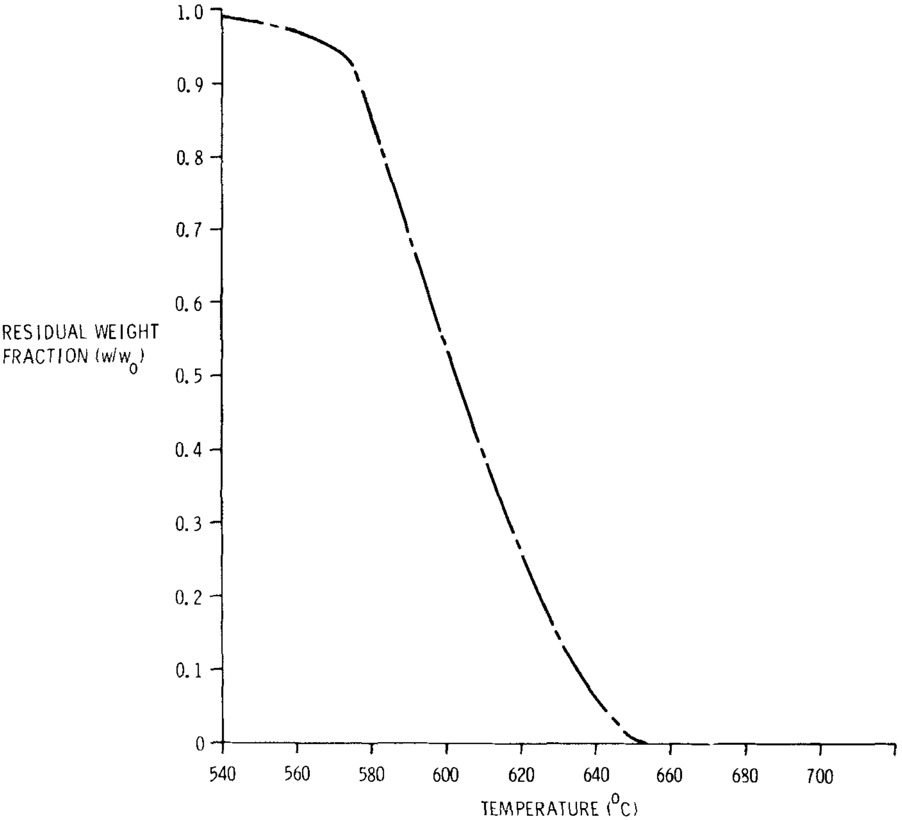

FIG. 1. Thermogram of polytetrafluoroethylene calculated from MTA data.

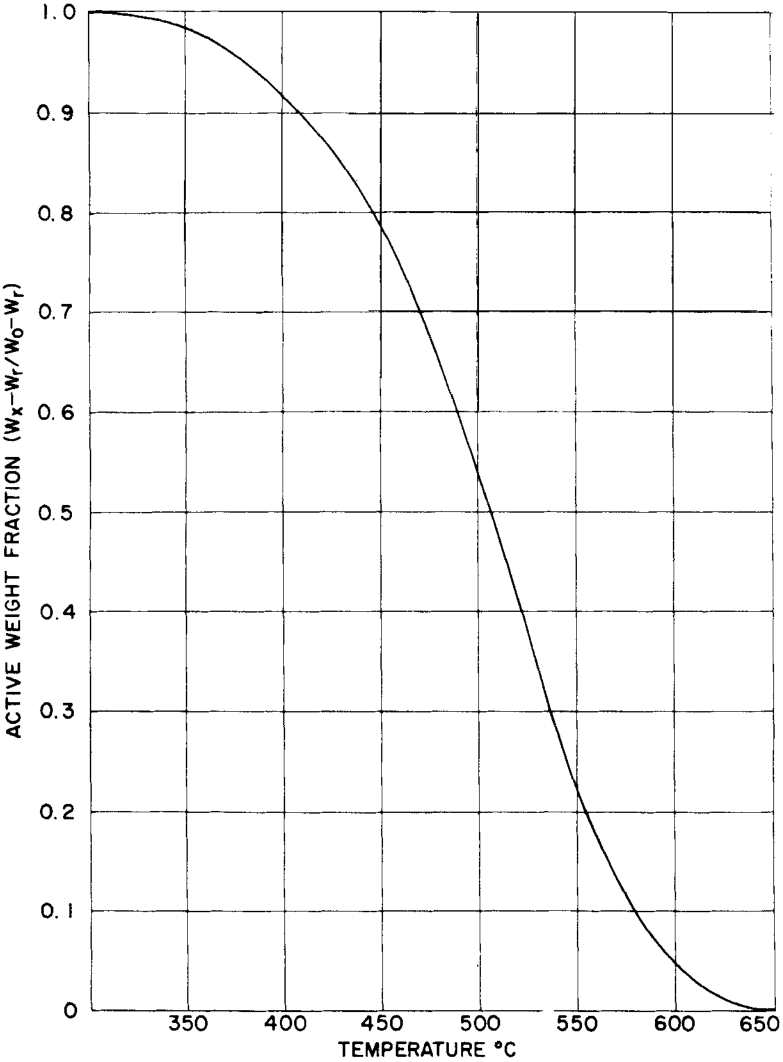

FIG. 2. Thermogram of silicone resin volatiles calculated from MTA data.

and Arrhenius plots (Figs. 3 and 4) are shown. Kinetic data were derived from a least-squares computer program applied to the individual datum points on the Arrhenius plots. From data recorded at various heating rates for m/e 31, a plot of log $\dot{T}$ vs. $1/T_{max}$ for polytetrafluoroethylene (Fig. 5) was prepared.

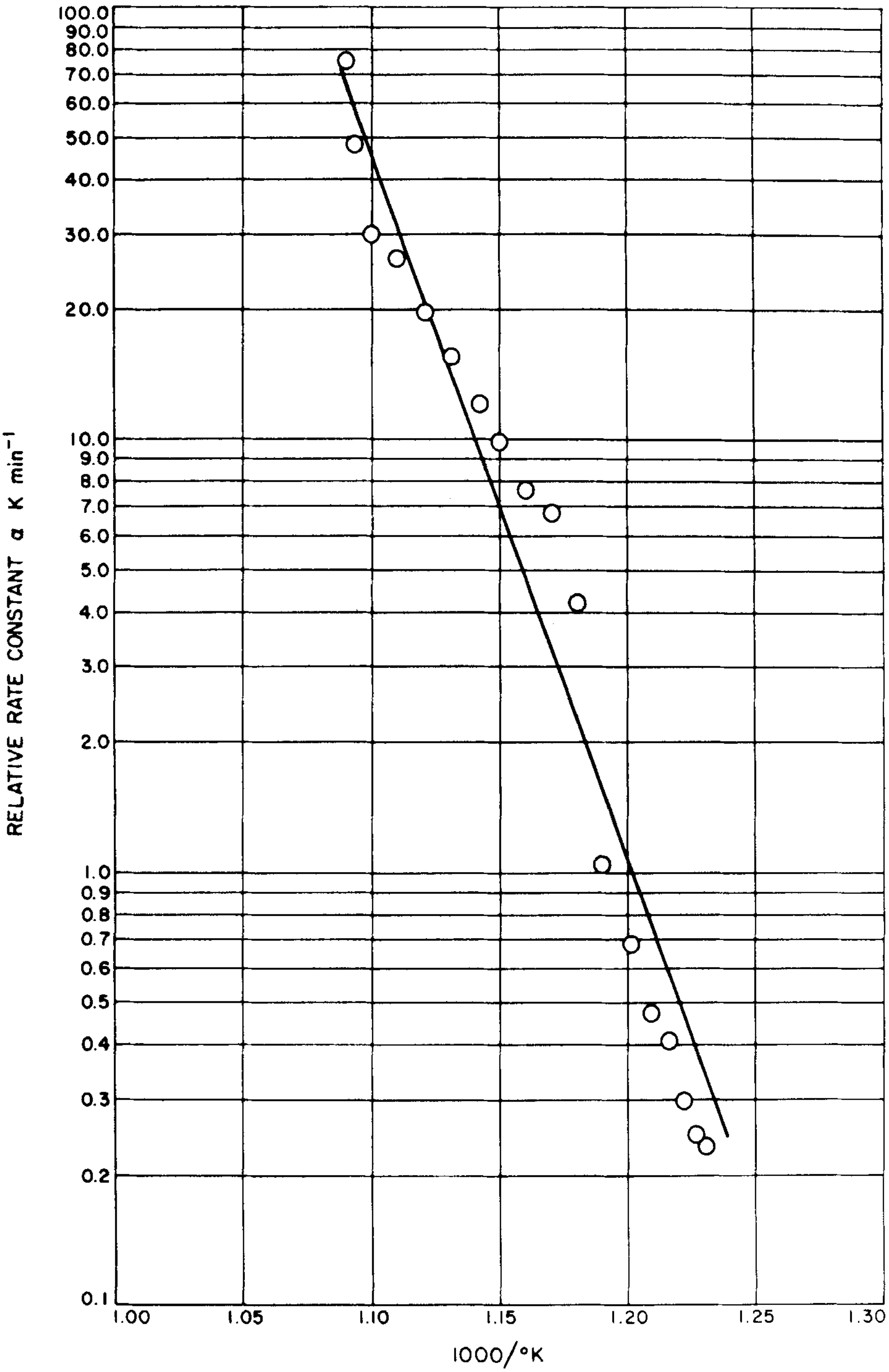

FIG. 3. Arrhenius plot for degradation of polytetrafluoroethylene.

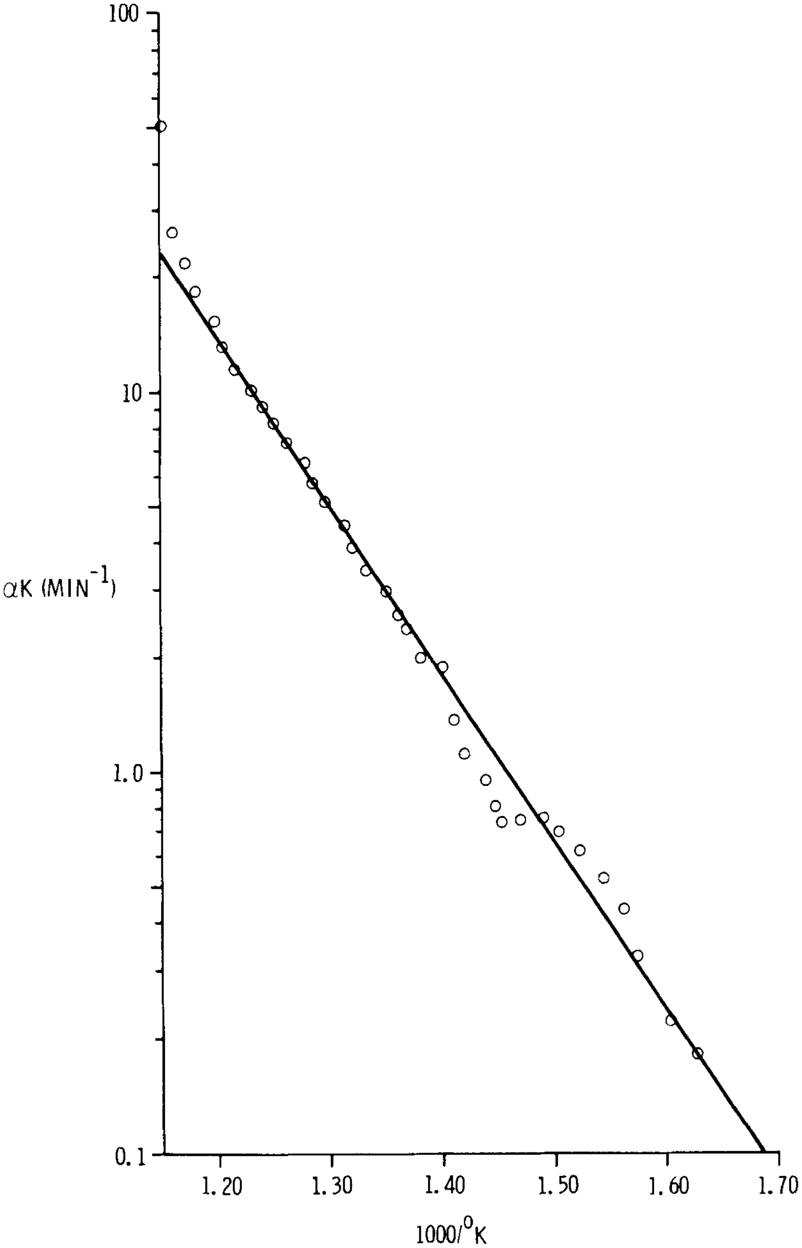

FIG. 4. Arrhenius plot for degradation of silicone resin.

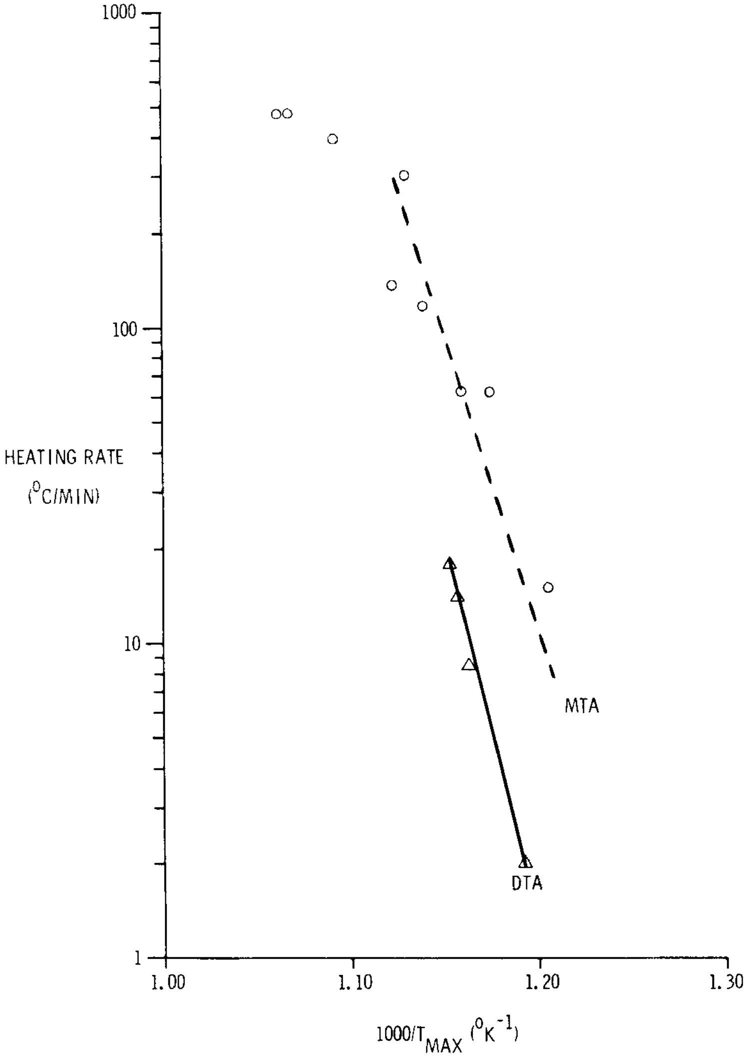

FIG. 5. Ozawa plot for degradation of polytetrafluoroethylene.

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Zusammenfassung

Mittels einer neuen Methode wurden kinetische und thermogravimetrische Daten aus massenspektroskopischen thermischen Analysen von Polytetrafluoräthylen- und Siliconharzen abgeleitet. Diese neue Methode der Datenauswertung lässt sich über den ganzen Temperatur bereich anwenden in dem Abbau erfolgt, sogar bei relativ hohen Erhitzungsgeschwindigkeiten (66 bis 118°C/min). Im Bereich von Erhitzungsgeschwindigkeiten bis zu 300°C/min wurde die Methode von Ozawa zur Abschätzung der Aktivierungsenergie von Polytetrafluoräthylen benützt. Diese Methode basiert auf einer Beziehung zwischen der Aktivierungsenergie und der Neigung einer Kurve, die sich beim Auftragen des Logarithmus (Erhitzungsgeschwindigkeit) gegen die reziproke Temperatur des MTA Maximums ergibt. Beide Methoden ergeben Resultate, die mit nach anderen Methoden erhaltenen Ergebnissen zufriedenstellend übereinstimmen.

Résumé

On a obtenu des données cinétiques et thermogravimétriques à partir des analyses de masse spectrométriques thermiques du polytétrafluoroéthylène et des résines silicones par l'usage d'un nouveau mode de traitement des données, applicable à l'échelle entiére de températures, dans lesquelles la dégradation se produit, mêma à des vitesse de chauffage elevées (66 a 118°C/min). Pour déterminer l'énergie d'activation du polytétrafluoroéthylène à des vitesses de chauffage jusqu'à 300°C/min on a employé la méthode d'Ozawa, qui rélie l'énergie d'activation à la pente du graphique du log (vitesse de chauffage) vs. température de MTA maxima. Les deux méthodes donnent des résultats en accord satisfaisants avec ceux obtenus par d'autres techniques.