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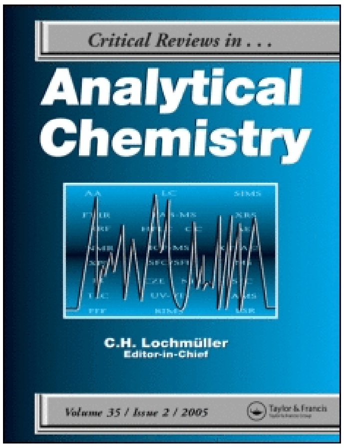

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MODERN METHODS OF THERMAL ANALYSIS

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PREFACE

The position and importance of thermal analysis among methods of material research and structure elucidation is well shown by the review which appeared in *Research and Development Journal.*[1] According to the review, about 42% of the laboratories surveyed are using, or expect to be using in the near future, thermogravimetric (TG), differential thermal analysis (DTA), or differential scanning calorimetric (DSC) devices. It is also characteristic that about 1 to 2% of the papers appearing yearly on analytical chemistry deal with the problems of thermal analysis.[2,3] It is clearly shown by these data that thermal methods of analysis cannot compete with electroanalytical, spectroscopic, and chromatographic methods with respect to practical applications. Nevertheless, they play an important part in material research. If used and interpreted properly, methods of thermal analysis provide unique information in both theoretical and practical respects about the thermal behavior of samples.

It is rather difficult to give a summary of the methods, due to their versatility and to the fact that it is not easy to draw lines between individual thermal methods. A further problem is that it is practically impossible to give a complete literature survey within the given size even for the past few years, as the number of papers appearing on the field is 1000 to 1200 per year in addition to books and conference proceedings. Therefore it is not intended for a complete list of literature to be given here as the scope of this paper is not to provide a literature review. In this respect the biannual reviews of Murphy published in *Analytical Chemistry*[4] which, although comprehensive and very useful, cannot be considered as complete, are to be consulted. Analogously, the references of abstracting journals cannot be considered as fully exhaustive either. The aim of the present paper is to provide a comprehensive critical survey of the methods of thermal analysis.

I. INTRODUCTION

As defined by the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA): "Thermal analysis: a group of techniques in which a physical property of a substance is measured as a function of temperature, whilst the substance is subjected to a controlled temperature programme."[5]

The definitions and suggestions by the Nomenclature Committee refer to an important question. Confusion with respect to terms and definitions was, and partly still is, characteristic of the field of thermal analysis. Any effort made to develop a uniform nomenclature and to define and exactly circumscribe the special fields is very welcome.

In the opinion of these authors, the field of thermal analysis includes not only the measuring techniques, but also the method of interpretation of results. The term in the definition that a physical property of a substance is measured by the methods can readily be accepted if one considers that in the course of a chemical transformation, one or more of the physical properties of the sample change simultaneously. Accordingly, the authors believe that from the practical point of view it is useful to give a detailed classification of the changes, transformations, and properties which can be studied by the methods of thermal analysis. They are the following:

1. Purely physical transformations such as enanthiomorphous or monotropic polymorphism, relaxation processes, phase transformations (melting-solidification, evaporation-condensation, sublimation), adsorption and desorption, etc.
2. Thermally initiated chemical transformations such as chemisorption, desolvation (dehydration), pyrolysis, solid to solid phase reactions, catalyzed or noncatalyzed chemical reactions in heterogeneous and/or homogeneous phase, etc.

These transformations start at a certain characteristic temperature and proceed within a relatively narrow temperature interval at a fairly high rate. Based on this fact, two data can be obtained: the characteristic temperature of a certain transformation of a sample and the signal and/or its integral recorded during the transformation. The latter, corrected by using appropriate proportionality factors, is related to the amount of substance transformed, if an extensive property has been measured. This, translated to the language of analytical chemistry, means that the methods of thermal analysis can be applied to both qualitative and quantitative analytical purposes.

In addition to the investigation of sudden physical and chemical changes, thermal methods of analysis enable a number of extensive and intensive material properties to be measured. It is characteristic of these properties that in the absence of transitions their change is a constant and predictable function of the temperature, e.g., specific heat, volume, electric resistance, various optical properties (reflection, refractive index, etc.), mechanical properties, etc. However, in the course of chemical and physical transformation, these properties usually change suddenly, too. For example, specific heat, volume, reflection, electric resistance, etc., may undergo a rapid change at the melting point.

In view of what has been said, the internal energy at constant pressure, the enthalpy, mass, dimensions, mechanical, electric, optical, magnetic, and acoustic properties of samples can be studied as a function of the temperature.

Chemical transformations can be characterized by mass transport in addition to heat transport, and if sufficiently high-volatility products are liberated from the sample, their analysis constitutes a special field of thermal analysis, the thermal-gas analysis.

The borders of the field of thermal analysis can only be drawn arbitrarily. Static calorimetry, enthalpimetry, and its titrimetric versions, etc., are also sometimes considered to be thermoanalytical methods. In spite of this, in accordance with the recommendation of the Nomenclature Committee of ICTA, only the dynamic methods will be dealt with in the present review; that is, with the questions of transformations taking place on programmed heat treatment (heating or cooling). The delimitation has some other aspects, too. Several methods provide profound information in such a way that a property of the sample is measured at known, stepwisely changed temperatures. For example, the dynamic NMR method, in which the spectrum is studied as a stepwise function of the temperature, enables hydrogen bridged structures, conformations, etc., to be studied more closely. Similarly, IR or ESR spectra can also be studied as a function of the temperature. In the opinion of the authors, these methods do not belong to the field of thermal analysis because the temperature — as an independent variable — provides derived, rather than primary, information.

It is not very easy to define analytical chemistry in a general and exact form. According to Malissa,[6] analytical chemistry is a system which consists of at least three elements — the sample, the reagent, and the signal — which, interacting with each other and with the environment, enable information to be obtained. The interaction can be schematically given as:

$$\text{Sample} + \text{Reagent} \rightarrow \text{Signal}$$

In terms of this definition, if the heat is considered as "reagent", as suggested by Šesták,[7] thermal analysis is really an analytical technique. However, an important restriction has to be taken into account; namely that the information obtained is basically connected with the thermal behavior of the sample. This may have several aspects from the point of view of the analytical task:

1. Analysis in the narrow sense, e.g., indentification, characterization, and concentration determination.
2. Investigations for technological purposes, e.g., processing, application, transformation of materials, etc., with special regard to production processes.
3. Determination of thermodynamic and reaction kinetic data for theoretical or practical purposes.

Some procedures which may be considered as thermal analysis were already known in the medieval times.[8-10] The fundamentals of modern thermal analysis were laid at the end of the last century. Applications were for a long time connected with the determination of data characteristic of the thermal behavior of various samples and with the homemade construction of laboratory thermal devices. Industrially produced devices appeared on the market only in the early 1960s and gradually became routinely applied tools for material research. However, the methods of thermal analysis are not as widely used as would be justified by their potentialities. Agreeing with the views of Earnest,[11] the authors think that the main reason for this is that the theory and practice of the thermoanalytical methods are not generally taught at universities. A further reason might be that the signals provided by these methods are not absolute values, but have to be calibrated, and the signals have to be freed from the distortions due to matrix effects and experimental conditions. Attempts in this direction are not entirely successful. Often data for the same material measured in different laboratories agree poorly or not at all. The methods of thermal analysis do not provide information as unambigous and general as, for example, spectrochemical and electroanalytical methods (chemical shift, coupling constant [NMR], absorption maxima [IR, UV etc.], half-wave electrode potential, etc. In this respect a comparison with chromatographic methods, with reasonable restrictions, is more justified. In this context the standardization of methods and importance of the furnishing of comparable data can be mentioned as the most important tasks of the field.

II. DESCRIPTION OF THE METHODS OF THERMAL ANALYSIS (CLASSIFICATION, NOMENCLATURE)

The definition of thermal analysis as given by the ICTA has been cited in the Introduction. It has already been mentioned that a number of different thermoanalytical methods exist, depending on the nature of the property of the sample studied under dynamic conditions, that is using a thermal treatment (heating or cooling). There are various known versions of classifying the methods of thermal analysis, the discussion and evaluation of which is of importance since, as already mentioned, the concepts of the field are not yet of uniform usage and interpretation.

The methods are usually grouped according to the technique applied for measuring the selected parameters. The field is treated according to this principle in most monographs.[12-20]

The classification given by Liptay[21] is different; methods in which the signal is produced by a measurement with respect to an inert reference substance (e.g., DTA, DSC) belong to one group, while those in which a parameter is determined directly

Table 1
IMPORTANT THERMOANALYTICAL METHODS

- Thermoanalytical methods in a narrow sense
  - Differential thermal analysis (DTA)
  - Thermometric titrimetry
  - Calorimetry
    - Differential scanning calorimetry (DSC)
    - Reaction and solution calorimetry
    - Calorimetric titrimetry
    - Combustion calorimetry
- Thermoanalytical methods in a wider sense
  - Cryoscopic and boiling point methods
  - Thermogravimetry
  - Dilatometry and thermomechanical analysis
  - Torsional braid analysis
  - Vapor pressure methods
  - Solubility methods
  - Low-resolution NMR

From Marti, E., *Thermochim. Acta,* 20, 1, 1977. With permission.

belong to the other group. The second group includes practically all the methods. This, however, does not mean a substantial difference. It would have been more effective to divide the methods into two groups according to whether the method need or need not be standardized with respect to the dependent variable. Temperature, as an independent variable, has to be standardized in each method for every single instrument. Marti[22] divides the methods into two groups also, as follows:

1. Thermal methods in the narrow sense, which allow the determination of a caloric dependent variable by a direct or indirect procedure.
2. Methods in the wider sense, which allow the determination of any physical property as a function of temperature, including dynamic and isothermal measurements.

In Table 1 the system suggested by Marti[22] is presented. This grouping is consistent as it includes, in the first group, methods enabling changes of internal energies and enthalpies to be measured. However, internal energy and enthalpy changes are generally involved in methods included in the second group. The most important objection to this grouping is that several important thermoanalytical methods, such as thermogas analysis, thermooptics, and thermomagnetic techniques, are not even mentioned.

According to Oswald and Dubler,[23] it is incorrect to speak of thermogravimetry as a thermal method in the wider sense since it is one of the most classical methods. Further, the authors do not agree with the description "most important", since a number of important methods are missing, whereas some of the methods mentioned are so special that they are actually less important and less widely used (e.g., solubility method).

An interesting grouping can be given based on the extensive or intensive nature of the parameter measured. The intensive properties do not depend on the number of moles of the sample. In view of this, the statement by Marti — namely that the method based on measurement of temperature difference (Δ T) is of intensive nature — is objectionable. While it is true that the temperature of the sample does not depend on its amount, the ΔT signal, measured under controlled experimental conditions, is proportional to the mass of sample. According to Garn,[24] the characterization of a property as extensive or intensive may be of decisive importance in thermokinetic measurements. A system has been developed by the authors of this review for the evaluation of the methods of chemical analysis by considering the differences due to the extensive and intensive nature of the properties measured.[25]

The authors think that the classification based on the nature of the property measured is the most expedient from the practical point of view, as already suggested by the Nomenclature Commission of ICTA (see Table 2) as follows in general form: "given" method is a technique in which a "given" property is measured as a function of temperature while the substance is subjected to a controlled temperature program. While these definitions are correct and flexible, do not hinder future development, and the work of the Commission is highly appreciated, there are some inconsistencies in the system elaborated, at least in the opinion of the authors of this review, some of which will be discussed below.

It seems needless to mention isobaric mass change measurement as a separate method since a constant stationary pressure sets up also in the course of thermogravimetric measurements after a transient state. The constancy of pressure does not justify a separate method to be defined. It is also unnecessary to deal with evolved gas detection (EGD) and evolved gas analysis (EGA) separately. In EGD, gas evolution is followed in some way. Detection is a less exacting form of analysis with a lower information content, but it is difficult to draw a methodological borderline between EGD and EGA. Similarly, the distinction of the emanation analysis and thermoparticulate analysis seems unnecessary. A gaseous substance released due to radioactive radiation can be measured by other methods of gas analysis and provide the same amount of information. On these grounds EGA methods using Katharometer, flame ionization detectors, etc., should be treated separately, too. Perhaps thermoemanation studies on samples into which radioactive materials have been incorporated artificially should be treated separately, whereas methods dealing with samples with spontaneous radiation should be classified simply as gas analytical methods.

Thermoparticulate analysis should not be treated as a separate method even though it was considered to be a new techique enabling a new physical property, namely the temperature at which particulates are emitted from heated organic substances, to be measured.[26,27] The task seems to be performable by a suitably designed thermo-gas analytical technique which has a suitably small time constant and high sensitivity, making the necessary qualitative and quantitative analytical data available.

In the opinion of the authors the definition of the DTA method is not exact either. Although the parameter measured is the temperature, the information yielded is based on the temperature difference between the sample and reference substance brought about by enthalpy changes. Accordingly, the enthalpy change, not the temperature, is a measured property! This is a typical sensor or signal-transformation problem. It can be considered analogous to the measurement, where conductance is converted to an analog voltage signal by the direct measurement of the ohmic resistance or the displacement or dilation is converted to a voltage signal by linear variable differential transformation (LVDT). It is a hard task to distinguish between the DTA and DSC. This is clearly shown by the quantitative DTA apparatus in which the disk itself is the thermal-flux-to-temperature converter. In this way there is no essential difference between real power-compensated DSC and dynamic heat-flux DSC. Knowing the debate concerning the definition and name of the two methods and also the differences, the authors think that this was only due to patent and instrument naming problems. Both are suited to the measurement of enthalpy changes. The distinction between the two methods seems to be similar to the distinction between TG measurements carried out by deflection-type, and a null-type or compensation balance.

Holba and Šesták[28] objected to the substitution of the terms "differential dynamic

Table 2
OFFICIAL CLASSIFICATION OF THERMAL METHODS PROPOSED BY THE NOMENCLATURE COMMISSION OF ICTA

Physical property	Defined techniques
Mass (change)	Thermogravimetry Isobaric mass-change determination Evolved gas detection Evolved gas analysis Emanation thermal analysis Thermoparticulate analysis
Temperature	Heating (cooling) curve determination Differential thermal analysis
Enthalpy	Differential scanning calorimetry
Dimensions	Thermodilatometry
Mechanical characteristics	Thermomechanical analysis Dinamic thermometry
Acoustic characteristics	Thermosonimetry Thermomechanometry
Optical characteristics	Thermooptometry
Electrical characteristics	Thermoelectrometry
Magnetic characteristics	Thermomagnetometry

From Mackenzie, R. C., *J. Talanta,* 16, 1227, 1969, and Proc. ICTA Kyoto, 1977, 561. With permission.

calorimetry" and "Calvet microcalorimetry by quantitative DTA" since, in the former, the measurement of the internal energy is carried out in a different way. Kambe[29] suggested the term "thermomechanometry," which is widely used in polymer studies, instead of thermomechanical analysis. By these critical statements the authors' intention has not been to underestimate the importance of the work done by the Nomenclature Committee, but to direct attention towards the need for refining and improving the existing definitions.

III. GENERAL DESCRIPTION OF THERMOANALYTICAL MEASURING APPARATUS

Depending on the property to be measured, a great variety of methods have been developed although modern instruments employed are similar in construction and technical design. The general scheme of thermoanalytical instruments is shown in Figure 1.

It is common for all thermoanalytical instruments to incorporate a heat source, temperature controller and programmer, and thermometer. Controlled atmosphere is not absolutely necessary. Signal and data processing may be of different levels.

Thermoanalytical devices differ in the nature of the sensor used for measuring a selected property and that of the transducer. A general, detailed description of the different parts of thermoanalytical devices will be given in the following section in accordance with Figure 1.

A. The Sample

Obviously the sample is not a technically designed and constructed part of thermoanalytical devices, but some of its parameters are to be considered from the

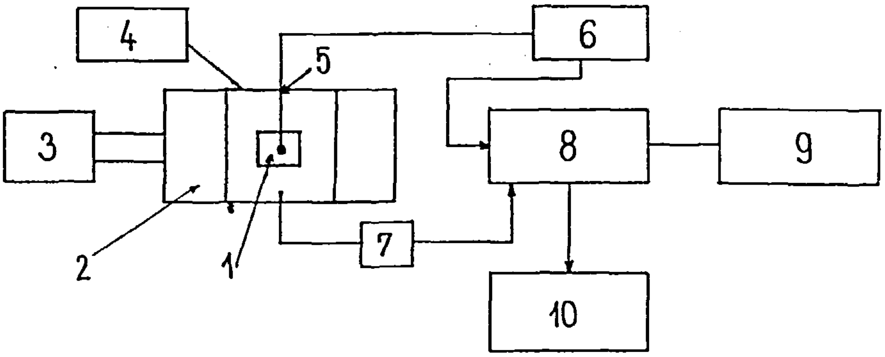


FIGURE 1. General scheme of a thermoanalytical instrument: (1) sample, (2) heat source, (3) temperature programmer and controller, (4) atmosphere controller, (5) signal transducer (element), (6) amplifier and electrical filter, (7) temperature measuring unit (element), (8) data acquisition system, (9) recorder, (10) data processing, storing, taping, punching, etc. devices.

measuring-technical point of view. The sample size depends on the method of sampling; the destructive nature of the method and the sensitivity and other characteristics of the instrument used. In the early stage of the development of thermal analysis macro (100 to 1000 mg) samples were used. Nowadays the usual sample weight is 1 to 10 mg. The reduction in sample size was made possible by the increased sensitivity of newly developed instruments and was justified by the fact that in this way the temperature gradient within the samples and, in the case of decomposition reaction, the pressure gradient become smaller. In some cases submicro samples are used. Menis and Garn[30] carried out successful studies on the modifications of silica important for environmental analysis using only a few μg of sample.

With the majority of samples, reproducible results can be obtained in repeated experiments under controlled experimental conditions provided that the decomposition temperature is not reached. The conditions of this are the thermal equilibrium of the sample as well as the rapidity of the modification and phase-transition processes. Experimental evidence shows that the characteristic temperatures and heats of transformation are the same or nearly the same at heating as at cooling. With a number of compounds — polymers and compounds with liquid crystal structure[31-33] and others, e.g., ammonium nitrate[34] — this condition is not fulfilled and subsequent heating-cooling cycles yield substantially different records. In addition to this, the shape of the curves may depend on the rate of heat conduction. This phenomenon is due to the fact that the amorphous, plastic, or crystalline structure of polymers depends on the molecular structure and on the temperature. Similar behavior can be observed on mechanical effects, e.g., rolled metals are inclined to a readily observable energy accumulation.[31,35] The phenomena mentioned are usually ascribed to the so-called thermal or mechanical history effects. These effects may occur also with natural samples (ores, minerals, and rocks) and may depend on the place of origin, method of sample preparation, and degree of grinding. The phenomenon is due to the difference in specific surface area and in the nature and amount of crystal defects. In the measurement of enthalpy changes by classical DTA method, an important role is also played by the size and nature of the reference material. In modern DTA and DSC devices, practically empty metal sample holders are used as reference.

B. The Heat Source

Sample heating can be accomplished using different heat sources, the proper choice of which is dictated by the heat effects necessary to the given measurement and the optimum temperature control and program to be used. The following methods can be used for heating:

1. Heat transmitting fluid, thermostat
2. Electric furnace
3. Heat radiation by infrared source, or by laser radiation
4. Induction heating

In constructing the heat source, three difference methods of heat transfer should be taken into account.

Heat can be transmitted by:

1. Conduction, represented simply as

$$q_1 = \frac{K(T_1 - T_2)}{L} \quad (1)$$

2. Convection, described as

$$q_2 = k(T_1 - T_2) \quad (2)$$

3. Radiation, represented as

$$q_3 = F \times \delta \times \epsilon(T_1^4 - T_2^4) \quad (3)$$

where q_1, q_2, and q_3 = heat transfer rate in each case, respectively, [$J/cm^2 \cdot sec$]; K = thermal conductivity of sample holder [$J/sec \cdot cm \cdot K$]; k = thermal convectivity of medium heat transfer coefficient [$J/sec \cdot cm^2 \cdot K$]; L = thickness of sample holder cap [cm]; F = geometric factor between heat source and receiver; δ = Stephen-Boltzman constant [$J/cm^2 \cdot K^4 \cdot sec$]; ϵ = total emissivity; T_1 = temperature of heat source; T_2 = temperature of receiver; and

$$q_{total} = q_1 + q_2 + q_3 \quad (4)$$

which of the three mechanisms is predominant in a given case depends on the nature of the heat source and technical design of the heater and receiver, and on the absolute temperature. *The mechanism and nature of heat transfer is of basic importance in some* methods (e.g., DTA and DSC).

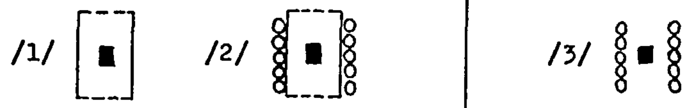
The relative position (geometry) of the sample and heat source may widely differ. In most methods they can be separated by air gap, which means that heat is transported by convection and radiation. In modern quantitative DTA and DSC devices, heat conduction is the predominating way of heat transport, either by inserting a heat-conducting disk or by placing the sample into a boring in a compact, heated block. The role of radiation is not negligible even in these cases; it becomes more predominating as the temperature rises, which accounts for the fact that devices based on heat conduction have an upper limit of operation somewhere between 900 and 1000 K. Heating by a fluid circulation thermostat is rarely used because of the thermostat's high heat capacity and consequent high thermal inertia, as well as a relatively narrow temperature operating range. It is difficult to find a heat transmitting fluid which can be used above 600 K since most are used at temperatures below room temperature, or in isothermal studies.

Electrical furnaces are the devices most widely used for heating in thermal analysis. Some practical requirements connected with the construction of electrical furnaces are given:

1. To enable, by means of a heating controller and programmer, any prescribed thermal treatment — heating or cooling, holding at constant temperature, or any combination of these — to be carried out within wide limits and with a high reproducibility.
2. Temperature distribution — the characteristic of the furnace — should be such as to have a constant temperature region exceeding in dimensions that of the sample within the entire temperature range.
3. To enable a wide variety of temperature speed programs to be ensured. The usually required range is 0.1 to 100 K/min, the most widely used 0.5 to 10 K/min. A linear heating program is to be ensured and the short-term fluctuation should be as small as possible.
4. Control of the atmosphere in the furnace made possible by the geometry, with no uncontrollable convection occurring.
5. No electrical noise or any induced magnetic field; therefore thorough grounding and bifilar wiring are necessary.
6. *Introduction of a cooling medium and realization of a cooling program should be* possible.

The choice of the size and insulation of the furnace is a result of a compromise. A big furnace ensures uniform distribution of heat, but has a big thermal inertia. For rapid temperature programs, smaller and less insulated furnaces are best suited. For the heating of low power, block-type sample holders, the so-called cartridge resistances incorporated centrally and symmetrically in the block can advantageously be used. In general, when resistance heating is used, the coils have to be situated in a way to ensure uniform, symmetrical heating. The maximum temperature depends on the material used to make the coils in addition to the nature of the structural materials of the furnace. Using platinum wire, furnaces working up to 1900 K can be constructed. The production of temperatures even higher creates special problems, although it is often needed when high-melting metals, ceramics, oxides, etc., are to be studied. High-temperature measurements require special constructions. At 1900 K the platinum wire has to be embedded in cement to prevent volatilization of platinum. For higher temperatures molydenum disilicide may be considered and, in this case, reflecting surfaces with different geometry are also to be used. Heating with tungsten wire and tantalum reflectors as proposed by Lecocq,[36] and alumina-coated tungsten coil axially focused on the sample by cylindrical platinum reflector, by Jouren et al.[37] The firm, Setaram, applied graphite heating elements in a commercial apparatus.

The problems in constructing furnaces for high-temperature thermogravimetry have been investigated by Steinheil,[38] who presented three solutions (see Figure 2). In the first case, high electrical current is used for heating using a tungsten coil and reflection chamber. According to the second suggestion, a carbon radiation chamber and induction heating are used to produce high temperature. In the third solution, a high-frequency induction coil is solely employed. Radiation heating can be used with both electrical conductors and insulators, whereas induction heating can only be applied in the case of electrically conducting samples. A great advantage of induction heating is the low thermal inertia. Rapid temperature programs are feasible, and by properly focusing the field, the sample alone, can be heated. However, the gradient of the electric field dramatically affects the weight measurement; it has been shown by the author[38] that a 0.1 mm deviation from perfect focusing causes an apparent mass difference of about 5.10^{-2}g. This highly exceeds the expected mass change case of micro samples and, therefore, the



Radiation	Induction
1. electrical conductors,insulators	1. electrical conductors only
2. hot radiation chamber reactions with gases coating of specimen radiometer forces	2. no hot parts except specimen
3. no fast changes in temperature possible	3. fast changes in temperature and quenching possible
4. no electromagnetic forces on specimen	4. electromagnetic forces on specimen

FIGURE 2. Methods for heating of specimens to about 3300 K. (From Steinheil, E., *Proc. ICTA Davos*, Vol. 1, 1971, 187. With permission.)

weight measurement must be carried out discontinuously when the high-frequency electromagnetic field is switched off. The method is difficult, but can be successfully used with methods of thermal analysis, with the exception of TG. In the majority of commercially available thermoanalytical devices two or more furnaces are used to cover the total temperature range. Usually one furnace is used between 300 and 1500K, a second at around 1500 to 2000 K. For temperatures above 2300 K there is no furnace commercially available — the furnaces used in this range are homemade ones and were constructed in research laboratories.

An example will be presented of the infrared heating which is rarely used. The device described by Japanese authors[39] incorporates an infrared image furnace with a high-precision temperature controller and programmer. With four halogen lamps, 1700 K could be reached. A trapeze-shaped program was realized at heating rates from 300 to 1300 K/min.

In the prospectus of Sauki Engineering Ltd.,[40] a laser heating is described, the principle of which is shown in Figure 3. This enables thermal diffusivity to be measured through which changes in other thermophysical properties (e.g., phase transition or Curie point) can be followed.

An electron-beam heating method was applied by Steffen and Wollenberger[41] to the investigation of processes involving small energy changes in an adiabatic twin calorimeter. Thus, for example, the release of the stored energy of copper polycrystal previously deformed at room temperature could be studied.

The importance and application of measurements below room temperature have recently increased. Sample study under the condition of programmed cooling means extending investigations. This made necessary the realization of the cooling mode of thermoanalytical devices. Cooling from higher temperatures to about 350 to 400 K can be accomplished relatively quickly at a rate depending on the heat capacity of the furnace. If cooling is to be performed at a high rate, a coolant is necessary even at higher temperatures.

Low-temperature measurements are usually carried out with the purpose of investigating polymorphism, glassy state, phase transitions, specific heat, electric conductance changes, magnetic transformations, etc.

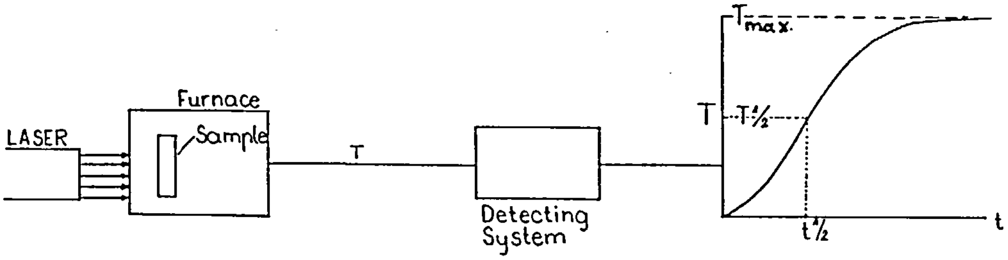


FIGURE 3. Heating system with laser beam for temperature measurement of surface. (From Bulletin of Sanki Engineering Ltd. With permission.)

The fundamental problems, applications, and data-processing questions of low-temperature calorimetry have been summarized recently by Gmelin.[42] Some of these considerations are also valid for dynamic measurements.

A summary of low-temperature DTA has been presented by Redfern and Treherne[43] and May.[44] In the former, a brief historical survey is also given. The coolants are treated as a function of the temperature range in which they can be used and the two most frequently applied solutions are outlined. The sample is either cooled previous to the required low temperature and heating is then started, or a dynamic, programmed cooling is applied. The practical solution has been dealt with by May[44] in detail. In the paper, considerations are presented on seven points, and an economical liquid nitrogen feeding device is proposed.

Finally, it is worth mentioning that all commercially available devices are equipped with special units for working at low temperatures.

C. Temperature Control and Programming (C-P)

The proper operation of the heat source is ensured by a temperature controller and programmer. This is a double-duty unit; the programmer contains all the switching logic circuit which determines the nature of heat transmission, the cycle and the rate of heating, the temperature holding, and any variations of the aforesaid as well as recycling; the controller actually controls the power supplied to the heater (cooler) which is determined by the selected program. Accordingly, there should be an interaction between the heat source and C-P unit to perform all the tasks mentioned and harmonize the instrumental parameters.

Modern C-P systems have the following characteristics:

1. They can offer linear and other programs within wide and arbitrary temperature limits in many stages.
2. There is very small, practically negligible fluctuation in time, that is, deviation from the prescribed program.
3. They can switch from a dynamic program to an isothermal one without overshot at a predetermined temperature, or, inversely, from an isothermal program immediately to a linear dynamic one.
4. There is negligible fluctuation in an isothermal program.
5. They are suited to control and program heat sources with widely different powers.

In Figure 4 the simple scheme of a C-P unit is shown. In Figure 5 a unit is demonstrated in great detail.[45,46] The operation principle of the latter is as follows: The analog voltage signal produced by thermometer "A" (thermocouple or resistance thermometer situated in the working area of the furnace as near as possible to the sample and modified by a

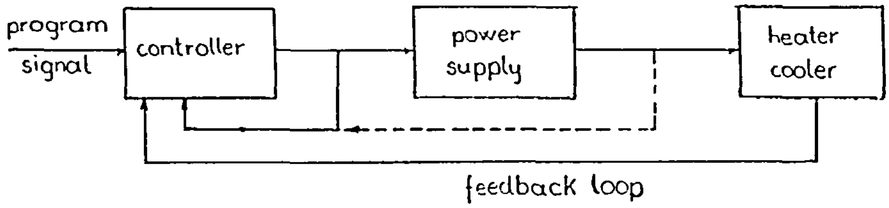


FIGURE 4. Simple scheme of a C-P unit.

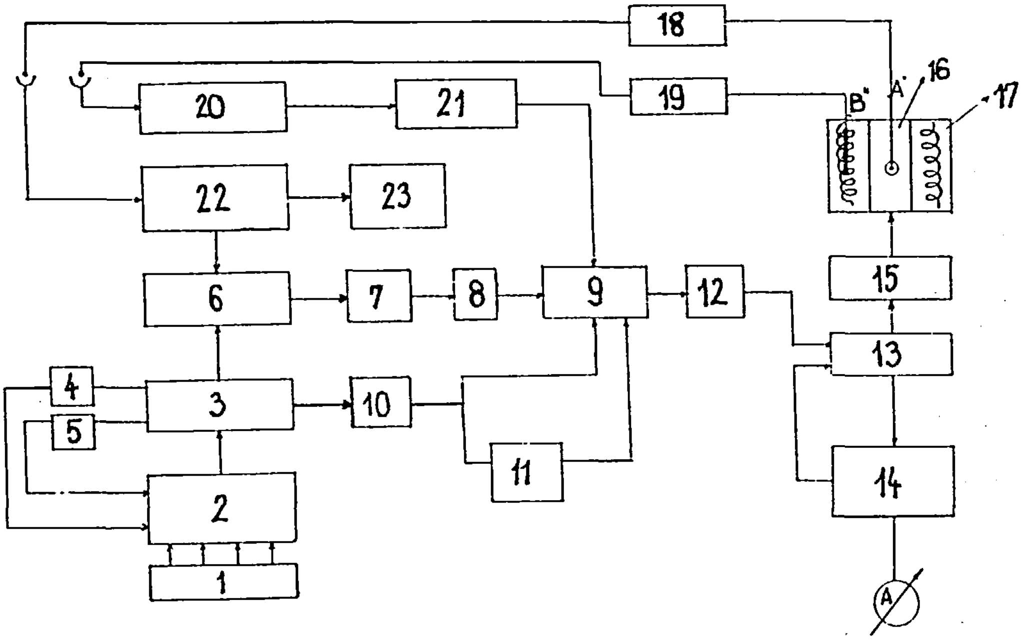


FIGURE 5. A versatile C-P, in detailed form. (1) operating panel, (2) control, controlling unit, (3) program counter, (4) upper limit selecting, (5) lower limit selecting, (6) error detector, (7) D/A converter, (8) P_2 controller, (9) summing amplifier and P_1 controller, (10) D/A converter, (11) ΔT controller, (12) I controller, (13) Thyristor controller, (14) current limiter, (15) power regulator unit, (16) sample space, (17) furnace, (18) cold-junction compensation, (19) cold-junction compensation, (20) amplifier of sensor B, (21) linearizer, (22) digital thermometer linearizer, (23) display. A and B are temperature sensors. (From Gál, S., Muráti, J., Polgár, I., Pungor, E., Sztatisz, J., and Zolnay, J., Hungarian Patent No. 173431, 1978. With permission.)

compensation for cold point) is transmitted to an A/D converter and to a display. The characteristic of the thermometer is linearized electronically. The digital signal is also led to a differentiating circuit where a digital error signal is produced from the difference between the actual signal and that corresponding to the position of the program. The error signal is converted to an analog signal and led to the proportional band controller. The signal produced is one of the control signals of the summing amplifier. A proper choice of the proportional band is one of the prerequisites of the correct operation of the unit. Adjustment of the proportional band expands or contracts the position of the full range over which proportioning of any sort occurs. If the deviation falls outside this range, the controller switches the power supply on and off. In simple devices the band-width is constant, in advanced ones it can be adjusted. For a given furnace it determines the time constant of the initial transient state of the heating and its choice influences the fluctuations in the heating power. Its effect on the ramp command response is shown in Figure 6a.[47] Similarly, it may influence the step degree of overshot in the case of step-command mode and the correctness of the switching from a linear program to a holding program (Figure 6b). In ramp command the effect of proportional band is combined with rate mode, which acts to modify the power applied as a function of the rate at which the temperature is approaching the control point. This can be thought of as modifying and shifting the proportional band as a function of the rate of change of temperature of the band. The use of rate mode has an advantageous effect on the response to a step command too.

Going back to the description of the apparatus, the control signal is compared by an amplifier with the cold-point compensated signal "B" which is produced by the thermocouple being in good contact with the heating element or coil. This signal controls the ignition circuit of the tiristor. Thus the power controller allows the required power to the furnace from the power supply. Overheating of the furnace is prevented by a current-limiting unit. The summary amplifier also incorporates a circuit for linearizing the characteristic of the thermocouple. The time-base divider serves for timing the program counter, the controller for accomplishing the program. The rate of programs is controlled by frequency division, but it can be done mechanically by voltage division or by a computer command. The T signal is produced by thermocouple A in the C-P discussed.

The temperature range covered by C-P depends on the material of the thermocouples used. Thus, in the case of a PtRh-Pt thermocouple the system can be programmed between 300 and 1900 K; in that of NiCr-Ni or chromel-alumel, between 200 and 1500 K. Although a lower accuracy can be ensured by the C-P system described, it can command various furnaces with different power consumption. C-P units constructed fit to a given heat source have generally better performances, but are not of universal applicability.

An important problem connected with C-P units is demonstrated in Figure 6. The temperature of the furnace and that of the sample usually lags with respect to that prescribed by the program. The lag ΔT depends on the thermal inertia of the furnace. The main problem is that ΔT is not constant; there is a transient section at the beginning of heating and at switching from linear program to holding mode. The furnace is sluggish. The time constant τ is the product of the thermal resistance and heat capacity of the furnace. The stationary value of ΔT depends on the rate of heating (β), that is $\Delta T \approx \beta\tau$. At the same time, the large time constant acts also as a filter—that is, it damps the noise caused by the voltage-fluctuations of the programmer. In the case of step function, delays also occur which can be interpreted similarly (Figure 6b). The thermal filtering effect can be replaced by electric, but the lag resumes its original value this way. This lag, however, can practically be eliminated by a suitable combination of the ramp and step function by the summed function (see Figure 6c). This correction can also be applied in the cooling cycle.

Modern thermoanalytical devices can ensure the programs preselected with smaller or greater deviations. Generally the predetermined programs can be ensured from about 100 K to 1900 K. However, deviations of temperature from the prescribed value have to be controlled; the apparatus has to be calibrated by means of samples with known transition temperatures. Deviations from the real value are not additive in the measuring range. Therefore a special T-calibration-correction circuit is incorporated in the C-P circuit depending on the properties of the apparatus. This way the temperature displayed deviates from the real value by a known constant value which can be corrected for by an additive term.

In calorimetric measurements the transition heats are proportional to the corresponding peak areas, to the integral of the curve (see later). However, the caloric sensitivity of

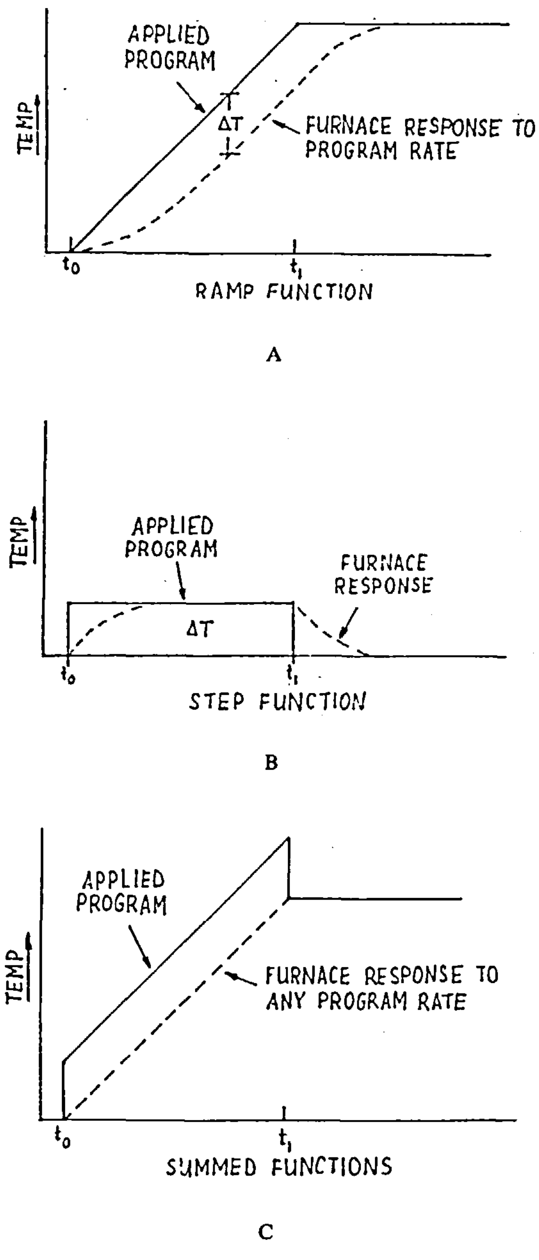


FIGURE 6. The effects of different command functions on the response of a furnace. (From Thermal Analysis Newsletter, Perkin-Elmer Corp., 10, 1972. With permission.)

DTA devices (e.g., mm^2/J) changes with the temperature. The temperature dependence of caloric sensitivity can also be determined experimentally using known amounts of substances with known transition heats. Based on this, sensitivity standardization can be carried out electrically. The signal's shape depends also on the rate of heating, which can be taken into consideration in the adjustment of the program rate. Quasi-isotherm technique has required the construction of a special C-P mode.[48] In the course of the thermogravimetric measurement, the furnace is programmed on the basis of the derivative (DTG) signal to produce a linear program in the heating periods where no transformation or isothermal conditions take place when the weight is changing, ensuring a controlled rate of the process. Using a specially designed sample holder, the so-called labyrinth crucible, partial pressure of the decomposition products can be made equal to atmospheric pressure, i.e., it is constant throughout the process except for a short initial and final period. This means quasi-isobaric conditions as well as the measurement itself can be considered as quasi-equilibrium, since P and T both are practically constant. A quasi-equilibrium TG curve is shown as a function of the time (Figure 7a) and of the temperature (Figure 7b), along with curves obtained under the usual experimental conditions.[49] The operation parameters of C-Ps generally meet the average measuring-technical requirements. In some cases, such as in apparatus for single crystal growing or in high sensitivity calorimeters used for measuring very small enthalpy changes etc., a higher precision is required. A high-performance programming unit has been described by Lewandowski and Randzio.[50] The extremely high sensitivity and stability (about $\pm 10^{-4}$ K) could be achieved by means of a high-performance thermometer. The time constant of the step function is very small.

High-performance C-P is necessary in DTA and DSC measurements; other methods of thermal analysis are generally less exacting in this respect. However, if we want to compare data obtained by different thermal methods, rigorous P-C requirements must be met.

D. Temperature Measurement With Special Regard to Thermal Analysis

Temperature measurement is a central question in thermal analysis. According to the definition of the technique, temperature is the independent variable and in measurements with a linear program may be substituted by time:

$$T = T_0 + \frac{dT}{dt} t \quad \text{or}$$

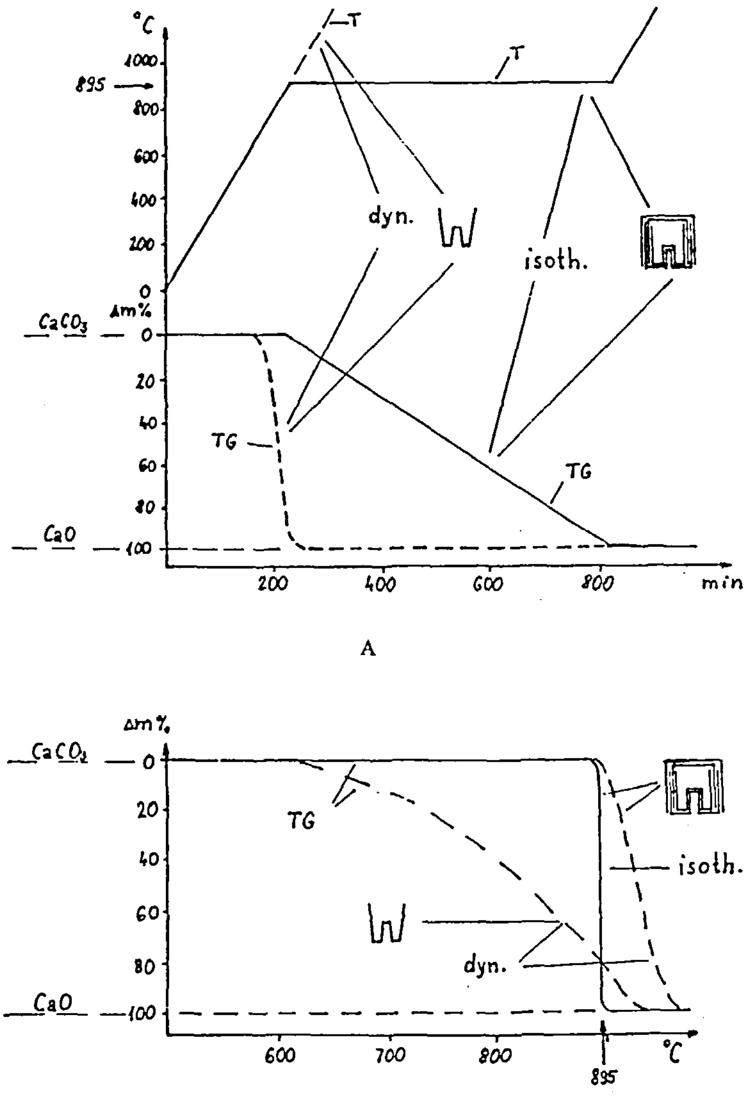
$$T = T_0 + \beta t \tag{5}$$

where $\beta = \frac{dT}{dt}$, the rate of heating, K/min.

From the initial temperature T_0 and the rate of heating, the temperature can be readily calculated for any point of time.

Measurement of the temperature is of basic importance in power-compensation DSC technique as well as in one of the most widely used methods of thermal analysis, DTA, where it is both an independent and dependent variable as in the old method of recording heating and cooling curves. Referring to the previous section, proper C-P operation assumes correct temperature measurement, too. The general requirements associated with temperature measurement in the thermal analysis are as follows:

1. Thermometers should output an analogue signal, preferably an electrical one proportional to the temperature.
2. Their sensitivity (mV/K) should possibly be high, constant over a wide interval, and well reproducible.
3. They should not be sensitive to changes in the environment, must be of stable composition, corrosion-resistant, and characterized by a long lifetime (no aging).
4. They should have a fast time response, must be rugged enough even with a small mass, and should not alter the temperature to be measured appreciably.



A

B

FIGURE 7. Quasi-isothermal, quasi-isobaric TG curves of calcium-carbonate, traced as function of time (a) and temperature (b). Dotted line is the usual dynamic curve. (From Paulik, F. and Paulik, J., *Proc. ICTA Budapest*, Vol. 3, 1974, 785. With permission.)

Considering the temperature range (1 K to 3000 K) used in modern thermoanalysis, one must realize that no single thermometer meets all the requirements in such a broad range. The thermometers mainly used in thermoanalysis are

1. Thermocouples with various composition and combination
2. Semiconductors/thermistors/
3. Electric resistance thermometers
4. Optical pyrometers.

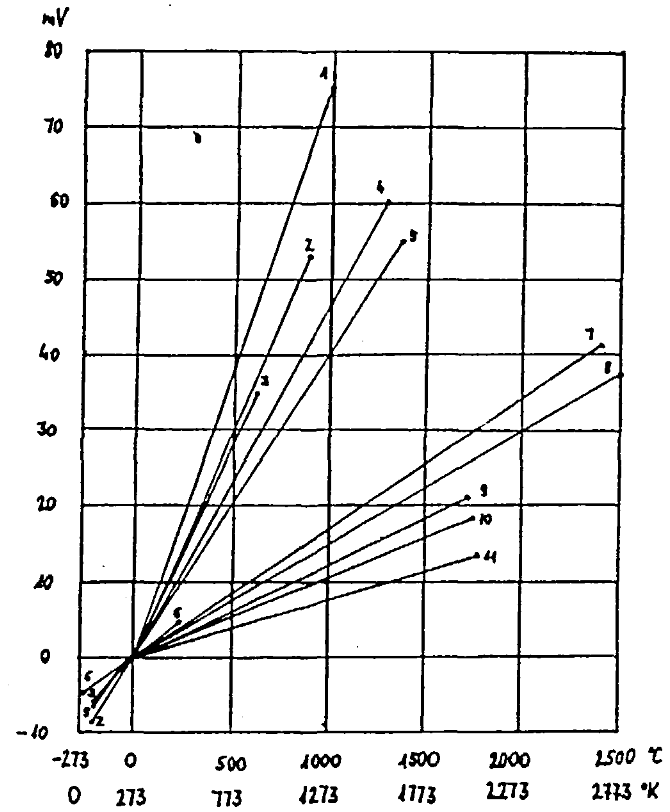


FIGURE 8. Linearized thermovoltage temperature correlations of various thermocouples. (1) NiCr — Const., (2) Fe — Const., (3) Cu — Const., (4) AuPd — Ni, (6) AuFe — Chromel, (7) WRe3 — WRe25, (8) WRe5 — WRe26, (9) PtRh13 — Pt, (10) PtRh10 — Pt, (11) PtRh30 — PtRh6. (From Handbook of Temperature Measurements, Linseis GmbH, Selb, BRG. With permission.)

1. Thermocouples

This is the most widely used thermometer in the thermoanalysis between near 0 K and 1500 K. Above the latter value their application is restricted, requires extreme care, and none of them work above 2300 K. On the theoretical and practical questions of high temperature thermometry an excellent review was published.[51]

Plotted on Figure 8[52] are the thermovoltage-temperature characteristics of some representative, important thermocouples in idealized (linearized) form. The basis of the measurement is the thermoelectric effect. According to its basic relationship, the thermoelectric power, E, is given for homogeneous A and B wires as

$$E = \int_{T_1}^{T_2} /S_A - S_B/dT \qquad (6)$$

where S_A and S_B are the Seebeck coefficients of the respective wires.

The relationship shows that temperature measurement is only possible when a temperature gradient is present, and that the constancy of the S_i is necessary for good reproducibility. According to Barnard[53] the magnitude of S_i depends on the mechanism that scatters the electrons, which is influenced by the chemical composition, the crystal structures, the impurities and by the imperfection of the lattice structure. Consequently, the composition of the wires and its stability are very important factors; recrystallization or contamination may cause a jump in the measured signal or a drift in the sensitivity in an uncontrollable manner and requires repeated calibration. The signal also depends on the form of the temperature gradient.

The usually non-linear characteristics of the thermocouples can be linearized by appropriate processes—nowadays by microprocessors—as was mentioned before. Reproducibility, however, poses a more severe problem: Anderson, in the review cited above, has given seven sources of possible errors, and after a detailed analysis recommended ways for reducing them. A critical comparison of the different thermocouples including their calibration problem is also given there.

The problems of low temperature thermometry were studied by Gmelin[42] in detail. In his opinion, despite the development of the field, very small reproducible thermocouples of extremely small heat capacites are still needed and further temperature measurement under high pressure or high magnetic fields has not yet reached the high standard of technical perfection.

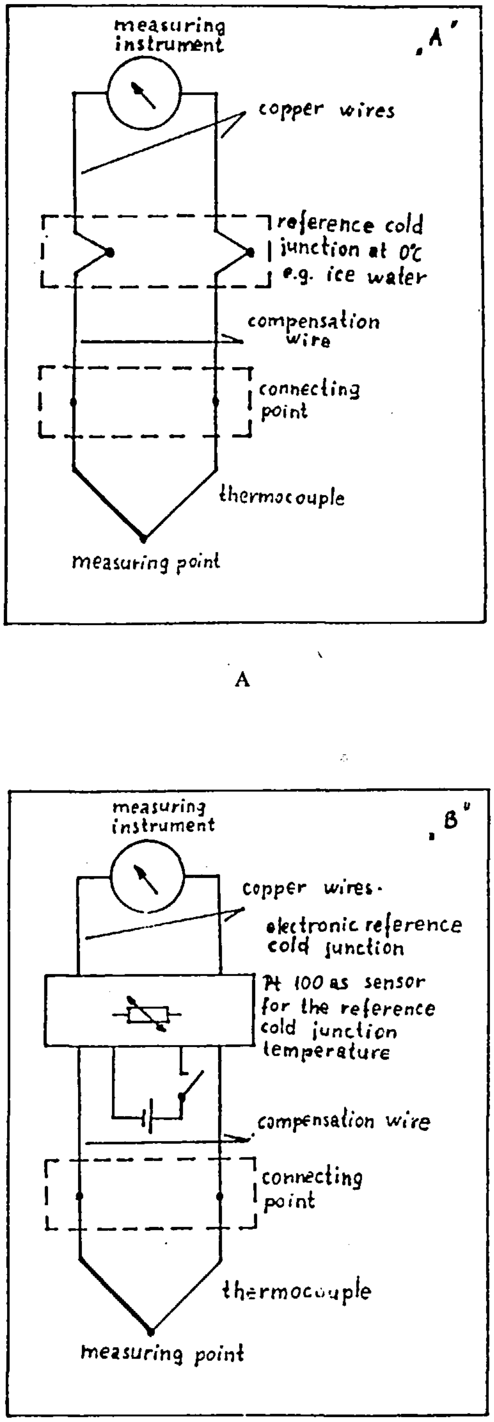
Figure 8 well illustrates the considerable differences in sensitivity of the various thermocouples. This, however, plays no important role today in determining the sensitivity of the thermoanalysis. The relatively small output voltage of the thermocouples can easily be amplified by a factor of 1000, and the sensitivity can further be increased by connecting several couples in parallel. The Calvet calorimeters are, in fact, thermocolumns.

Figure 9 shows the most widely used set up for measuring thermovoltage. The cold junction correction is done either by using melting ice or an electric cold junction for reference. The measuring instrument may serve as a null detector when using compensation techniques, or can be directly followed by an A/D converter, giving a digital readout. Processing the signal is fairly common now and it is usually fed into data collecting systems.

The operation of resistance thermometers is based on the fact that the electric resistance of metals and alloys is a nearly linear function of the temperature in a given interval. The most widely used platinum thermometers are treated in the detailed review of Riddle et al.[54] The resistance of a Pt thermometer as a function of temperature is shown in Figure 10. As can be seen, their high temperature application is rather limited mainly because of sheath and insulation problems. To reduce the oxidation and impurity by migration, Evens and Burns[55] proposed a "bird cage"-type construction for the metal case.

The accuracy of the resistance thermometers considerably exceeds that of the thermocouples. As a further advantage, no cold junction is needed. The change in resistance as a function of temperature is fairly constant, although it can be usefully applied in 100 K steps only. Linearization is generally unnecessary except for high-precision and especially for low-temperature works. One disadvantage is that they are not suited for point temperature measurements. In the power-compensation DSC technique, being of good mechanical strength and easy to fit, they are successfully applied when measuring in small areas. In this case they give the integrated value of the temperature distribution and serve as a heating resistor, too.

The application of thermistors is based on the fact that many semiconductors have a resistance and a logarithmic temperature coefficient exceeding that of the metals by orders of magnitude, thus offering a very sensitive method for temperature measurement. They are mainly used in the static calorimetry. In dynamic thermoanalysis their use is severely limited by the fact that their linear response is limited to about 10 K. A few applications are given in the DSC method from 253 to 473 K by Dosch.[56] Noto et al.[57]



A

B

FIGURE 9. Setup for measuring the thermovoltage. "A" = natural, "B" = electric-compensated cold junction. (From Handbook of Temperature Measurements; Linseis GmbH, Selb. BRG. With permission.)

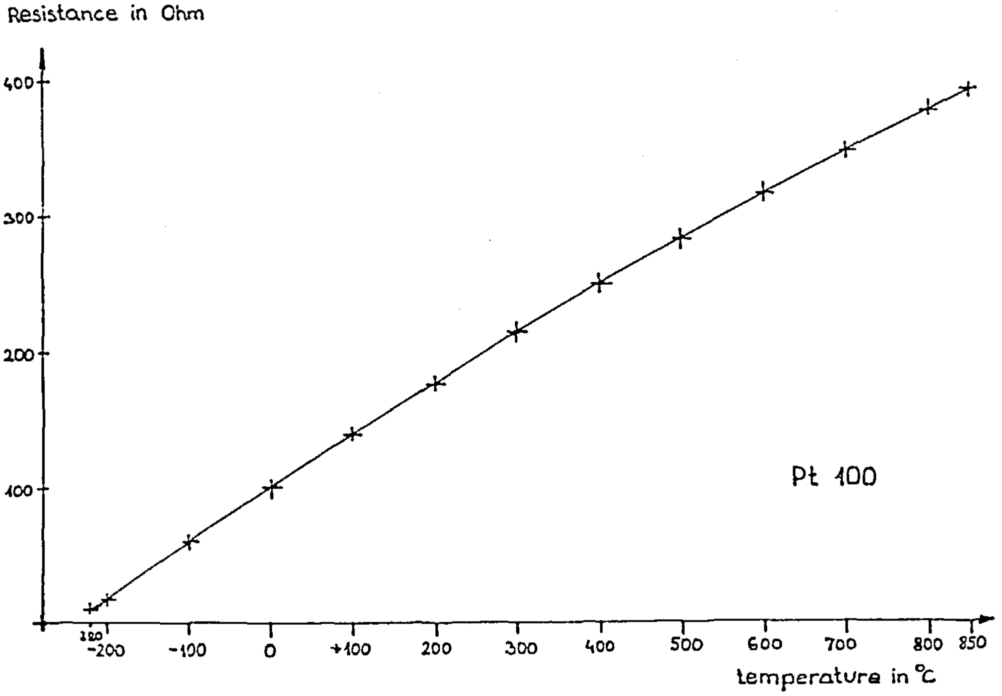


FIGURE 10. Ohmic resistance vs. temperature function of Pt resistance thermometer. (From Handbook of Temperature Measurements, Linseis GmbH, Selb. BRG.)

found the application of thermistors from 1 to 10 K in magnetic field to be advantageous. Til and Johnson[58] used a hybrid coupling of NTC and PTC (negative and positive temperature coefficient) thermistors and achieved better linearity and higher sensitivity.

The optical pyrometers are mainly used in the high temperature region. Their use starts at 1100 K, but their main significance becomes apparent at temperatures higher than 1800 to 1900 K. They work on the principle of black body radiation. The balanced visual pyrometers work around 0.65 μm, but modern photoelectric devices are characterized by a broader range. Most of the laboratory instruments have a strip lamp as a reference source, the brightness temperature of which is determined by calibration. A main feature of the pyrometers used nowadays is that the emission of the heated body is measured by photodiodes, its current being calibrated to temperature by a filament pyrometer. A critical review of the optical pyrometers is given by Anderson.[51] In his opinion, the commercial photoelectric instruments have uncertainties about ±2 K at 1800 K and ±7 K at 3100 K. A good example of their application was given in the paper of Wehner et al.,[59] who investigated the phase diagram of metal-oxide eutectic systems (Figure 11).

Temperature measurement in thermoanalysis is not only a measurement of a certain property in the strict sense, but possesses several special relationships, too.

The absolute calibration of the thermometers is not discussed here. Using primary standards with known transition temperatures *in situ* in the given instrument is the practical solution for calibration in thermal analysis.

Different methods require different precision and accuracy of the temperature measurement or, more precisely, the limits of the compromises are different. For example, in the TG method—where the reliability of the mass change measurement is controlled by the balance and the thermometer cannot touch the sample, but be only in its close proximity—the reproducibility is considered to be more important than the

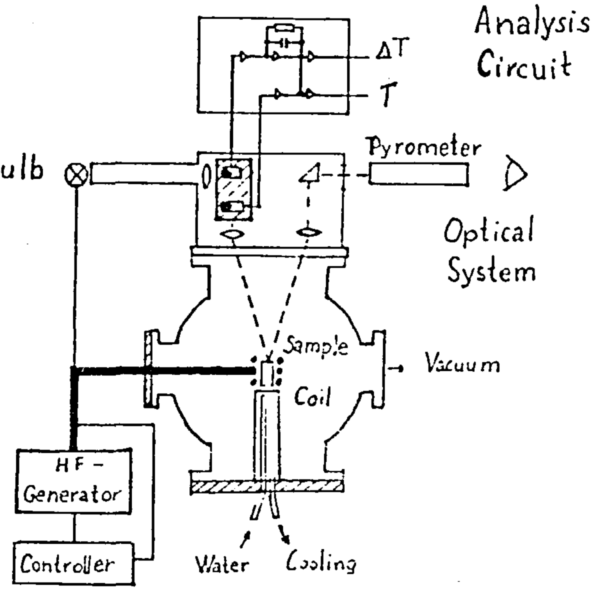


FIGURE 11. Schematic construction of DTA device; temperature measured by optical pyrometer. (From Wehner, F., Henig, E.-Th., and Lukas, H. L., *Thermochim. Acta*, 20, 17, 1977. With permission.)

knowledge of the exact values. In most thermoanalytical measuring techniques the sample and thermometer are separated by a (third) medium. Consequently, the thermometer readings always differ from the true temperature of the sample. It is very important for this difference to be known and, preferably, constant. A temperature gradient exists in the sample itself, the magnitude of which depends on the sample mass, its heat conduction, and properties of products evolved, etc. This gradient may be nearly constant, but when at a given transition, a heat flux is created in the sample, the original temperature distribution is altered. What temperature is characteristic to the process or where to measure it is not obvious. This is one of the most serious problems of data processing. It is generally accepted now that reducing the sample size reduces, but does not eliminate the problem. From the other point of view, small sample masses may create additional difficulties.[15] In dynamic calorimetry, the signal shape may be influenced by the position of the thermometer depending on whether the sample, the block, or the reference temperature is read as a function of the programmed temperature or time (see Figure 12) at various endothermic or exothermic processes.

Measurement of temperature is a problem of several aspects in thermoanalysis and its realization needs a careful consideration.

E. The Atmosphere of the Working Space

The atmosphere of the space of the furnace may have different effects on the processes studied by thermoanalytical methods and may change the signal shapes to be observed. In the interpretation of data, the features of the atmosphere must be taken into account. Reproducible results are obtained only in controlled atmospheres. This explains the ICTA recommendation: upon publishing data the atmosphere composition, pressure, and the flow circumstances must also be specified.[11]

The atmosphere in the thermoanalysis is classified by various aspects. The working

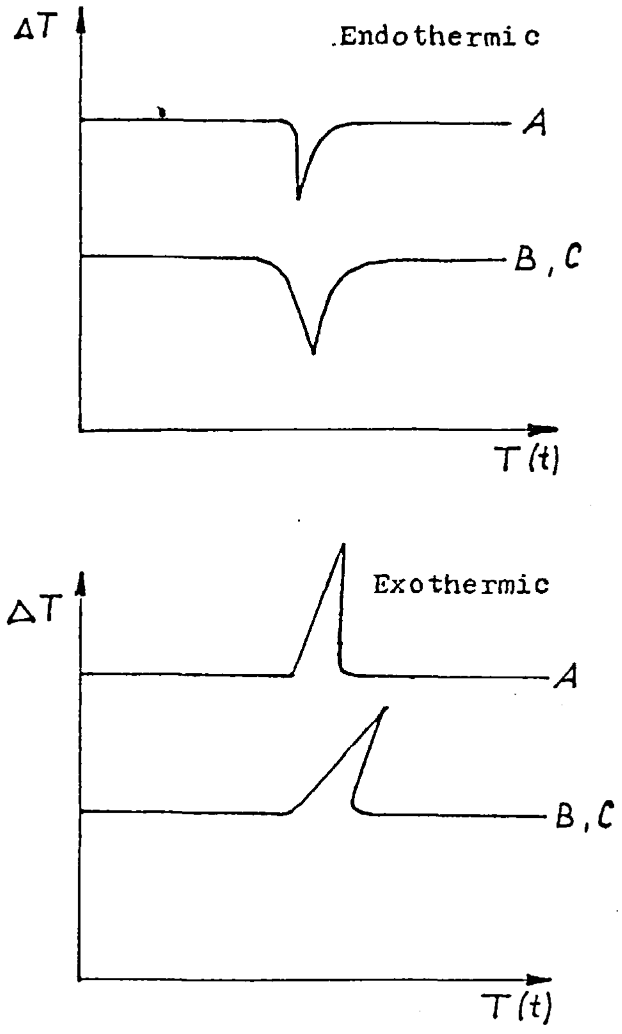


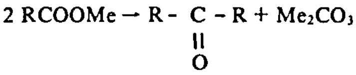
FIGURE 12. The shape of DTA-curves, depending on abscissa parameters. A = temperature measured in the sample; B = temperature measured in the reference or in the block; C = signal traced as function of time.

space may be either inert or reactive depending on the atmosphere composition. The atmosphere is said to be inert if it does not enter into chemical interaction either with the sample or with its decomposition products in the thermal interval scanned. The active atmosphere shows the opposite behavior. Air, oxygen, and halogens may start oxidation reactions, hydrogen may give a reduction step, etc. These mainly solid-gas reactions may be either reversible or irreversible. A simple example is

$$MeO + CO_2 \rightleftharpoons MeCO_3$$

Here the equilibrium constant K is determined by P_{CO_2}. It immediately follows from this that the characteristic temperature of the decomposition of a metal carbonate depends on the partial pressure of carbon dioxide in the working space. It must be stressed that the strict reversibility is not realized with $CaCO_3$ (which is known to be a very simple case) even when using a very thin sample where the heat transport plays no practical role in controlling the process. Incomplete reversibility was explained morphologically by Pokol and Gál.[60] Similarly, the formation and decomposition of crystal hydrates is also irreversible to some extent. It is evident from this that reproducible results are obtained only in atmospheres with strictly controlled partial pressures.

If the decomposition process is wholly irreversible, e.g.,



$$2\,\mathrm{RCOOMe} \rightarrow \mathrm{R}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R} + \mathrm{Me_2CO_3}$$

the fatty acid salts ketolysis is complicated by side reactions and the partial pressure influences the investigated process by changing the rate of diffusion of the products. Earlier, following the recommendation of Garn and Kessler[61] it was quite popular to measure in the so-called self-generated atmosphere in the DTA-TG method. Usually a near-atmospheric partial pressure of the decomposition products was maintained in the neighborhood of the sample soon after decomposition. By this method occasionally well-reproducible results were obtained for decompositions with high transition temperatures but narrow transition interval. Their significance at the time was a little overestimated. The quasi-isobar method of Pauliks[48,49] is similar to this.

Another type of classification is possible according to the pressure used: there are vacuum, atmospheric, and high pressure techniques. The effect of pressure is clearly demonstrated with processes where gaseous phases are concerned. Most importantly, the chosen pressure must be stable (free from fluctuation) since lack of this may cause an error comparable to that caused by nonlinear temperature scanning. The high-pressure modification of a series of thermoanalytical methods is described by Wendlandt et al.[62-64] It is considered to be only partial interest, mainly for gaining a better understanding of the decomposition processes and, in other cases, it is more of a technical virtuosity. The application of high-pressure techniques for polymer chemical studies was demonstrated by Wunderlich and Bopp.[65] As a special case, the mematic liquid crystals can be treated where different orientations occur.[66] Processes accompanied by a small volume change are remarkably affected by very high pressure only.

Some interesting results were obtained by Rouquerol and Rouquerol[67] in the field of high-vacuum studies. The diffusion control of the process can be greatly enhanced this way. The application of high vacuum is one of the basic problems of the simultaneous DTA, TG, and MS techniques: the authors will return to this point in Section VI. A. 2.

It is advisable to change the atmosphere of the working space in all the methods, preferably with a constant flow rate. This forced flow standardizes the temperature distribution of the furnace space, eliminating the uncontrollable convections. When using an inert gas, attention must be paid to its heat-conduction properties as these may change the heat transport, especially at higher temperatures. In the TG method, another correction is necessary to compensate for the buoyant forces depending on the gas density.

The control of the atmosphere is an absolute necessity in up-to-date instruments. For this reason a gas of carefully chosen composition is introduced into the measuring space: preferably prepurified and known pressure in a stable flow pattern. Because of this, all thermoanalytical instruments have accesories for gas production and, purification oxygene, for example, has to be removed from an inert gas. Further accessories include vacuum systems of high capacity, manometers, etc. The high-pressure systems, apart from a few exceptions, are usually homemade. Nowadays the construction of safe electrical and mass-flux inlets and outlets poses no severe technical problems even in high-pressure apparatus.

F. Signal Amplification and Filtering

The measurement of temperature always—and that of other parameters almost always—yields an electrical output signal, commonly a voltage. Nowadays, as was mentioned before, microsampling is quite general and usually the small signal levels are to be amplified and filtered. Description of the electronic processing of the signals is, however, beyond the scope of the present paper.

The amplifiers must have no zero drift. The amplification factor is determined by both the signal amplitude and the recorder sensitivity, and by the S/N ratio and the long-time drift. The usual amplification factors in thermoanalysis fall in the range of 10^2 to $10,^3$ the typical problem being to amplify μV signals to the mV range.

The RC circuit used for smoothing the signal must be designed carefully because changing the time constant may distort the shape of the signal (mostly peak broadening occurs), as was demonstrated by Theall.[68] The task is to chose a condenser to give the optimum performance as a compromise.

As was mentioned previously, the signals coming through the C-P system are conditioned in its circuits while processing of the electrical signals of the other variables may be done by a microcomputer.

G. Methods of Signal Generation in Thermal Analysis

Figure 1 showed the general scheme of the thermoanalytical instruments. The unit denoted there by 5, the sensor-transducer, is that which distinguishes among the various thermoanalytical processes. The sensor is an element by which the value and temperature dependence of a given variable can be measured. From the system-theory point of view, the sample is identified as the signal carrier since all the physical and chemical properties, along with their changes, may induce signals. This signal carries information characteristic to its source. The signal itself is generated by the sample in the sensor or measuring element. The sensors used in thermoanalysis are usually direct, simple signal converters, i.e., they deliver an analog electric signal proportional to the sample condition or its change. The sensor may also be a direct, multiple, or multi-element signal converter. For example, dilatation is accompanied by displacement and this induces a voltage signal in a differential transformer. There are also compensational sensors in use, e.g., electrically compensated null-type balances or thermometers using null indicators, etc.

In thermoanalytical processes, signal converters meet similar requirements as they do in analytical chemistry or other measuring techniques. Sensitivity, selectivity, proper response time, long-time stability, precision, and accuracy are what analytical literature regards as primary characteristics, those secondary being various stability factors towards environmental changes. Most of thermoanalytical sensors meet the sensitivity requirement since, most frequently, extensive properties are to be measured for which the methods available are orders of magnitude more sensitive than those for measuring intensive ones. The methods for measuring the most important intensive parameter—temperature—are satisfactory. Selectivity in the first approximation poses no problems either as, for the selective measuring of the individual properties, appropriate special methods are available. For example, where measuring the overall values of weight change, processes such as simultaneous enthalpy change or changes in the electrical, optical, and in other properties do not interfere. However, external magnetic fields may affect the mass measurement. The shape of the TG (DTG) curve may be altered by the exo- or endothermicity of the given process, the heat transfer properties, etc. Optical or electrical resistance measurements can similarly be affected when a gas-solid heterogeneous system is formed in a decomposition process accompanied by a mass change, but this is usually a technical problem only. In fact, thermoanalysis is not one of the methods yielding "fine-structured" information.

The question of response time of thermoanalytical sensors is a complex one as the observed response time may be the result of the combination of several response times. Summarizing the response time requirements in the DSC technique, Flynn[69] found that three different response times were involved. Matching time response is crucial in simultaneous techniques. The long-time stability is important only for the period of measurement and determines the frequency of the necessary calibrations. Corrosion and aging of certain parts of the instrument can, of course, deteriorate stability. For example, the DTA instruments using a heat-conducting disk are sensitive to the corrosion of the alloy the disk is made of since this leads to a change in the thermal resistance. A similar requirement is the constancy of electrode surface at the measurement of conductivity or that of the sensitivity of the balances used, etc.

Questions of precision and accuracy of thermoanalytical methods as well as the effect of environment will be dealt with further in Section V. B. Experience shows that the main effect in determining the reliability of thermoanalytical data is that of the environment, especially if it acts spontaneously.

H. Thermoanalytical Sensors

DTA in its classic or semiquantitative form is characterized by simultaneous measurement of the temperature differences of the samples and the reference material with thermometers, most frequently thermocouples being embedded in the respective substances. The direct signal, the thermovoltage, is proportional to an intensive parameter, the temperature, but since the difference of the sample and reference temperature is finally measured, this measurement is of extensive type.

The so-called quantitative DTA instruments (or rather DDCs—dynamic differential calorimeters—a name advocated by Šesták[28]) measure heat flux by thermocouples. The appropriate choice of the thermal resistance and the reproducible positioning of the thermocouples allow quantitative, low standard deviation measurements to be performed.

In the power-compensation DSC method, two resistance thermometers form the sensor in a special circuit design driving a definite amount of electrical power into the sample and the reference material necessary to keep them at the same programmed temperature during measurement. To achieve this, a power proportional to the heat of transition is necessary.

The sensor of thermogravimetry is the balance, either a deflection or null-type one, operated in forced equilibrium. The displacement in the first, and the force necessary to maintain the equilibrium position in the second case are converted into electrical signals by various means. Wendlandt[18] has written a good review of the balances used in thermogravimetry.

As thermoanalytical gas sensors, all usual gas analytical instruments can be used, including pressure and volume change-measuring devices, flame ionization detectors (FID), gas-chromatograph (GC), and mass spectrometers (MS), etc. Using a two-step or multistep conversion, the final signal is again an analogue electrical one.

The thermomechanical methods measuring volume change dilatation, contraction, penetration, tensile strength, torsion, etc., use linear variable differential transformer (LVDT) and other converters, finally yielding an analogue voltage signal.

Thermoelectric measurements use impedance, capacitance, and current- and voltage-sensitive detectors.

The sensor of thermomagnetic measurements is the thermobalance, which measures forces created by an external magnetic field as virtual weight changes. A few examples are for ferro-paramagnetic and para-diamagnetic, etc., transitions.

Thermosonimetry uses stethoscopes as sensors with piezoelectric crystal, etc.

I. Data Acquisition and Processing

Thermoanalytical signals are registered as a function of time or temperature on strip charts, XY recorders, or on multichannel recorders in simultaneous techniques. Generally an analogue graphical display is used even when digital data acquisition techniques are applied, i.e., parallel data storage is realized. The reason for this is obvious: starting with an unknown sample, optimal registration and data acquisition circumstances can readily be established and used to optimize the second run when the appearance of the curve is visually observed, simultaneously.

Appropriate attention must be paid to the recorder sensitivity settings to avoid loss of information due to under- or overflow. The paper speed must also correspond to the main task of the measurement (e.g., area measurement or temperature reading precision).

The early stages in the development of thermoanalytical methods were characterized by homemade instruments and primitive data acquisition, e.g., by periodical reading of galvanometers and balances and subsequent plotting of the data as a function of time or temperature read simultaneously. Apart from being time-consuming and wearisome, this method had a considerable source of subjective errors. Rapid development in electronics allowed substantial improvement in data acquisition techniques as well as in the precision and capacity of the instruments. The appearance of line recorders, photoregistration galvanometers, and multichannel recorders was the next step, although redrawing the recorded curves was inevitable at the time. Powerful instruments supplied with appropriate data processing units (linearizer, differentiator, integrator) appeared in the late 1950s and were subsequently followed by digital instruments. This facilitating of data analysis offered a practical basis for investigating basic theoretical relationships. Recently, instruments with digital storage and on-line operating, programmable calculators have appeared in the market. The last few years also witnessed the application of microprocessors. The rapid development of thermoanalysis in the field of data handling and analysis was first summarized by Wendlandt.[70] Most of the systems he reviewed use a passive calculator (computer), interactive organization being rather an exception.

In what follows, only the digital data acquisition and analysis systems will be dealt with in some detail. Their simplified general scheme is given in Figure 13, showing three main functional units, namely data acquisition, data analysis, and display units.

Data acquisition is realized basically in two ways, off-line or on-line. With off-line, the data are stored in a background memory and the measurement and its analysis are separated in space and time. This method has the advantage that the computer is available for other users. On-line methods store the data directly in the computer memory and at the end of the run the results are available. This method is especially justified when process control or feedback is done on the basis of the results.

Depending on whether the signals take analogue or digital form in the given instrument, data acquisition systems are preceded by analogue or digital multiplexers, or sometimes by a combination of both. Fast processes prefer channel-by-channel A/D conversion and subsequent digital data transfer. The A/D converter design may be of importance since fast converters are noise-sensitive while the integrating ones give some noise-filtering effect.

Recently, quite a number of papers have been devoted to the data analysis of thermoanalysis along with its mathematical methods. A few selected examples are listed in the References.[71-75]

Instead of electronic linearization, the thermocouple characteristics can also be precisely linearized by computers; using low-order polynomials for fitting, the noise filtering is considerable. The computer coupled to the DTA-DSC instruments computes

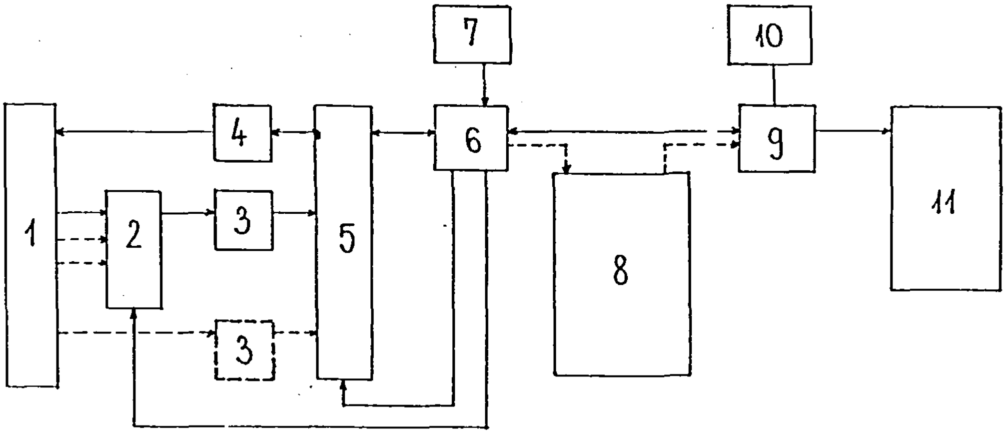


FIGURE 13. Generalized scheme of a data acquisition and processing system used advantageously in thermal analysis. (1) experimental device, (2) analog MPX, (3) A/D converter, (4) D/A converter, (5) digital MPX, (6) interface, (7) clock, (8) temporary storage: punch-tape, punched card, magnetic tape, magnetic disc, (9) computer, (10) software, (11) readout: digital display, printer, plotter, graphic display.

peak area integrals, converts them by appropriate conversion factors, and displays or prints the transition enthalpies in joules per gram. It also computes and displays the transition temperatures. In many cases, useful additional information is obtained by numerical differentiation, although its application needs a careful consideration as possible rounding errors can lead to catastrophic consequences. First or higher derivatives are also used in kinetic measurements.

In the specific heat determination based on the comparative baseline shift measurement, the general equation for temperature dependence can be realized by a computer if necessary.[96] A substantial part of the data analysis in this field is the application of different regression methods. Purity determination[77-80] (see Section V. C.) and thermokinetics (Section V. D.) also need a computerized data analysis owing to the complicated mathematical apparatus used.[84-86] Typically, elaborated algorithms are supplied now with up-to-date measuring systems. The computers greatly assist in modeling the processes and apparatus operation; i.e., possessing the adequate information, the circumstances of the signal generation, the thermospectra evaluation, and the interaction of different parameters are readily established with a precision depending on the approximations used, thus eliminating troublesome and time-consuming experimental work. Apart from offering a better insight into the basic relationships, the computer also facilitates the optimal instrument design.[87]

Summarizing what has been said, it is evident that computer-assisted data acquisition and analysis has recently gained—as in other analytical processes—increasing importance in the field of thermoanalysis. As a future development of the field, it is expected to find an even broader range of application in helping to solve thermokinetic problems and assisting in process control in an interactive way. In the authors' opinion, the temperature programming units can be replaced in the near future by computers. They can also play an active role in stepwise-type purity checks and in the active adjustment of the input rate in the simultaneous techniques (e.g., in TG-MS) and torsional braid analysis.

IV. MULTIPLE THERMOANALYTICAL TECHNIQUES

In the practice of thermoanalysis, the application of multiple methods giving complex information about the sample by measuring several parameters, is fairly common. In this case, the different thermoanalytical methods are used simultaneously in a combined form, organized at various levels of sophistication. To avoid confusion sometimes appearing in literature concerning the organization levels, the ICTA Nomenclature Committee recommended the distinction of three different levels of sophistication:

1. Simultaneous techniques are characterized by the simultaneous measurement of two or more parameters of a given sample (e.g., simultaneous TG-DTA).
2. Coupled simultaneous techniques are characterized by the use of two or more interfaced instruments for measuring a given sample. This can be viewed as a tandem instrument with continuous sampling for the second one (e.g., simultaneous DTA-MS, TG-MS). A hybrid technique of this group and the preceding group is the DTA-TG-MS combination.
3. Discontinuous simultaneous techniques are the combination of two or more coupled techniques for measuring a given sample with periodical sampling for the second and subsequent units. Examples of this group are the DTA-TG instruments from which discrete samples are fed to MS or to GC.

It should be stressed that when using homogeneous materials and performing different measurements separated in space and time the results obtained on individual samples in the same instruments or units using different sensors are well comparable by now. A necessary condition is, of course, that properly calibrated thermometers be used.

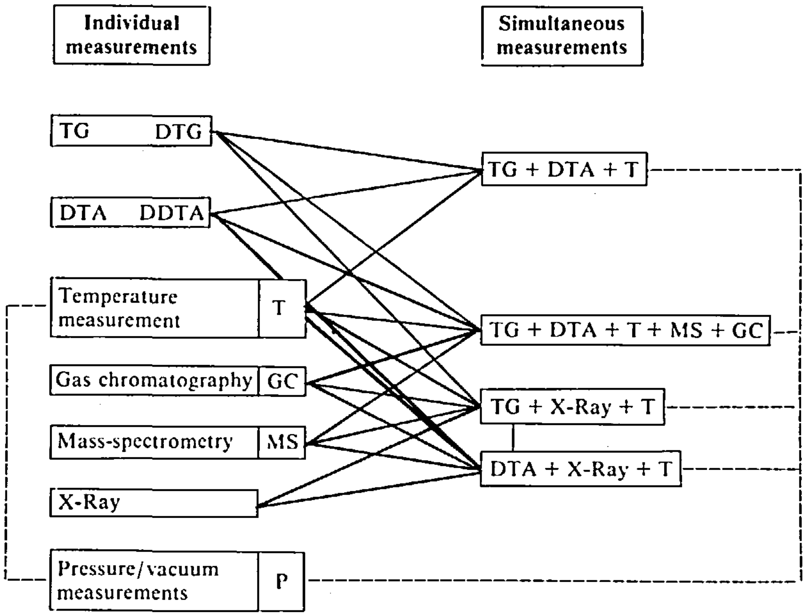
Consequently, simple comparison of individual measurements cannot be considered a multiple method except in a very broad sense.

The application problems of simultaneous techniques are treated in detail in the review of Paulik and Paulik.[88] These authors, besides being pioneers of the field, are still active in its further development. In its original form, their instrument, called Derivatograph, registered DTA, TG, T, and DTG (first derivative of TG) curves on photosensitive paper as a function of time using a single sample.[89] Further development provided it with dilatometric and coupled simultaneous gas analytical units.[90,91] Another variant is supplied with a special adapter for selective water analysis.[92] As was previously mentioned, by modifying the temperature programmer and using a labyrinth-type sample holder, they worked out the quasiequilibrium thermogravimetry, too.

The development of the simultaneous techniques was initiated by previous experience which found the results of the individual measurements rather difficult to compare. This was especially true for the decomposition processes which are known to be very sensitive to environmental effects. The comparison was greatly facilitated by the simultaneous DTA-TG method since, in this case, the environment affects both parameters to be measured in a similar sometimes identical manner. A further advantage is that the DTG curve is obtained by differentiation simultaneously with the TG and DTA signals. The DTA curve is, in fact, a density function while the TG is a distribution function. The two types of curves are mutually defining each other; by integrating the density function, the distribution function is obtained and visa versa. This means that the comparison of DTA and DTG curves — two functions of the same kind — is more reliable than that of the DTA and TG curves. For stoichiometric studies, the TG method is best suited as it gives an absolute mass change. The overlapping of consecutive decomposition steps seems to be more precisely separated, however, by the DTG signals. It should be pointed out that, in accordance with the ICTA Nomenclature Committee, the DTG signal derivation is not a sample measuring technique, but only a mathematical transformation. This can be done either by on-line or off-line computers, or by graphical, numerical, and electronic methods.

The fact that DTA indicates the processes with gross enthalpy change while TG

Table 3
COMBINATIONS OF DIFFERENT METHODS INTO MULTIPLE TECHNIQUES



From Maurer, R. and Wiedemann, H. G., Proc. ICTA Davos, Vol. 1, 1971, 184. With permission.

does only those with mass change gives some selectivity to the methods. Consequently, the mutual correspondence and/or difference offers a basis to determine the type of the given process. Simultaneous techniques are very common now. Table 3 summarizes some possible combinations of the individual methods following Maurer and Wiedemann.[93]

The application of simultaneous techniques requires several construction considerations and always involves compromises. Some of them are the following:

1. Signals of two or more sensors must be generated without mutual distortion or interference. This condition requires a severe compromise in the TG-DTA method. A problem is encountered, for example, in the matching of the thermoelectric sensor to the DTA unit if the two measuring electric circuits are isolated from each other. This may, however, affect the DTA signal shape owing to the change in the thermal resistance.
2. The two sensors must deliver comparable signals, otherwise they must be differently and appropriately amplified.
3. The setup configuration must be optimized for heat transport taking into account the requirements of both units, sometimes contradictory to each other. This sometimes means a very severe restriction: for example, no coupling may exist between the heat transfer disk-type quantitative DTA (a very advantageous method) and the TG instruments. In TG, to avoid the uncontrolled loading of the balance, heat transfer is always done through a gap of air. Even so, the connection of the DTA

signal on the arm of the balance requires extreme care in design. This is advantageous to the TG, but offers a rather limited precision for measuring heat and temperature.

In spite of this, the DTA-TG combination is a source of important additional information, its application being especially advantageous with instruments using semimicro or macro sample amounts. Garn[12] drew attention to the fact that under improper experimental conditions, loss of information may occur.

The coupled simultaneous techniques, either in their continuous or noncontinuous forms, offer special advantages towards a deeper understanding of decomposition processes. DTA-TG measurements for independent, parallel, or considerably overlapping consecutive decomposition processes do not give a well-resolved picture. The study of the individual steps of the decomposition processes is especially informative when selective gas analyzers, preferably MS and GC, are used. Usually the weight change is easy to detect and/or the total heat of decomposition is easy to determine, but these leave several questions unanswered. Has the sample been evaporated, sublimed, or decomposed? If so, what are the decomposition products? What is their relative amount and proportion? Were the processes simultaneous or consecutive? What rate did they have? What characteristic temperature or temperature interval did they occur in? The purpose of measurement is to answer all these questions on a given confidence level.

The following requirements are to be met with the coupled simultaneous techniques for gas analysis if reliable results are wanted:

1. Interface design. Coupling the TG(DTA) and the MS techniques is done in either of the next two ways. The thermoanalytical instrument and the MS may be built together in the same high-vacuum system. A basic fault inherent in this combination is that the operation of the thermoanalytical instrument is restricted to the low pressures in which the given MS operates. The other possibility is a pressure gap between the two systems. This requires the interposition of several complicated pressure-reducing units, valves, capillaries, orifices, etc.
2. The true nature of thermal decomposition processes is sometimes difficult to establish since deciding whether the fragmentation took place as a result of heat or ionization is no trivial task. Usually a low-energy ion source is applied. The advantageous properties of the chemical ionization quadropole MS were pointed out by Baumgartner and Nachbaur.[94] Using a carrier gas they are operational up to 1.10^{-3} bar. A further advantage is the weak fragmentation; intense molecular peaks are obtained.
3. With continuous sampling, only one fragment can be measured accurately by MS. Measuring the whole spectrum is not possible this way. Continuous but less selective detectors (e.g., katharometer, flame ionization detector, etc.) can do the job, but they yield integrated, nonresolved information (e.g., total organic content as a function of temperature). As fast-scanning GCs and MSs are available (quadrupole, TOF) the sampling rate can be adjusted to the scan times and to the rate of the decomposition reaction, e.g., through the appropriate choice of temperature program.
4. If the temperature dependence of the difference decomposition products is also to be determined, the delay between the two measurements must be known and kept low.
5. Attention must be paid to avoid further secondary reactions, adsorptions, and condensations of the primary decomposition products in the unit connecting the two instruments.

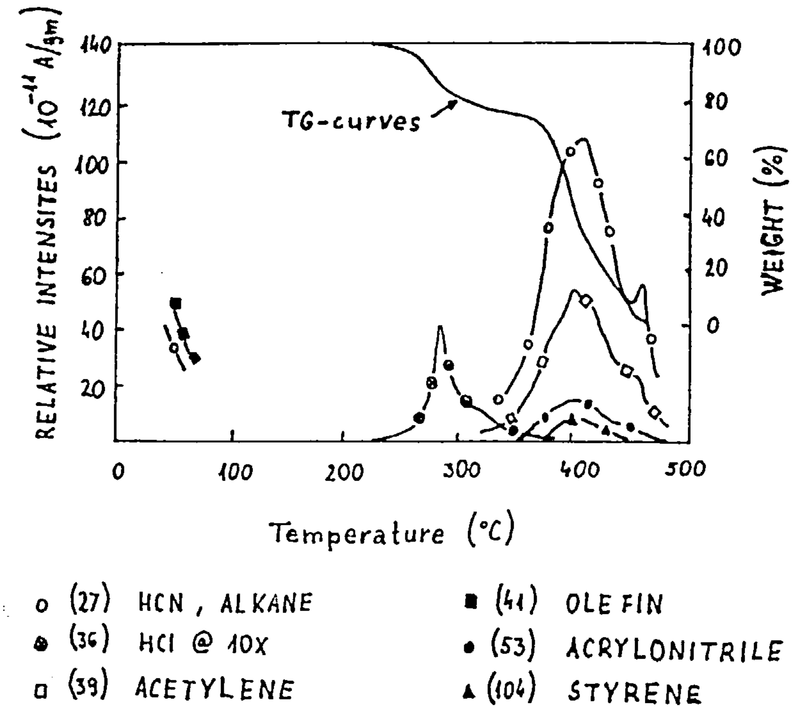


FIGURE 14. Thermal profile of decomposition products of ABS (styrene, butadiene, acrylonitrile) measured by MS and TG. (From Mol, G. J., *Thermochim. Acta*, 10, 259, 1974. With permission.)

Essentially similar considerations apply to the coupling of GCs except, of course, vacuum problems. It is difficult to achieve a fast scan with GCs if the products are of complicated composition; in this case "process chromatographs" are used.

Figure 14 shows an MS spectrum obtained by computer-aided data acquisition and processing.[95]

In discussing simultaneous techniques it must be pointed out that the reasons which originally explained their application are much less valid now. This does not imply that the simultaneous characterization of a single sample from different aspects is unnecessary, but simply that the results, obtained with individual, highly sensitive and precise measuring techniques of today, can be compared with a high confidence. This is guaranteed by the proper operation of the C-P system, the temperature measurement, the uniqueness of heat transport, etc.

The application of small samples yielded substantial improvements. In 0.1 to 1-g samples, 10 to 30 K temperature gradients may exist at a transition. Moreover, in the practice of the authors, a heat-initiated organic substitution reaction was encountered where the temperature of a 0.2-g sample exceeded that of its environment by as much as 120 to 150 K. Milligram sample sizes may reduce this value by at least an order of magnitude. Similarly, the diffusion control is much less pronounced when using small samples and the pressure is easier to regulate. This way it is possible to find the optimum in precision, sensitivity, and signal resolution for a given sample. Approximating the ideal state as being free from experimental distortion, this assures a reasonable comparability of the results of individual measurements. Similarly, microsampling simultaneous techniques are giving more definite results, hence less severe compromises are needed. In many cases, as was indicated before, simultaneous techniques are of great significance; neither their under- nor overestimation is justified.

V. ANALYTICAL INFORMATION OBTAINED BY THERMAL ANALYSIS

A. Analytical Information on Qualitative Level

Various methods of thermoanalysis are used to obtain analytical information, in the strict sense of the word, by analytical chemists. The majority of monographs and papers published in the field report such studies.

The analytical information obtained can be summarized as follows:

1. Qualitative data for sample identification and characterization by investigating its thermal behavior.
2. Quantitative results for heats of transition and reaction coordinates for processes with weight change, etc.
3. Information concerning the fine structure and composition of different phases.
4. Purity check.

Another aspect is to study the thermal behavior and reactions of a given material from the technological point of view, i.e., modeling its large-scale production, processing, and application. On the other hand, a significant amount of theoretical and experimental work appears in the literature oriented towards thermodynamical and kinetic aspects.

Thermoanalysis, the beginnings of which can be traced back to the end of the last century was for a long time restricted to collecting empirical data. Mainly studied was the thermal behavior of inorganic compounds, minerals, ores, and metals. A later period was characterized by phase equilibrium studies. The first experimental method was the classic DTA technique, followed by TG, the others having been developed in the 1940s and 1950s. Writing the complete history of thermal analysis would be interesting, although attempts have already been made in particular fields.[8-40,96-98]

Every substance can qualitatively be characterized by the temperatures at which its polymorphous or phase transition, decomposition, etc., occurs. A so-called "thermospectrum" can be obtained for every substance by the DTA-DSC method; on a theoretical base, these can be expected to be of fingerprint nature. Displayed in Figure 15 is the thermospectrum of a hypothetical substance. Similarly, the thermospectrum of substances suffering weight change can be obtained with the characteristic parameters being the temperature of the onset of decomposition and the weight change. Other thermoanalytical methods also give data characteristic to the quality of the substances by indicating temperatures where an abrupt change is occuring in some property.

Upon the analytical utilization of thermoanalysis the following questions emerge:

1. How reliable are the data; what is their accuracy and precision?
2. To what extent are they characteristic and specific to the given molecule?
3. Is there a matrix, instrumental, or environmental interaction going on; if so, does it yield additional information or rather distort the results?

It should be repeatedly emphasized that temperature mesurement is a crucial point. On considering its precision, two different groups are to be considered; one, where there is an air gap between the sample and the thermometer for construction reasons, and the second where a thermometer in well-defined heat-transfer contact with the sample is used. In the first case a time delay, characterized by different time constants, always exists; moreover, deviations from the programmed temperature occur at endo- or exothermic processes in an uncontrolled way. The measured (displayed) temperature may differ from the transition or sample temperature depending also on the heating rate.

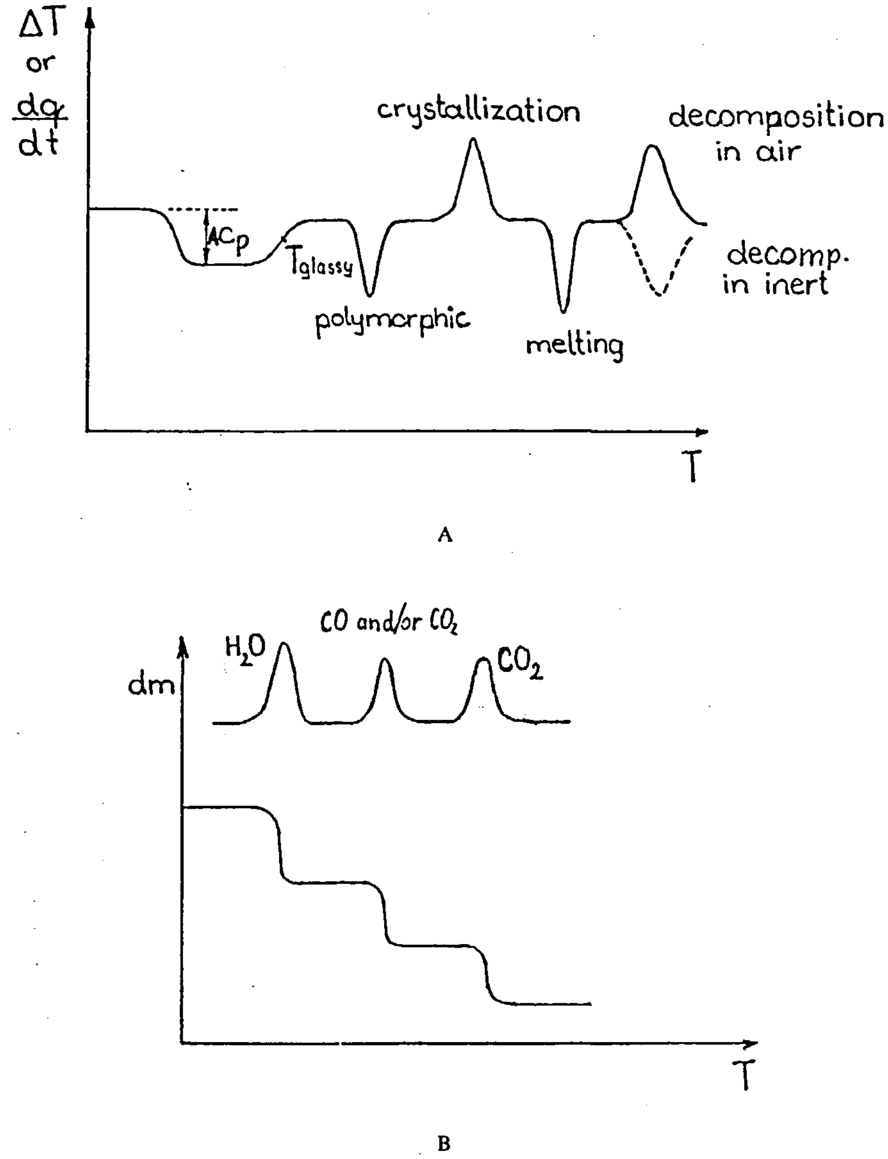


FIGURE 15. An idealized DTA "thermospectrum" (A) and TG-EGA curves for calcium-oxalate-hydrate (B).

Modern instruments correct for this by using internal calibration procedures.[99] In an instrument with good heat transfer, the deviation of the real and the displayed temperature is minimal.

The measurement of temperature, after proper calibration, can be used for identification and characterization of the substances; keeping in mind, however, that the thermospectrum is poorly intensive to get fine structure information. It is far from being as specific as the IR or NMR spectrum but, rather, comparable to the UV-VIS spectrometry or to GC.

It is generally true that thermoanalytical measurements of processes with mass transfer yield better precision for the mass change than for the characteristic temperature of transition. The relative error in measuring a thermogravimetrical step is determined by the balance sensitivity, sample size, and process stoichiometry. High-precision measurements require the calibration of the balance, taking into account the buoyant force along with its temperature dependence. A further experimental task is the elimination of the undesirable, uncontrolled convective flows from the working space. Several nonoverlapping processes can be measured without interference. For processes with overlapping weight changes, precise results are only obtained for the final weight constancy. The extent of overlap determines the precision of the deteermination of the individual processes. Different curve-resolving techniques are to be applied with appropriate caution. The strictly parallel reactions, of course, do not give a resolved signal, as the subsequent gas-phase reactions of decomposition products cannot be followed by TG either. TG thermospectra are far more informative when supplied with "thermo gas spectra." The measurement of quantitative parameters, especially in complicated multicomponent systems, requires extreme care, but in the best case the concentrations of all the components formed can selectively be measured by EGA after proper calibration. A coherent picture can be obtained for the decomposition reaction. On determining the characteristic temperatures, the interface dead volume and the time response of the gas detector may cause problems. With quantitative gas analyses two types of error estimates are to be made: one involves the error of the gas analytical method itself and the other is associated with the effectivity of the product gas transport. The extent of these can be estimated by measuring samples with known composition and decomposition processes.

The application of thermoanalytical methods to sample identification and characterization is subject to a two-purpose consideration. As processes initiated by heat are encountered, these requirements are met as the study of the thermal behavior on course to a reaction with a specific reagent, namely heat. Probably there is no pair of substances behaving identically, in all aspects, upon thermal treatment. This fact, however, cannot always be fully utilized since most thermoanalytical methods have a limited resolution, their sensitivity being insufficient for studying low-energy transitions. This strongly limits their application in discriminating between samples with similar properties. Beyond certain limits other methods are called for. These problems are especially well-pronounced in thermoanalytical identification and characterization of multicomponent systems. A few examples are known, however, when their application is very economic. Preference is made here to water content analysis, where the adsorbed crystal and so-called structure water content can be selectively and quantitatively measured by the stepwise thermal dehydration, using one sample and run. It also offers unique possibilities for measuring organic content in inorganic materials, specific heat (heat capacity), and some special properties (glassy state, degree of crystallization) of several groups of compounds, mainly polymers.

In conclusion, thermal methods offer a unique chance for studying heat-induced changes in the sample. In the so-called qualitative and quantitative analysis, their application, apart from special cases, is rather limited, however.

It is clear from what has been said above that the results obtained by thermoanalytical methods are very sensitive to instrumental and environmental interactions. Probably this is the reason why the results of the different laboratories obtained on identical samples by identical methods are rather difficult to compare. The most important effects are

1. Those arising from sample parameters and features
2. The interaction with the atmosphere
3. The operational parameters of the instrument

Effects caused by sample features can be approximated as characteristic effects of chemically homogeneous, or heterogeneous samples.

The reproducibility of data obtained for samples with homogeneous composition may dramatically be influenced by the thermal history of the sample. Apart from *a priori* memory effects, the different behavior of the same sample after several measuring cycles is to be considered. It is quite common that the first run gives a thermospectrum different from that obtained in subsequent runs; even these may differ from each other with different cooling rates. These differences become apparent not only in the DTA-DSC curves, but also in thermomechanical, thermoelectrical, and X-ray diffraction measurements, etc. Thermal history generally plays no role in processes accompanied by decomposition.

Irradiation may, however, change the transition temperatures and gas analytical results, etc. In this case, the original substance is no longer dealt with, but a more or less degraded one.

Chemically homogeneous samples, apart from single crystals, cannot be considered homogeneous from a morphological point of view. The crystal structure is always imperfect and possesses dislocations. An illustrative example of the dependence on the phase fine structure was observed by the present authors[100] as a thermoelectrical anomaly of smectic liquid crystal structures of certain fatty acid salts. Thermoanalytical behavior of homogeneous samples is substantially influenced by their specific surface area; porosity and average grain size may affect the DTA signal shape. Grinding may result in such surface deformation (e.g., quartz) which may seriously alter the thermospectra. Solid-gas reactions are especially sensitive to the specific surface area. By careful experimental design, however, the specific surface area of the residue can be controlled.[101,102] Heat-transport properties of the sample are not negligible either, as they are determined by the average grain size and apparent average density. Specific heat (heat capacity) determines the baseline shift of modern DTA-DSC instruments in a well-determined manner, giving rise to the most frequent and economic way for quantitative determination for C-P (see Section III.C.).

In order to analyze thermoanalytical data obtained on heterogeneous samples, whether interactions between the components and the decomposition products can be neglected or not must be known; more precisely, whether the resolution of the given measuring technique is sufficient for identifying a given interaction. The sample dilution technique, mainly used with the classic DTA method, was considered to be free from from interaction. Suitably the reference material, most frequently aluminium oxide, was used as diluent; in the first approximation this really could have been considered as inert. (The purpose of dilution was to achieve identical thermophysical properties in the two measuring cells.) Many examples showed, however, that the adsorptive characteristics of samples with high specific surface area changed the gas transport and consequently the registered signal parameters considerably. Now, DTA-DSC instruments use empty cells as reference. In practice, however, multicomponent systems can be examined under such circumstances that the main component behaves as "inert" in a given temperature interval (i.e., measuring the water content in solids, etc.). A special study of multicomponent systems is done on DTA-DSC instruments for checking purity. This involves the shape analysis of the registered curve and is based on melting-point depression. This process, because of its great importance, is described separately in Section V. C. It is only indicated here that thermoanalytical curve shapes can drastically be changed even by the presence of small impurity amounts (Figure 16).[403]

This forms the basis of the experimental determination of phase diagrams which are also of great practical importance. On the theoretical and experimental problems of phase transitions, specially those of the DTA studies of binary and multicomponent systems, Gutt and Majumdar[104] gave a detailed review. Franzosini[105] described the

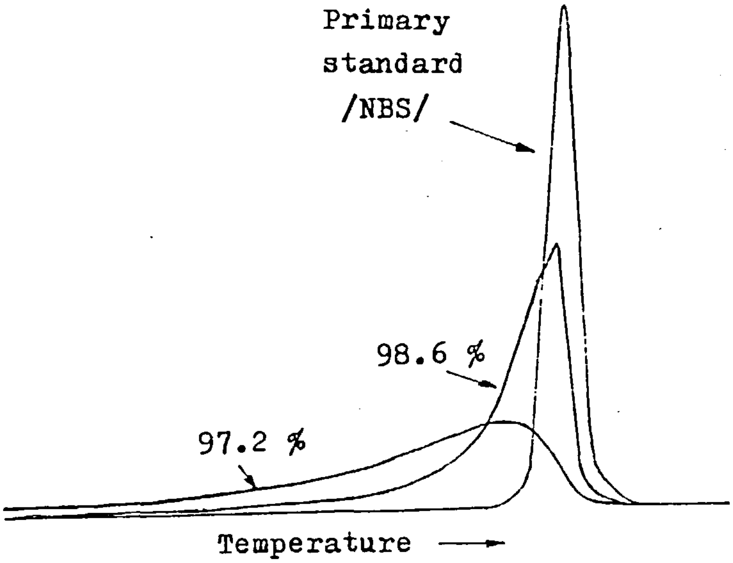


FIGURE 16. Effect of purity on DSC melting peak shapes of benzoicacid. (From Thermal Analysis Newsletter, No. 5, Perkin-Elmer Corp. With permission.)

phase diagrams of hundreds of organic and inorganic compounds in a systematic manner.

Apart from physical and physicochemical interactions, sometimes heat-initiated chemical reactions may occur among the components, i.e., carbonates and quartz, or calcium carbonate and sulphur dioxide may react, this latter should be the decomposition product of a sulfate. Hydropyrolitic reactions may also occur as water released from the sample reacts with an alkali sulfide sample to produce hydrogen sulfide, etc.

The influence of atmospheric parameters has already been dealt with in section III.E. Some of the effects of instrumental parameters will be summarized below.

The effect of sample holders depends on their geometry, on their being closed or open, and on their material. The connected problems have been dealt with in detail in monographs. Without offering detailed explanations, the effect of the geometry of the sample holder is demonstrated in Figure 17. One of the most important instrument parameters is the rate of heating and cooling. For reasons of economic point of view, the heating rates are usually chosen high. However, there are other factors to be considered when choosing the appropriate rate. The heat flux, which is proportional to the rate of heating, should not limit the rate of transformation to be investigated. As the rate increases, an increasing temperature gradient develops within the sample, its magnitude depending also on the thermal resistance of the sample and, in addition to this, the time lag between the block and sample also increases. It is also important that the deviation from the equilibrium state in any process depends also on the heating rate, having the consequence that the characteristic onset temperature of a transformation is shifted to higher temperatures, except when the temperature is measured in the sample and the curve is taken as function of the temperature of samples.

In DTA and DSC measurements the sensitivity does not depend on the rate of heating within reasonable limits. It has been found in modelling studies that the peak area is not affected by the rate of heating, but the leading edge of the peak becomes steeper with increasing heating rates.[88]

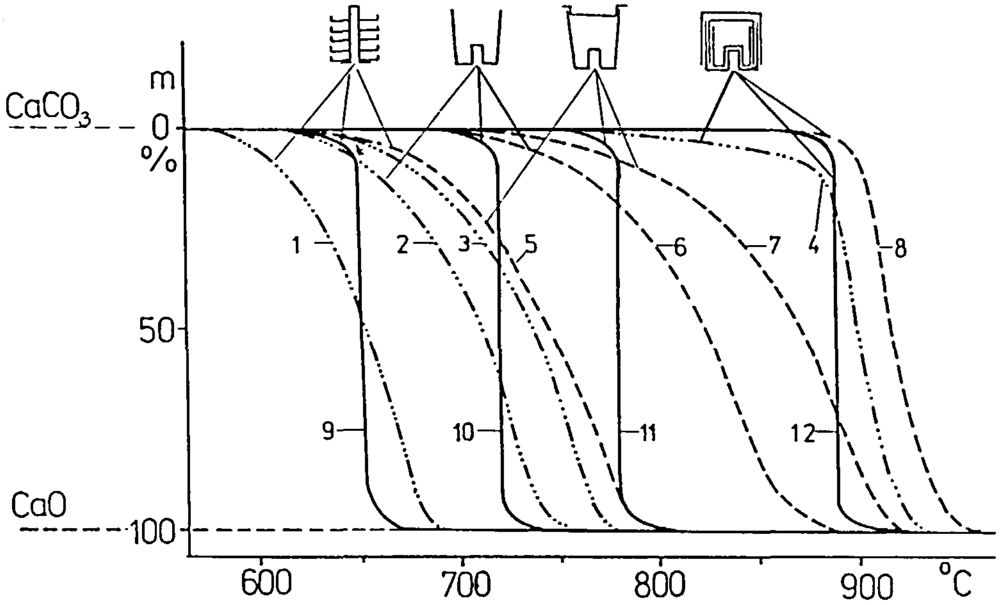


FIGURE 17. Effect of the shape of sample holders on the TG-curves of calcium-carbonate. 1-4, in inert dynamic atmosphere; 5-8, in carbon-dioxide atmosphere; 9-12, under quasi-isothermal conditions. (From Paulik, F. and Paulik, J., *Proc. ICTA Budapest*, Vol. 3, 1974, 785. With permission.)

The dependence of the signals on the heating rate has been described by Baxter[106] for DTA and by O'Neil[107] for power-compensation DSC as follows:

$$\frac{dH}{dT} = \frac{T_S - T_R}{R_D} + (C_s - C_r)\beta + C_s \frac{d(T_s - T_r)}{dt} \frac{R_D + R_C}{R_D} \qquad (7)$$

$$\frac{dh}{dt} = -\frac{dq}{dt} + (C_s - C_r)\beta + RC_s \frac{d^2q}{dt^2} \qquad (8)$$

From these equations it is clear that the term describing the baseline displacement is proportional to the rate of heating (β), too. The rate of heating has no significant effect on the temperature characteristic of polymorphous transformations and melting. However, for phase transformations characterized by overcooling and for polymorphic ones having a relatively long relaxation time, there may be a marked difference depending on the rate of heating or cooling.

The dependence of the characteristic temperatures may significantly differ if a mass transfer is taking place. In this case change is greater, although it is not strictly linear, as the reversibility and the rate of the decomposition reaction also play a role. This accounts for the different effects of the rate of heating on the three decomposition steps of calcium oxalate monohydrate (see Figure 18).[108] It is also obvious that the heat resistance of the different parts of the apparatus — in the case of DTA, the heat-conducting disc (R_D) and so-called contact resistance (R_C), due to the air gap between the disk and the sample holder — may affect the shape of the signal.

The shape and intensity of the signal may be modified remarkably by atmosphere. Equations 7 and 8 do not account for any heat transfer through the atmosphere in the furnace in addition to conduction, when the properties of the atmosphere may influence the signal. Thus, e.g., in hydrogen atmosphere, the peak area is smaller than in nitrogen under otherwise unchanged conditions.

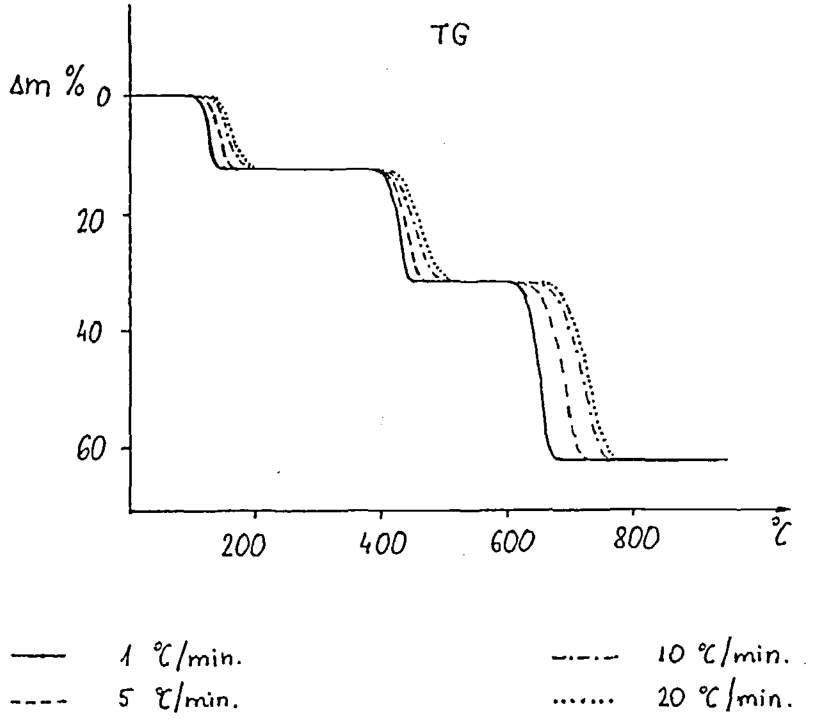


FIGURE 18. Effect of the heating rate on the three decomposition steps of $CaC_2O_4 \cdot H_2O$. (From Gál, S. and Meisel, T., unpublished results.)

In Figure 19 the different effect of thermal resistance on the intensity and leading edge of the signal is shown as given by Gray[109] which is indicative of the essential difference in the operation of DTA and DSC devices, too. The actual values of resistances also affect the time constant of the signal return to the baseline. Consequently the resolution is influenced from two different sides in these methods. Other methods of thermal analysis are generally not as sensitive to the design with respect to heat transfer. Summing up, in constructing an apparatus, speed of operation is one of the primary requirements which can be ensured by using a furnace with small thermal inertia, a properly operating C-P optimum conditions of heat transfer, small sample weight, and a proper optimum combination of these parameters.

B. Quantitative (Caloric) Data

It was already realized in the early state of development of the method that peak areas on DTA curves are proportional to the molar heat of transformation and the number of moles of substance. However, due to the uncertain and not very well-controlled operation of the instruments, the data yielded could only be considered as semiquantitative. The reasons have already been dealt with; the deviations are due to differences in instrumental and measurement parameters. Instruments developed during the past 10 to 15 years, however, enable reliable quantitative data to be obtained. The conditions for the application of dynamic calorimetry for the purposes of quantitative analysis have been summarized by Šesták et al.[110] as follows:

1. The working conditions of the apparatus must be constant when the temperature increases linearly.
2. The physical properties of the sample and the reference must be as close as possible.

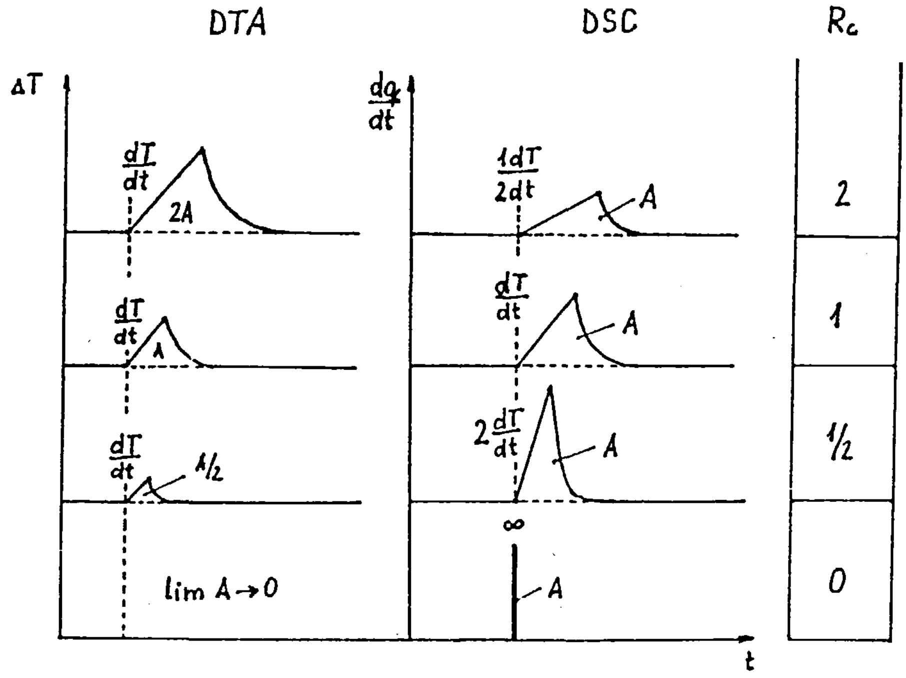


FIGURE 19. Effect of the contact thermal resistance (R_c) between sample holders and discs on the shape and sensitivity of DTA and DSC traces respectively. (From Gray, A. P., in *Analytic Calorimetry*, Vol. I, Porter, R. S. and Johnson, J. F., Plenum Press, New York, 1968. With permission.)

3. The baseline must be determined correctly. (This is, however, rather difficult to carry out in the case of asymmetric peaks where the specific heat of the substance before and after the transformation is markedly different.)
4. The apparatus must be calibrated carefully in the working range using compounds with known transformation heats.

It is noteworthy that a characteristic feature of power-compensation DSC is that its calibration factor is a real constant not depending on the temperature. This means that it is sufficient to calibrate with one substance. In instruments based on measurement of temperature or heat flux differences the calibration factor changes with the temperature; that is, the sensitivity of caloric measurements is temperature dependent (Figure 20). This function can be eliminated by properly designed compensating circuits. It should be pointed out that in addition to this, the factor also depends on instrumental parameters. For this reason a separate calibration has to be made for every single instrument. In spite of this, derived caloric quantities exhibit a substantial scattering, as shown by data in Table 4.[111-115]

As pointed out by Šesták,[110] calibration with standard substances is unusually uncertain and much better accuracy could be achieved by using joule heat. This calibration procedure can be accomplished in various ways: using a micro-heater which requires double calibration, a wattmeter, or a separate heat-impulse generator.[116] The apparatus is shown in Figure 21 along with the simulated DTA signals produced by it at different temperatures, and a comparison of the two calibration procedures is taken. The deviation between the results yielded by the two calibration procedures is due to the uncertainty of literature data and to nonuniformity in the standard measurement

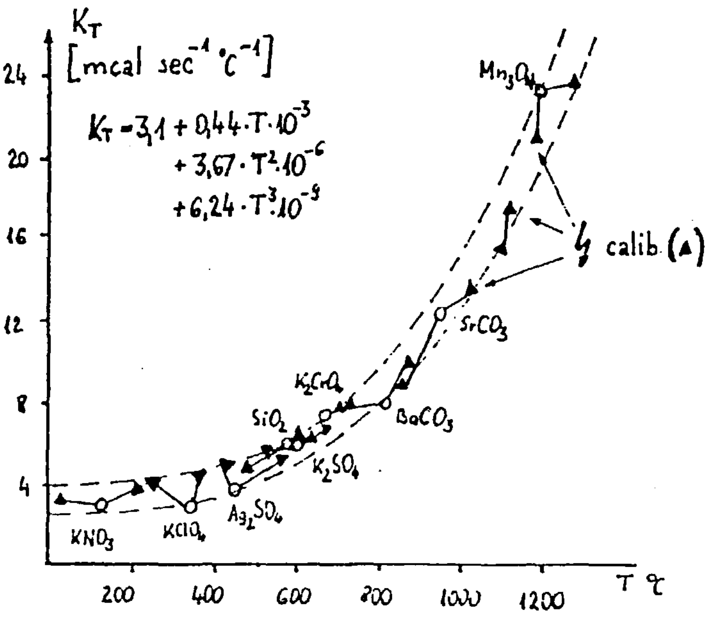


FIGURE 20. K/T/ versus T diagram, calculated by means of electric calibration (full triangles) and standard compounds (empty circles). (From Šesták, J., Holba, P., and Lombardi, G., *Ann. Chim. (Rome)*, 67, 73, 1977. With permission.)

Table 4
ENTHALPIES OF TRANSFORMATION (kcal/mol^{-1}) FOR ICTA TEMPERATURE STANDARDS

Sample	Ref. 111	Ref. 112	Ref. 113	Ref. 114	Ref. 115
KNO_3	1.30	1.30	—	1.34	1.20
$KClO_4$	3.29	3.29	3.3	4.43	3.39
Ag_2SO_4	1.90	3.75	4.2	4.44	3.73
SiO_2 (quartz)	0.15	0.18	0.19	0.14	0.095
K_2SO_4	1.94	2.14	2.1	2.08	1.35
K_2CrO_4	2.45	2.45	1.8	2.25	1.65
$BaCO_3$	4.52	4.52	4.3	5.29	4.48
$SrCO_3$	4.70	4.70	4.1	4.42	—

conditions with respect to the volume, internal structure of the sample, etc. The authors of this review have some disagreement with Svoboda and Šesták[116] as to the probable uncertainty caused by air environment. The systematic errors of calibration have been discussed by Sturm.[117]

The other fundamental question of quantitative evaluation is the accuracy in setting out the baseline. For this there is an ICTA recommendation (see Figure 22). In simple cases this is a reliable approximation; however, if an appreciable baseline displacement occurs due to changes in the specific heat, significant errors may arise. Marking out the baseline can be made rather difficult due to instrumental noise, by contaminants of sample which alter the shape of the curve, and by changes in the specific heat. As has been pointed out by Heuvel[118] in work nowadays considered classical, the baseline changes in a

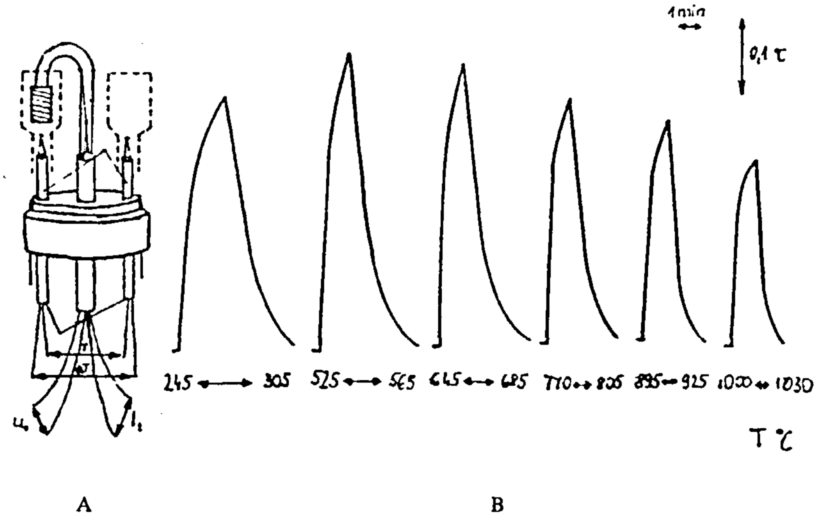


FIGURE 21. DTA measuring system (A) with the accessory for transmitting known electric impulses in the reference block and the artificial DTA peaks (B) obtained with a constant heat input of 1 cal, "generated" by means of an impulse generator. (From Svoboda, H. and Šesták, J., *Proc. ICTA Budapest*, Vol. 3, 1974, 725. With permission.)

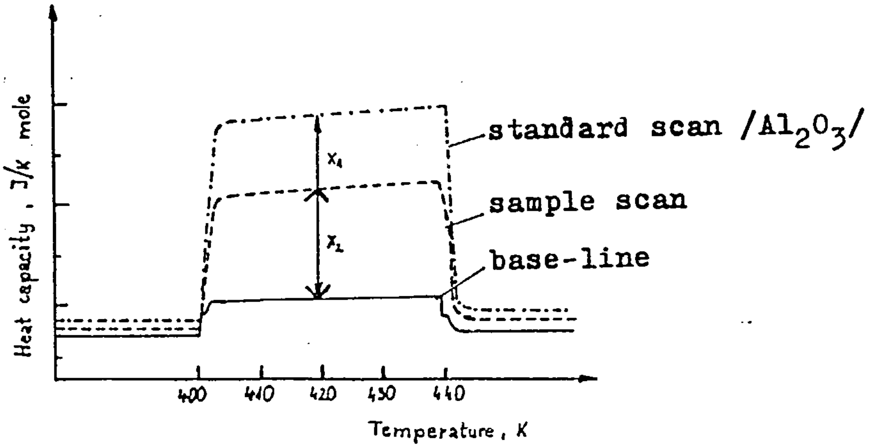


FIGURE 22. DTA, DSC-experiment for the determination of specific heat of samples. x_1 = baseline displacement in the case of a sapphire standard, sample weight, and specific heat are known; x_2 = baseline displacement in the case of measured amount of sample. C_p is not known. (From Mackenzie, R. C., *Proc. ICTA Kyoto*, 1977, 561. With permission.)

rather complicated way during transformations, and any practical marking out means only a partial error compensation. The measurement of peak areas is carried out by techniques usual in the practice of analytical chemistry; namely by weighing, planimetry, and graphical or electronic integration with baseline correction. Numerical integration as well as digital display or printing of transformation heats have become widely used recently.

In addition to the determination of transformation heats, the main field of application of dynamic calorimeters is the determination of specific heats and temperature

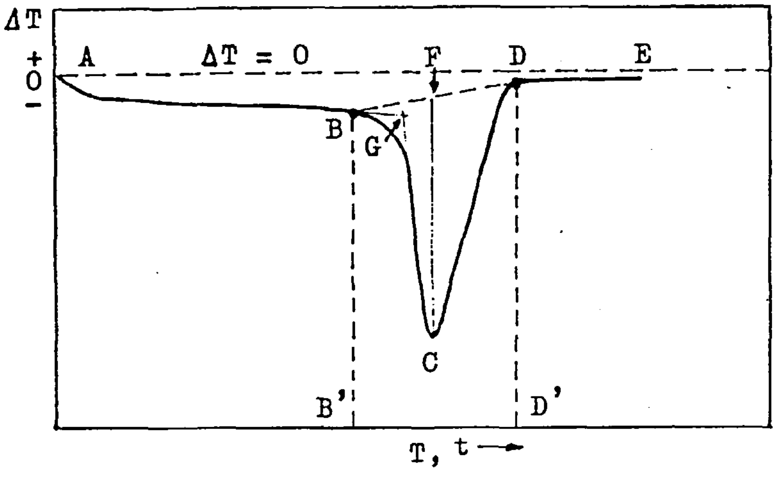


FIGURE 23. Quantitative evaluation of DTA curves, according to ICTA recommendations.

coefficients thereof. Concerning the concept of the specific heat, the authors refer to the literature.[119,120] In this review only measurement techniques will be dealt with.

Accurate specific heat determinations were carried out earlier by means of static calorimeters using large samples in a procedure rather lengthy, but with a high accuracy. DTA and DSC devices enable specific heats to be determined rapidly with a few milligram samples and with acceptable accuracy. Cassel[121] has described a highly accurate method of specific heat measurement by which a standard deviation of 0.1% can be approached. The procedure itself is derived from a consideration based on Equations 7 and 8. The principle of the method is that the baseline is determined with empty sample holders and the baseline displacement with a standard sample of known specific heat. The principle of the measurement is demonstrated in Figure 2~~3~~ 2 with data in the figure:

$x_1 : x_2 = m_1 c_{Saf} : m_2 c_x$, β = constant at temperature T_i.

$$c_x = \frac{x_2 m_1 c_{Saf}}{x_1 m_2} \tag{9}$$

If c_x is determined for different temperatures, the constants of the equation describing the temperature dependence of the specific heat can be computed, too.[96]

According to Vučelič et al.,[122] the reproducibility in simple cases is about ±2%, which is in most cases sufficient. The accuracy of measurement depends on the reproducibility of the baseline. The measurement takes 5 to 50 min depending on the rate of heating. Obviously, specific heats can be determined only in temperature ranges where no physical or chemical transformation takes place. This method of specific heat determination is widely used in the field of polymer compounds; it may help in the realization and interpretation of the properties of the polymer structure.

The tracing of the changes in the baseline may be valuable in detecting and characterizing so-called second-order transitions, such as the glassy to liquid transition in polymers which is described in the literature by the temperature T_g. Transitions of this type are characterized by the fact that there is no associated enthalpy change and no abrupt volume change, but the heat capacity and the expansion coefficient changes discontinuously and the entropy of the system increases. Figure 24[123] shows the DSC

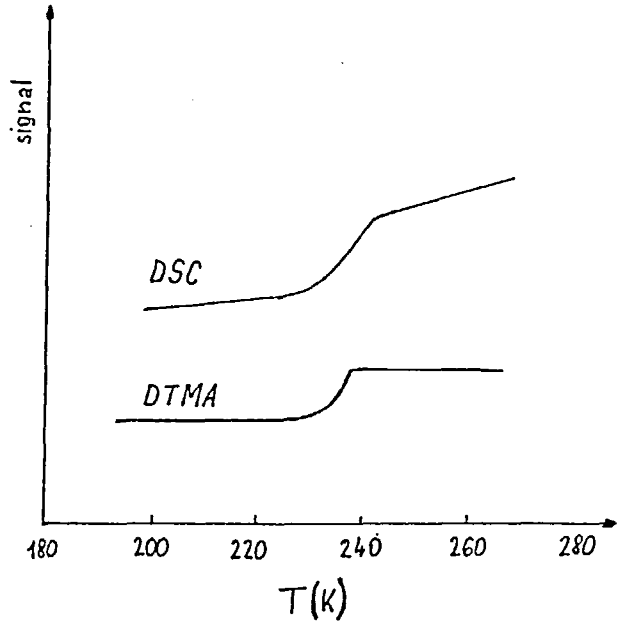


FIGURE 24. Glassy transition of neoprene (heating rate 10°/min), measured by DSC and differential thermomechanical analysis (DTMA). (From Thermal Analysis Application Study 7, Perkin-Elmer Corp., 1973. With permission.)

curve and a derivative signal of a thermomechanical analyzer (TMA) taken of a neoprene sample as a function of the temperature, which indicate a glassy transformation.

In Reference [123], a valuable summary is given on the phenomenon of glass transition, the possibilities of its measurement, and the factors affecting it. In practice the phenomenon is successfully used for quality control in technological processes.

The α to β transformation of quartz can be considered as a similar change, as well as magnetic transitions which can be studied similarly by DTA or DSC method.

C. Purity Control by DTA and DSC Methods

A further important field of application of DTA and DSC techniques is purity control and the determination of contaminants present in low concentrations (about 0 to 5 mol %). The determination is based on the measurement of melting-point depression, according to the general equation given by Mastrangelo and Dornte:[124]

$$T = T_0 - \frac{\bar{x} R T_0^2}{\Delta H_0} \frac{1}{\frac{k}{1-k} + F} \qquad (10)$$

where T_0 is the melting point of the the pure substance, ΔH_0 is the heat of melting (J/mol), $\bar{x}$ is the gross mole fraction of the contaminant,[125] and k is the distribution coefficient of the substance distributed between the solid and melt phase ($k = 0$ in the case of an eutectic, and $0 < k < 1$ if solid solutions are formed).

Based on experiments, Equation 10 is considered valid for eutectics; however, its validity is questioned in the case of solid solutions. Some good results are given in References 124 and 126, and significant deviation of calculated from experimental values in References 78 and 79. In using Equation 10, it has been assumed that ΔH_0 is constant.

As will be discussed later, this is not true, especially at the initial stage of the process. This face gives rise to unreliable results. Another practical problem is connected with the determination of the upper concentration limit of the validity of the equation. In the opinion of the authors, the limit of validity depends on the concentration dependence of the activity coefficients of contaminant in the system studied, as the deduction is valid only in the case of ideal solution systems. According to estimations, the upper limit is generally 5% or, in some cases, 10%.[127,128]

Measurements can be carried out in two different ways, either by continuous[103,129] or stepwise procedure.[130,131] In the continuous method, one melting curve is recorded and evaluated. The principle of the method can be understood from Figures 25a and b, where the evaluation is demonstrated schematically.

The phase-equilibrium state, the only one which yields valuable results, can be approximated by the proper choice of the heating rate. The conditions for the phase transition to be heat-transport controlled are usually ensured by using small samples and a low rate of heating (practically, about 0.2 to 1.0 K/min).[78,79,128,132] However, very often it cannot be checked whether or not a process has taken place under equilibrium conditions. Furthermore, the sample temperature must be corrected for the thermal lag. Lag may also cause uncertainties in that respect, as small differences in the position of the sample may affect the thermal resistance of the system, which gives rise to deviations in the original thermal lag[133,134] and changes in the curve shape.

The results of purity tests carried out by the continuous technique are very often unreliable (see Marti[22]) because of uncertainties in marking out the baseline, sluggish premelting which may also cause difficulties, as well as the reasons already mentioned.

The reliability of purity tests has increased after the introduction of the stepwise technique.[130] Recording obtained by using this technique is shown in Figure 26. In this method the problems connected with the deviations from the equilibrium state are eliminated. In this case the temperature intervals and the magnitude of the steps are to be chosen so as to yield about seven to eight steps for evaluation. A disadvantage of the method is that it takes a rather long time, about 30 to 150 min.

In the discussion of the evaluation of the data of purity test or contaminant determinations, Equation 10 has to be applied to eutectic systems. In this case the equation has the form

$$T = T_o - \frac{\overline{x}RT_0^2}{\Delta H_m}\frac{1}{F} \tag{11}$$

where F is the fraction melted which can be calculated as the enthalpy change up to temperature T divided by the enthalpy change of the entire process:

$$F = \frac{\Delta h(T)}{\Delta h_0} = \frac{\Delta h(T)}{n\Delta H_0} \tag{12}$$

where $\Delta h(T)$ is the enthalpy change up to temperature T (joule), Δh_0 is the enthalpy change needed to the melting of the entire sample (joule), ΔH_0 is the molar heat of melting, and n is the number of moles of the sample. Inserting this into Equation 11, we get

$$T = T_0 - \frac{xRT_0^2 n}{\Delta h(T)} \tag{13}$$

The deviation found between experimental and theoretical values is as if $\Delta h(T)_{measured} < \Delta h(T)_{true}$. This finding is explained by the fact that the initial portion of the recording

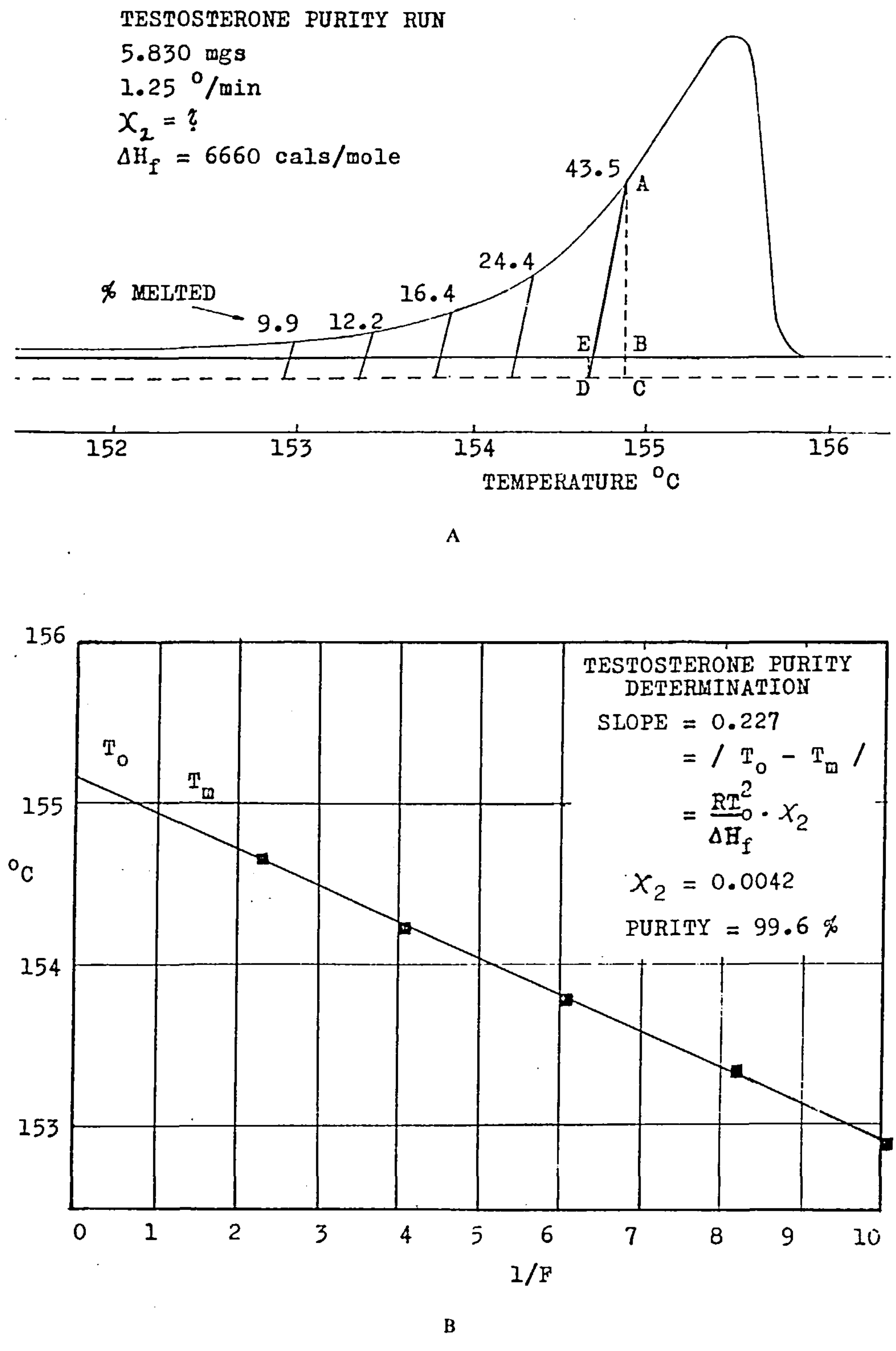


FIGURE 25. Purity determination of Testosterone by DSC, single run (A). B represents the method of evaluation. (From Thermal Analysis Newsletter, No. 5, Perkin-Elmer Corp., With permission.)

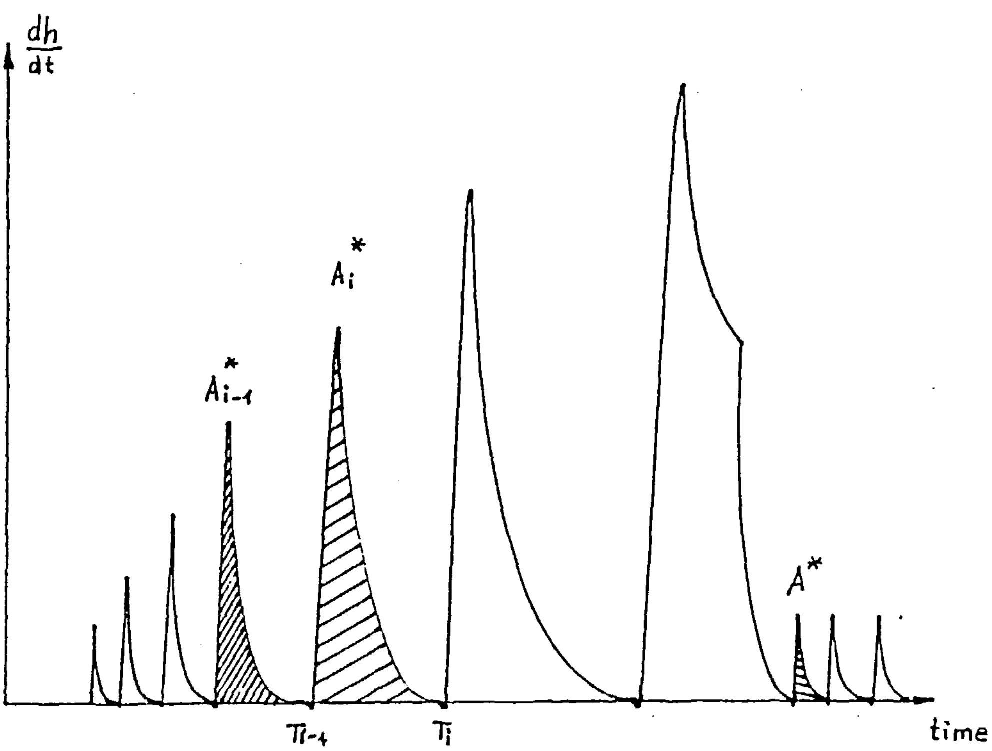


FIGURE 26. Mode of evaluation of DSC traces, obtained by stepwise technique for purity determinations. $\Delta T = T_i - T_{i-d}$; $A_i = A_i^* - A^*$.

cannot be evaluated; that is, part of the enthalpy change is merged in baseline. This can be corrected for by a correction term Δ which is determined so as to yield as good of agreement of corrected experimental and theoretical values as possible.

According to Palermo and Chiu,[128] the deviation between measured and theoretical data is not only due to the loss of peak area, but also to the dependence of ΔH_{melt} on the concentration of contaminant. It means that

$$d(\Delta h) = d(n\Delta H_{melt}) = (nd[\Delta H_{melt}] + dn[\Delta H_{melt}]) \tag{14}$$

where changes due to the first term cause losses which cannot be separated from the losses discussed above.

The concentration of contaminants can be calculated from the recording taken using the stepwise technique in two ways. According to Gray,[135] it can be calculated from data of two subsequent peaks

$$x = \frac{2\Delta T}{Rn} \quad \frac{A_n A_{n-1}(A_n + A_{n-1})}{(T_n[A_n - A_{n-1} + 2\Delta T\, A_n])^2} \tag{15}$$

In using the other method, the evaluation is made based on the data of five to ten peaks using the equation:

$$\min_{x,\,T_0,\,\alpha} \sum_{i=1}^{n} \left(T_0 - T_i - xRn \frac{T_0^2}{\sum\limits_{k=1}^{i} A_k + \alpha} \right)^2 \qquad (16)$$

The evaluation can be carried out by computer based on appropriate programs. The authors[436] have estimated the standard deviation of the evaluation methods, and have found that the stepwise technique yields more reliable data than the continuous technique, and the standard deviation is smaller if a greater number of experimental data are used.

D. Some Questions of Thermokinetics

A significant proportion of papers which have appeared on thermal analysis since the middle of the 1950s was devoted to thermokinetics problems.[137] In most papers either experimental results are presented or problems of data processing are dealt with; a smaller number are of polemic nature. A comprehensive, versatile, and extensive survey of thermal kinetics has been published by Garn in Critical Reviews,[138] followed by another paper with a less optimistic view.[139] The points of view expressed by representatives of the well-known Czechoslovakian thermoanalytical school are to be mentioned, namely, that the initial optimism concerning the usefulness of thermokinetics has been gradually replaced by a less optimistic view.

Dynamic thermoanalytical methods — TG, DTA, and DSC — at first glance seem to be suited to the investigation of the kinetics of heterogeneous thermal reactions and decompositions, or generally to all kinds of thermal transformations. The aim of the measurements in this direction is similar to homogeneous reactions; to derive data such as reaction rate, specific rate constant, activation energy (E_a), order of the reactions (n), the frequency or pre-exponential factor (A), and for complex reactions the individual steps from data yielded by the methods mentioned using suitable data acquisition and processing techniques.

Heterogeneous thermokinetics, however, differ from homogeneous fluid-phase kinetics in various respects. In the latter case, the concentration distribution is homogeneous as the system is stirred and isothermal. It is characteristic of heterogeneous thermokinetics that the temperature is increased according to a program and the system, being solid or heterogeneous, is not stirred. Consequently, the heat and mass transport may play an important role in the system and in addition to the reaction rate, the mass, shape, specific surface of the sample, and crystallization conditions of the new solid product, etc., are factors of importance. This means that in addition to the nature of the reaction, a number of factors affect the rate and kinetic parameters of the reaction. According to Paulik and Paulik[140] even the relatively simple equilibrium reaction described by the general equation

$$A_{solid} \rightleftharpoons B_{solid} + C_{gas}$$

consists of several partial processes which are important from the point of view of kinetic considerations (Figure 27). The partial processes are as follows:

1. Formation of the gaseous product characterized by the reentering into, and release from the crystal lattice. According to the authors,[140] these processes are generally not rate-controlling since they are fast compared with the heating program used.
2. Capillary diffusion of the gaseous product, which is also considered fast; diffusion into the environment, the rate of which is commensurable with that of the heat trans-

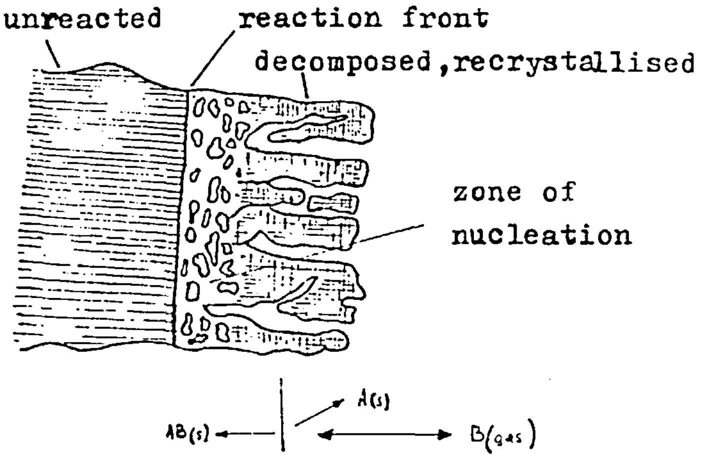


FIGURE 27. Considerations on the decomposition reaction of $AB_{(s)} \rightleftharpoons A_{(s)} + B_{(gas)}$ type. (From Paulik, F. and Paulik, J., *J. Therm. Anal.*, 5, 253, 1973. With permission.)

mission which, therefore, can be rate controlling. In this case also, the rate of diffusion depends on the temperature, pressure, and concentration gradients; thus it is difficult to describe.

3. Formation of a new solid phase taking place in several steps; namely the formation and growth of nuclei, then rearrangement, the rate of which may be commensurable with that of the heat transport.
4. Heat transmission which is considered by the authors[140] as being the slowest process due to the air gap between the heat source, the thermal resistance of the wall of the sample holder, and that between the surface and center of the sample.

The above statements are valid even if the conclusions drawn concern relatively large samples and unfavorable conditions of heat transmission.

As will be shown, the mathematical evaluation of the shape of DTA, DSC, and TG curves is a method of thermal kinetics. It has been pointed out in previous sections that the shape of the curves is affected by instrumental parameters and experimental conditions, which means that random and uncontrollable deviations may occur which are independent of the rate of the process investigated. In kinetic studies the temperature of the sample should be measured with a high accuracy. However, this cannot always be carried out exactly.

According to Garn[139] a number of problems arise when kinetic parameters are to be calculated. In addition to the factors mentioned above, the problems are of a philosophical, epistemological nature; some depend upon definition of terms, some depend upon the validity of assumptions adapted for mathematical convenience, and some are related to human ability to carry out suitable measurements.

In spite of the outlined difficulties and problems connected with thermokinetics, a short section is devoted to the subject in this review, the reasons being that:

1. It is thought that thermokinetic studies have promoted the development of the methods of thermal analysis. The requirement that the results of measurements have to be independent of the technique used has stimulated the designers and constructors to consider the conditions for the exact operation of the devices.

2. The ceasing of the exclusively descriptive, speculative, and interpretative nature of thermal analysis was in many respects due to the demand for kinetic treatment. It has inspired the development of thermal analysis from a method into a theory.
3. It has provided some data to the description of solid-state reactions which are generally rather complicated.
4. Finally, although in its present state of development it does not provide accurate kinetic data, some of the parameters calculated may be characteristic of processes and useful for comparison purposes.

The general rate-equation of processes taking place in the homogeneous fluid state is as follows:

$$\frac{dc}{dt} = kc^n \qquad (17)$$

Under isothermal conditions similar to Equation 17, the following equation can be given for solid-phase reactions:

$$\frac{d\alpha(t)}{dt} = kf(\alpha[t]) \qquad (18)$$

where α is the reaction coordinate, k is the rate constant, and t is the time. α can be determined on the basis of TG, DTA, or DSC curves, e.g.,

$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \text{fraction decomposed} \qquad (19)$$

m_0 = initial mass of sample, m = mass of sample at t (time), and m_f = final mass.

Several equations are known for the description of the function f (α).[141] In the case of dynamic heat program,

$$k(T) = A\,e - \frac{E}{RT} \qquad (20)$$

At a linear heating where β = const, the normal differential equation model can be given:

$$\frac{d(\alpha[T])}{dT} = \frac{A}{\beta}\exp - \frac{E}{RT}(1 - \alpha[T])^n \qquad (21)$$

In another form:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta}e - \frac{E}{RT}dT \qquad (22)$$

Several procedures have been developed for solving this equation. By inserting

$$x = \frac{E}{RT}$$

we get

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{AE}{R\beta} - \frac{e^{-x}}{x^2}\,dx \tag{23}$$

In the integrated form:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{AE}{R\beta}\,p(x) \tag{24}$$

where

$$\int_x^{\infty} \frac{e^{-x}}{x^2}\,dx = p(x) \tag{25}$$

According to the assumed mechanism of solid-phase reactions a number of mathematical descriptions are possible and the solutions are different due to the different assumptions made. As regarding the mechanism, e.g., a 1,2,3-dimensional topochemical process can be assumed for the decomposition, or in the induction period nucleation is the rate-controlling process, or the growth of nuclei, which can be one- or two-dimensional. Further, the processes may be diffusion-controlled in 1 to 3 dimensions, etc. There are cases where a mixed mechanism is assumed. An interesting approach was presented by Draper and Sveum,[142] namely that in solid-phase reactions the heat transport is rate controlling. Accordingly, their equation derived only contains material constants in addition to α and t.

In the kinetical evaluations the experimental data were inserted in one of the models mentioned above. The choice of the model is based on hypothesis related to physical and chemical considerations. The model is considered as valid if the experimental curves or a transformed form can be obtained by simulation and if the log k vs. 1/T plot is linear. In this case the mechanism and the rate-controlling step are rendered probable and a physical-kinetic interpretation of the constant determined is offered. (E_a, A, and n values are presented) As pointed out by Garn,[139] this approach is formal and subjective and the estimation of the reliability of the data is, in most cases, missing. In many cases various mechanisms can be assumed for the very same process according to the procedure and evidence outlined above. Garn[139] has summarized ways for testing reliability in six points, which are very interesting and worthy for consideration. The essence is that for the mechanism to be justified it is necessary to have physicochemical proof supported by experimental evidence, in addition to mathematical evidence. The problem is that this experimental evidence is impossible or very difficult to obtain. A basic question connected with the calculated kinetic parameters is, whether it is allowed to attach an interpretation similar to the corresponding constants determined for fluid-phase isothermal and homogeneous reactions where the procedure is theoretically well-established. In this context the interpretation of the reaction order n and pre-exponential factor A for heterogeneous, non-isothermal reactions is highly questionable even on logical grounds. Namely, it is not justified that the concentration of the unreacted fraction may be used at all. The calculated values depend on the geometry of the sample and on other experimental parameters. A may include in its value a number of constants related to the initial state, thermal history, density, the stoichiometric factors of the reaction, active surface, lattice imperfections, pressure, or surface adsorption; but it can be assumed to include also the frequency factors of elementary processes. It is very difficult to assume the formation of the transitional complex characterized by A.

In most papers dealing with reaction kinetics, E_a data are presented. The interpretation of E_a in homogeneous kinetics is well known and accepted — its calculation is based on the temperature dependence of the specific rate constant.

$$k(T) = Ae^{-\frac{E}{RT}}$$

from which

$$\frac{d\ln k(T)}{d\frac{1}{T}} = -\frac{E}{R} \qquad (26)$$

Plotting lnk(T) as function of 1/T, a straight line is obtained with a slope −E/R.

The similar interpretations of E_a values obtained in heterogeneous thermokinetics is questionable even if the mathematical treatment is correct. As it is not known for certain to which rate-controlling process it belongs, there is no evidence for assuming that it is the activation energy of a chemical reaction. For an equilibrium process it is generally valid that $\Delta E_{reverse} + \Delta H_{trans} = \Delta E_{forward}$

However, very often this is not true in the cases of solid reactions.[143] It is striking that E_a values given by different authors for the very same reaction vary widely and different equations may yield the "best" fitting. On logical grounds, the reason for this is that the value of E_a calculated from experimental results depends sensitively on the uncontrollable changes in experimental conditions. As this is a fact, according to Garn:[139]

1. There is no uniquely describable activated state and consequently the Arrhenius equation has no application to solid reaction, or
2. The assumption that the rate is a function only of temperature and the fraction remaining, is incorrect, or
3. Both may be true

The limitations of the non-isothermal thermokinetics are pointed out in the paper by Arnold et al.[144] based on a critical evaluation of data from thermogravimetry and quasi-isobaric-isothermal TG. Their starting argument is that Equation 18 and the like cannot be considered as the true physicochemical model of the process investigated. To construct a true model all the factors affecting the process should be taken into consideration. Probably the equation

$$\frac{d\alpha}{dt} = f(t,T,N,\Theta,\rho,p...x) \qquad (27)$$

would fulfill this requirement in which the number of nucleation centers N, the specific area Θ, the density of the sample ρ, the geometric factor characteristic of the particles, partial pressure of the gas p, and further quantities or parameters x are considered in addition to the ones already dealt with.[144]

The function has not been given yet in an explicit form or solved, most probably due to measurement-technical reasons, especially if we consider that the dependence of the factors on time and temperature is also to be known. Instead of this, Arnold et al.[144] have found the use of a more simple approach advantageous — the investigation of the reliability of the estimation of the kinetic coefficients and the relationship which can be considered as an apparent model. The possibilities of improving the reliability of the estimation were studied and characterized. As a result of simulations with various orthogonal polynoms, it has been concluded that the simultaneous estimation of A and E

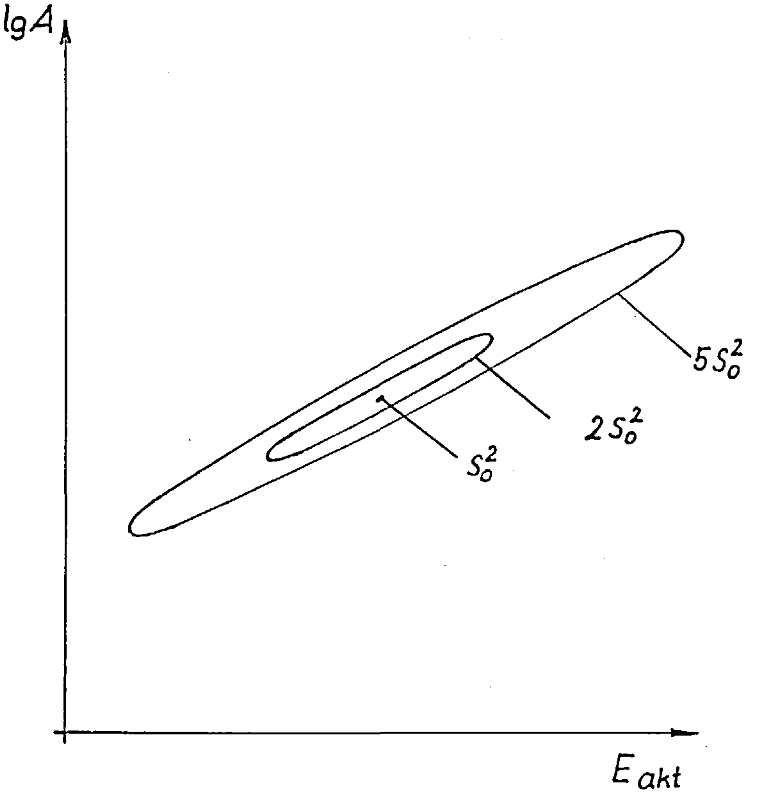


FIGURE 28. Confidence range of estimation of lgA and E_{akt}. The changes of the sum of the squares of the deviations in functions of lgA and E_{akt} in the case of parameter estimation based upon the least square method. S_o = the minimum level of the sum of the squares of the deviations.[146]

on the basis of one TG curve taken with a single dynamic program yields rather poor results which are of little practical usefulness. This can be expected in view of the so-called kinetic compensation effect.[145] As can be proved mathematically, deviations in the value of A and E_a due to varying experimental errors are of the type shown in Figure 28, according to Arnold.[146]

To characterize the fitness of the parameter estimation, the so-called "conditional" number of the system of equations has been calculated by suitable mathematical means.[147] In this estimation based on TG curves in the least favorable case, the measurement should be made with an accuracy of 0.0001% to enable the parameters to be estimated with an accuracy of 10%. In an average case an accuracy one or two orders of magnitude smaller than the value specified above is sufficient which, being between 0.001 and 0.01%, is still unattainable experimentally. It may be interesting to mention that in the case of the quasi-equilibrium TG technique yields contradictory results, and therefore the parameters cannot even be estimated in this case. Accordingly, the conclusion was drawn that even formal kinetical data can hardly be expected to be obtained for heterogeneous reactions from thermoanalytical (TG) data.[144]

The authors of the present review do not deal with thermokinetics on the level of research, and perhaps this is the reason for their optimistic view that a more exact solution of the problems can be expected in the future due to the improvement of measurement techniques and data processing. Further, they believe that thoroughly

Table 5
SOME SELECTED CHARACTERISTIC DATA ON PERFORMANCE OF DTA, DSC, AND TG METHODS AND APPARATUS

Parameter	**Approximative value**	
	DTA, DSC	**TG**
Temperature range	120—1000 K (2500 only for DTA)	300—1500 (2500) K
Sample	0.1—50 mg	0.1—10 mg, 10—500 mg
Output signal	20—150 μV/K	—
Sensitivity	0.1—0.5 mW/full scale	10 μg—1 μg/full scale
Precision of T measurement	± 0.1—0.5 K	1—2 K
Precision of DTA, DSC/TG signals	± 1 %	± 0.2—1 %
Time constant	1—3 sec	1—3 sec
Baseline stability	0.5—2 mW/full T range	0.05 μg/full T range
Long-term stability	recalibration about monthly	
Program modes	linear, heating and cooling, isothermal and their combination	
Program rate	0.03—150 K/min (320)	0.03—80—100 K/min
Program speed selection	6—12	6—12
Temperature deviation of program	± 1 % (± 2 % above 1000 K)	± 1 % (±2 % above 1000 K)
Maximum load	—	10—100 g
Pressure	10^{-6} bar—200 bar to 50 kbar	10^{-6} bar—200 bar

checked formal kinetic data may yield conclusions useful in the design of technological processes involving thermally initiated reactions.

VI. VARIOUS METHODS OF THERMAL ANALYSIS

This section summarizes the available methods of thermal analysis and gives a brief description and evaluation of each. However, a thorough review could not be aimed for and therefore does not reflect the complete significance of the methods in question. As the most important procedures, the DTA-DSC and the TG have already been discussed and only the most relevant operational data are presented in Table 5.

A. Thermal Gas Analysis

Considerable amounts of information can be gained by qualitative and quantitative analyzing of the volatile products of thermal decomposition processes. Thermal gas analysis might be applied as a single method although most frequently it is combined with other thermal methods, mainly TG or DTA-DSC.

1. Single Methods

One of the simplest procedures is to measure pressure and temperature while the volume is kept constant. It is somewhat more complicated to record the volume change while pressure is maintained constant during thermal decomposition. Recently, Wendlandt[148,149] has given examples of both ways and pointed to applications. Monographs contain the description of many earlier combinations as well. According to Wendlandt[149] the pressure might be monitored by measuring the resistance of a wire submerged in a mercury manometer. The information offered by this method is rather poor—accuracy is limited when there are condensing products, and pressure changes due to thermal dilation of the whole system should be taken into account. Only processes separated from each other could be identified; simultaneously occurring processes give gross pressure signal. The constant-pressure equipment contains a variable-volume motor-driven gas syringe. Performance compares with that of the aforementioned ones.

The decomposition products of the sample are usually carried into the detector of special equipment operating as thermal gas analyzers by constant-velocity gas stream. The composition of this gas should be chosen according to the operational principle of the detector. The samples may be heated in temperature-controlled furnaces, but flash pyrolysis and Curie-point destruction are often used as well. An example for temperature-controlled analysis is Du Pont's wet measuring instrument.[150] The detector contains phosphorus-pentoxid which binds the released water to produce phosphoric acid. This product is electrolyzed, and the recorded electric work utilized in electrolysis measures the wet content. The instrument has a high sensitivity: even 0.1 μg of water is detectable. Another instrument with high sensitivity applies a flame ionization detector to measure thermal decomposition products of organic materials.[151] Similar devices are available with gas detectors measuring thermal conductivity, flame temperature, flame ionization current, gas density, etc. Kaisersberger[152] made a comprehensive study on detection techniques by means of thermal conductivity, gas density, and emanational and quadrupole mass spectrometry (QMS). In this way, these measurements give relatively little information and are able to follow only the overall processes since their selectivities are rather limited. When calibrated, these methods can be used for quantitative analysis; however, there remain several sources of error (i.e., sensitivity might depend upon material properties of products or operational mechanism of detector, etc.)

When identification of decomposition products is required, a simple method of rapid pyrolysis and subsequent washing out into a low-temperature trap is usable and the condensate may be analyzed conveniently by gas chromatograph. From the practical point of view, this is equivalent to the well-known pyrolytic gas chromatography. Decomposition products of complex organic compounds and polymers may successfully be investigated this way, although one has to take into account the secondary products that may form in the reaction of thermally decomposed fragments. In mass spectrometry also, pyrolytic sample inlet is a useful means when the tension of studied material is negligible even in a high vacuum. In cases of mixtures, the sample to be analyzed may enter the ionization chamber after fractional distillation. When temperature is well controlled, the selectivity is quite satisfactory. The GC-MS method works well to identify components of a complex condensate separated by gas chromatography. As to the resolution of the method, Lumme et al.[153] could identify[44] different organic compounds by means of IR and MS in the case of Ni(II)-aniline-nitrate-hydrate. Their working method consisted of pyrolysis, product freezing out, and chromatographic separation. During pyrolysis, radical reactions may give rise to many complicated products unexpected at the first approach. The GC-MS method is also able to identify many organic compounds is airborne particulate matter satisfactorily.[154] Pyrolisis, freezing out, and product analysis together give reliable results but no information on decompositon temperature. In contrast, temperature-controlled degradation gives rise to uncertainty in product analysis.

Risby and Yergey[155] reviewed linearly programmed, temperature-controlled MS. Since fragmentation is carried out in the MS device, no transportation problems exist and the possibility of analyzing large characteristic ions is increased. It is more convenient to use the chemical ionization than the electron impact one. In the former case, fragments are fewer and the magnitude of Parent peak is larger. The relative appearance of the two fragmentation processes, thermal and chemical ionization, could be efficiently studied in this manner.

We have already dealt with thermoparticulate analysis from the point of nomenclature. Originally this technique was used for the detection of condensation nuclei evolved from polymers undergoing degradation when subjected to programmed heating.[156] Recently this was successfully applied to study predecomposition of different organic materials. In particular situations, this method gives way to investigate the onset of thermal decomposition at substantially lower temperature, determined earlier. Methods made feasible with the high-sensitivity detectors used some of the organic materials considered as particulate emission sources in these studies. The ion-chamber detector utilizes the change in current output of an ion chamber as a function of particulate concentration. The condensation nuclei detector utilizes the principle of a cloud chamber. In Table 6[157] thermoparticulate characteristics of a few compounds are listed. The suggested use of the detection method might lie in sophisticated technologies as an alarming system to avoid overheating but not in thermal analysis.

2. *Multiple Methods*

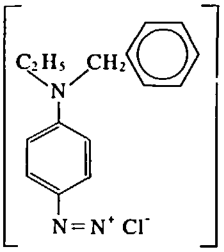
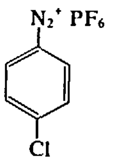
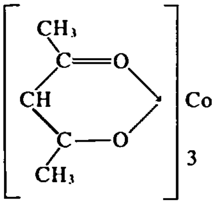
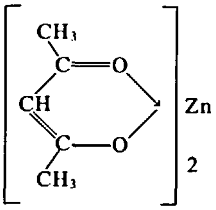
One example is the adapter, referred to as thermogas-titrimeter, connected to a Pauliks derivatograph that is used in simultaneous measurements.[88,90] The stream of gas carries the thermally degraded products from the furnace into the fluid absorber where absorbed products are hydrated and titrated continuously to endpoint by an automatic burette. The piston of the burette is motor driven, its command signal obtained as potential difference between preset working and reference electrode. The displacement of the piston is recorded photographically. By this method one can analyze acidic and basic products by means of glass electrodes and can titrate redox systems, including water, when using a waterless solvent and Fisher's solution by means of platinum indicator electrodes. The titration curve follows the thermogravimetric changes with a small time lag and is a useful tool in evaluating the latter in detail. The applications of the method are limited by the inability to measure electrode-inactive materials, and the poor selectivity. It is mainly used for inorganic compounds, complexes, etc., or to measure organic impurities by tracing the carbon dioxide brought about in oxydizing atmosphere.

Combining TG, DTA, DSC, and GC, the decomposition products can be selectively determined. Apart from the time lag, further difficulties may arise from different methods of operation as the samples should be discretely entered in the case of GC.

However, the loss of information may be avoided even for rapid reaction by properly adjusting the time constant of TA and GC. The frequency of samping is determined by the scanning rate of GC. Summing up the data of consecutive chromatograms, one obtains the concentration distribution of components over temperature, and quantitative analysis also can be done. Combining the two devices, care must be taken to minimize the dead volume and to prevent selective condensation, and the temperature of the connecting tube should be kept high and constant.

Although somewhat sophisticated, it is increasingly common to connect a mass spectrometer to TG, DTA, and DSC devices. This combination is commercially[162] available, also (see Figure 29). It is advantageous with respect to GC that MS does have a substantially higher scanning rate or could be set to continuously monitor a chosen fragment. Friedman has published a comprehensive review on thermoanalytical use of mass spectrometers.[158] According to this review, Zemany[159] made the pioneering introduction of MS for thermal analysis, while the first equipment complying with today's standard was described by Langer and Gohlke.[160] According to Friedman, in selecting or designing a system it is important to keep in mind what information is desired. In

Table 6
THERMOPARTICULATION CHARACTERISTICS OF ORGANIC COMPOUNDS

Compound	Chemical formula	Organoparticulation temperature range (°C)	Melting (or decomposition) temperature (°C)
Malonic acid	$CH_2(COOH)_2$	126—132	132
Methylmalonic acid	$CH_3CH(COOH)_2$	127—131	135
Dimethylmalonic acid	$(CH_3)_2C(COOH)_2$	147—151	190
p-Amino-N-benzyl-N-ethyl benzene diazonium chlorostannate (diazo 453-M)	 1/2 $SnCl_4$	155—160	160—162
p-Chlorobenzene-diazonium hexa-fluoro-phosphate (phosfluorogen "A")		130—140	150
Cobalt (III) acetylacetonate		150—152	213
Zinc acetylacetonate		85—120	138

From Phillips, D. C. and Smith, J. D. B., *Ind. Res.*, 18, 57, 1976. With permission.

choosing the mass spectrometer it is important to consider mass range, resolution, sensitivity, scanning rate, and structure of the inlet system. Generally, one must have a way to remove the excess gas produced and yet obtain a representative sampling. The two systems should be connected in the shortest way, and this is a crucial point in investigating intermediates. As to ionization, it is most important to minimize the possibility of fragmentation for this reason instead of the conventional excitation of about 70 eV; working with lower-energy electrons is advisable.

Earlier studies applied time of flight MS,[161] for it was rather easy to combine with the

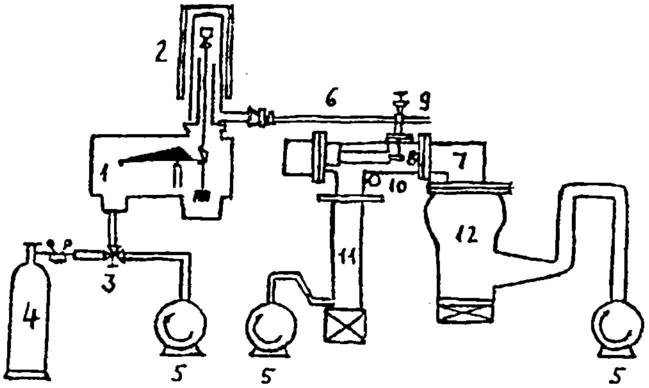


FIGURE 29. An arrangement for TA-QMS using chemical ionization. (1) thermobalance, (2) furnace, (3) 3-way valve, (4) reaction gas cylinder, (5) rotary pumps, (6) coupling line, (7) quadrupole mass spectrometer, (8) Cl-ion source, (9) metering valve, (10) ionization gauge, (11) analyzer diffusion pump, (12) Cl diffusion pump. (From Baumgartner, E. and Nachbaur, E., *Thermochim Acta*, 19, 3 (1977). With permission.)

TA devices. Those, however, had the drawback of limited resolution and mass range, plus that simultaneously only a few fragments could be studied. With these limitations it could be used in analyzing products of compounds which were not too complicated. The most fruitful applications lay in studying the circumstances in which H_2O, CO, CO_2, NH_3, SO_2, etc., occurred from mainly, but not entirely, inorganic origin.

Using a programming and demultiplexing unit and a multichannel recorder, multiple ion monitoring is possible (i.e., the intensity of different products as a function of temperature can be recorded). The latest generation of QMS with digitized control unit is extremely versatile if control and data processing is computerized.

Eppler and Selhofer[163] discuss the problem of connecting TA and QMS in detail and propose several designs for bridging over different temperature and pressure. Székely and Till[164] suggest to use (instead of the usual capillaries) of short and relatively wide tubes, high-capacity vacuum pumps, and gas bypasses in interfacing devices without a pressure gap. According to Emmerich and Kaisersberger,[165] platinum capillaries and orifices make out a working interface up to 1800 K. A simple, simultaneously recorded result is shown in Figure 30, obtained by equipment made by Baumgartner and Nachbaur.[94]

The use of thermoananlytical methods in combination with MS in the polymer degradation is widely known. This requires a high-performance MS and gives information on solvent and softener content, on degree of depolymerization, and on destruction stages.

In many cases the spectrum is rather difficult to interpret and to distinguish between thermal and ionization degradation. The fragmentation rules, use of small excitation energies, or sophisticated combination of TA, GC, and MS might help to overcome this difficulty.

B. Emanation Thermal Analysis

A special method in thermal gas analysis is based on gas release from solids and/or melts. The emanated gas is radioactive, and detectors well known from radioanalysis could be used. One particular method of emanation thermal analysis is when a

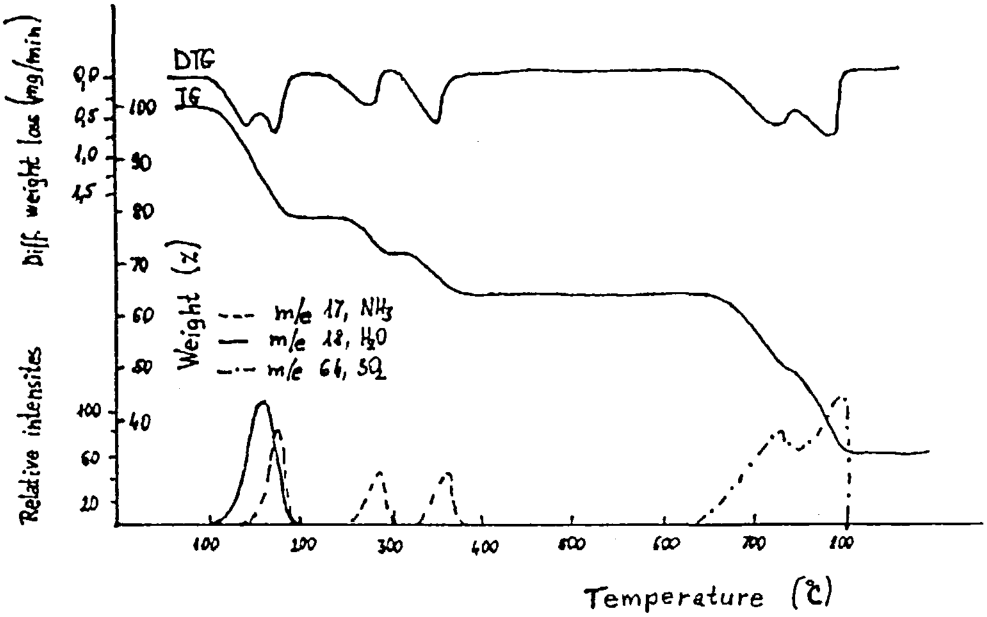


FIGURE 30. TG/DTG curves and MS-profile of copper tetramine sulphate hydrate. (From Baumgartner, E. and Nachbaur, E., *Thermochim. Acta*, 19, 3, 1977. With permission.)

nonradioactive gas is incorporated into a solid and the release of this is measured by a suitable detector as a function of temperature.

There are two ways to have radiating material in the sample, either natural or artificial. An example of the first case is when investigating *a priori* radioactive materials. In this case, according to

$$228_{\mathrm{Th}} \xrightarrow{\alpha} 224_{\mathrm{Ra}} \xrightarrow{\alpha} 220_{\mathrm{Rn}} \xrightarrow{\alpha}$$

which is the decay scheme, the sample emits α radiation. The intensity of 220_{Rn} release, determined by its α radiation and provided other factors are kept constant, depends upon the structure of solid and the surface properties. On the other hand, the similar situation arises when the lattice is labeled by some tracer, for example Zn-oxides may be labeled by coprecipitating Th-salts together with hydroxides and heating the sample to obtain oxides.[166] Barium compounds similarly may be labeled by thorium and/or radium. It is somewhat different when a radioactive gas (for instance ^{85}Kr) is incorporated into the sample. This can be accomplished by bombardment of sample surface or by high pressure and temperature diffusion. The gas may be incorporated at

1. Lattice vacancies when Kr atoms assume substitution positions
2. Between the levels of lattice structure elements with interstitial function
3. Lattice cavities in case of klathrate structure of matrix
4. Microbubbles in the matrix

For the case of different incorporations, the thermal releasing probabilities will differ also. The release rate depends upon the fine structure and surface energy of the host matrix. The gas release steeply increases as the matrix undergoes physical or chemical transformations.

The following equations describe the decryptonization process:[168]

$$E = E_r + E_d \tag{28}$$

where E_r is the emanation released due to the recoiled emanation atoms, in detail:

$$E_r = \frac{r_o S}{4m} \rho \tag{29}$$

and

$$E_d \approx \sqrt{\frac{D_o}{x}} \frac{S}{m} \rho \exp \ - \frac{E_{act}}{RT} \tag{30}$$

where D_o = diffusion constant of ^{85}Kr for the matrix, x = decay constant of ^{85}Kr, S = surface area of the grain in the matrix, m = mass of the grains, E_{act} = activation energy of ^{85}Kr diffusion in matrix, R = gas constant, T = temperature, and r_o = the range of recoiling atoms. E_d is an exponential function of inverse temperature. There is an upper limit of the usage of this method which lies in the range of 750 to 1050 K depending on material properties of the sample.

Both first- and second-order transitions are detected as peaks. The peaks can reflect dehydratation, thermal dissociation, glassy and polymorph phase transition, stabilization of metastable state, and when lattice defects concentrate. One can usually get quite reliable signals in some cases when the DTA or other methods fail. Figure 31 displays DTA, EGA, and ETA signals of calcium-carbonate labeled by thorium, the mother element of radon.[169] The DTA and EGA signal correspond entirely to each other; the small effect at 400° C on the thermoemanation curve may be attributed to the dehydratation of calcium-hydroxide brought about on the surface by vapor. The peak, well recognizable on ETA but hardly on the EGA curve, around 900 K is a result of an irreversible transition and does not occur on repeated measurements. According to the authors[169] it is caused probably by the annealing of surface defects which are present as a consequence of the high dispersity of sample and it could not be detected by DTA.

The emanation method is complemented reasonably by DTA and EGA. These methods usually give the same information, but occasionally, as in the case above, additional data become available. On the other hand, the emanation method occasionally falls behind the others. It is particularly sensitive for variations in surface energies; Balek recently reviewed the principle, practice of method, and fields of applications.[170] Readers interested in additional detail will find his paper profitable.

C. Thermosonimetry and Thermoacoustimetry

The ICTA Nomenclature Committee suggested the classification of the measurement of temperature-dependent acoustic properties into two groups. Sonimetry measures sound-emission characteristics; while in acoustometry, characteristics of imposed acoustic waves are measured as a function of temperature after passing through a substance heated in a programmable way. Practically, variation of ultrasonic propagation time is measured in the latter case.[171] According to Lønvik[172] the actual signals under considerations are transient bursts of elastic distortion with a frequency range from audio up to several megacycles, depending on the processes and material in question. There are three readily measurable characteristics of sound emission upon heating:

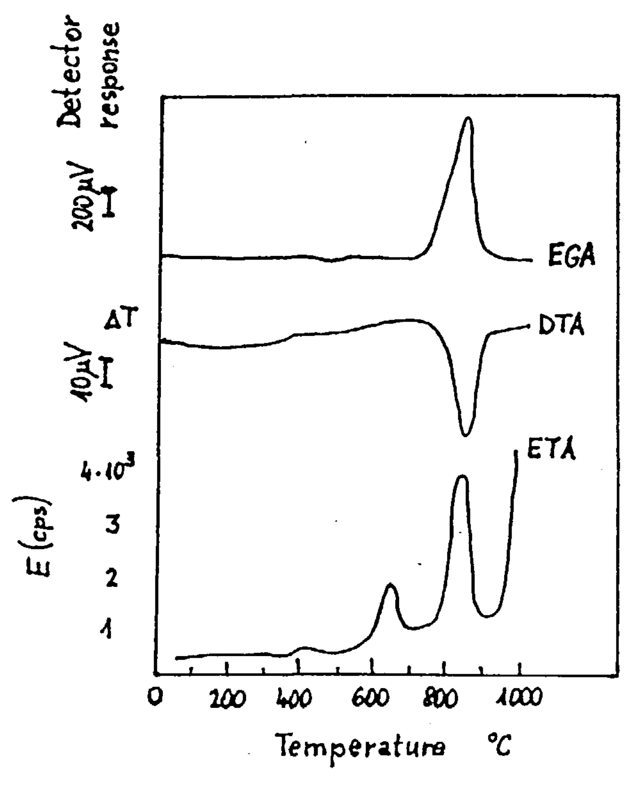


FIGURE 31. ETA, DTA, and EGA traces of calcium-carbonate (From Habersberger, K., Balek, V., and Srámek, J., *Radiochem. Radioanal. Lett.*, 28(4), 301, 1977. With permission.)

1. The mean rate of the appearance of burst events (cps)
2. The mean amplitude level of the signal
3. A direct frequency monitoring by the count of half cycles in the elastic vibrations

The measurement of the distribution of signal-frequency components has become an important part of the information; all of their quantities have to be simultaneously recorded as function of temperature. The resulting thermosonic curves will give a characteristic pattern and peaks reflecting the temperature-dependent processes in the sample. The sonic activity may be followed by:

1. The oscillations established in a specially built resonant stethoscope
2. Directly recording the actual signal of sample picked up and transmitted by the stethoscope as a sensor
3. An analog electric signal may be obtained by a conventional piezoelectric converter

The thermally excited elastic distortion is a rather complicated phenomenon. The difficulties are enhanced by the modulation caused by the response characteristic of the sensor itself. In the course of the measurement this modulation should be taken care of. The sound signals may be related to the following structural properties:

1. Thermodynamical properties — strength of the substance, crystal defects, structural damages, cleavage

2. Physical changes — polymorphic and phase transitions, chemical changes
3. Dynamics of migration processes — effects of sliding, flow of dislocations or diffusion, and partial displacements of constitutents by crystalization

Lønvik[174] and Clark[173] reviewed the method and technique (see Figure 32). This method usually gives the same information as DTA and DSC.[175] The recorded signals for individual transitions are complex and likely to bear additional information, but those could not have been recognized yet. The frequency distribution of signals may be remarkable: for instance, brucites of varying origin exhibit significantly different frequency distribution on dehydration.[175]

D. Measuring Dimension and Mechanical Properties of Samples

Both linear thermodilatometry and volume thermodilatometry are used to follow dimensional changes in one and three dimensions, respectively. The thermomechanical analysis (TMA) investigates the deformation of the sample on simultaneous heating and loading. When the load is not oscillatory then it is referred to as mechanical analysis and the type of stress should always be specified (compression, tension, torsion, flexure, etc.). On the other hand, when dynamic modulus and/or damping of a substance is measured under oscillatory load then it is consistent, particularly not for ignoring time dependence of defórmation phenomena. Such examples are non-equilibrium viscoelastic deformation or tixotropic and antitixotropic behaviors. Kambe is likely to be right in assuming that accepting the term TMA may be fortunate for instrument manufacturers and the users of these instruments. In any case, it is to be realized that these instruments are suitable because of their modular design for measuring dimensional changes upon both heating and stresses.

From elementary thermodynamics it is known that

$$dV = \left(\frac{\delta V}{\delta P}\right)_T dP + \left(\frac{\delta V}{\delta T}\right)_P dT \qquad (31)$$

$$dV = \beta\, VdP + \alpha_v\, VdT \qquad (32)$$

where

$$\alpha_v = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_P \qquad (33)$$

is the volume coefficient of thermal expansion and

$$\beta = \frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_T \qquad (34)$$

is the thermal compressibility. For the enthalpy change of system can be described as

$$dH = V(1 - \alpha_v T)\, dP + c_p dT \qquad (35)$$

Increasing temperature causes the bodies to dilate while cooling causes contraction, disregarding for the moment dilations and/or contraction induced by physical and chemical transformations. Isotropic thermal energy transfer produces uniform expansion in three dimensions, causing an isotropic change of volume. For structural reasons the dilation of sample may be anisotropic. In these situations measurements in different directions may be carried out, but averaging for three dimensions is also

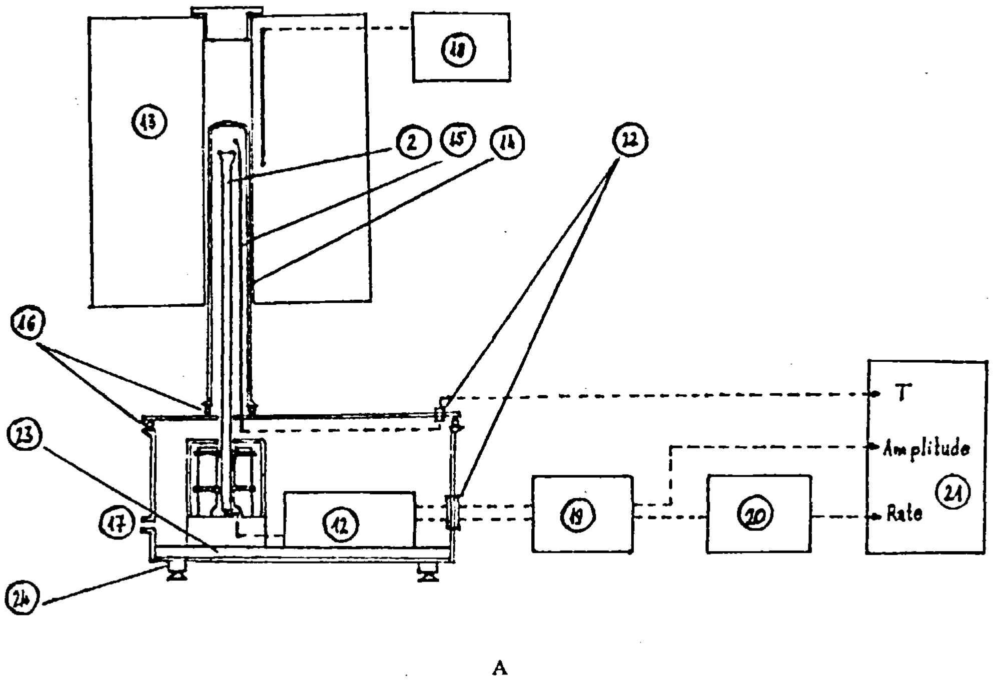


FIGURE 32. (A) General layout of a thermosonimeter. (12) preamplifier, (13) furnace, (14) silica sheath, (15) thermocouple (Pt/Pt, Rh), (16) silicone rubber vacuum seal rings, (17) vacuum/gas port, (18) temperature programmer, (19) main amplifier, (20) rate meter, (21) recorder, (22) vacuum leadthroughs, (23) acoustic foam, (24) vibration mounts. (B) Elevation of Waveguide assembly. (1) PZT transducer crystal, (2) silica waveguide, (3) sample platform, (4) sample cup (alternative to number 3), (5) steel ballbearings, (6) tension spring (shown for 1 ballbearing only), (7) adjustment screw (shown for 1 ballbearing only), (8) silvered resin, (9) steel base (recoil mass), (10) duralumin foil, (11) lead to preamplifier. (From Instrument News, Perkin Elmer Corp., 19(4), 8 (1969). With permission.)

possible. Linear thermodilatation measures in one direction alone; this method is suitable for bar, fiber, plate, and film samples to record changes in length or thickness. When the aforementioned method is carried out, α_v is almost constant in a given temperature range, so the recording has a baseline with a characteristic slope. When at a definite temperature there is a sudden change taking place, we could record either a step or a break. The step is characteristic of processes with enthalpy changes while the break reflects so-called second-order transformations. Obviously these are meaningfully valid for compressibility, also. Isotropy or anisotropy in α_v and β is a material property, and the temperature where sudden change occurs and the magnitude of that change is a material property as well. For example, in many solid-isotropic fluid-phase transitions, the volume change is around 15 to 20%, while for smectic liquid crystals the volume change associated with mesomorph-isotropic liquid-phase transition is only 3 to 5%.

It is important to study the deformation of many materials (polymers, fibers, structural materials, etc.) for changing loads. This sort of load, besides changing the volume and the shape of the sample, can produce discontinuity — a break. These properties may be studied in a sample with maintained load: for example, compression, measure of penetration, characterized softening properties, or, in special cases they are giving information on glassy transition. Flexure and tensile stretching may be important primarily for films and fibers. Also, it is important to study the creeping or, generally, the response for different strains. Temperature-dependent viscosity measurement belongs to this category also. For this measurement it is generally not enough to consider the

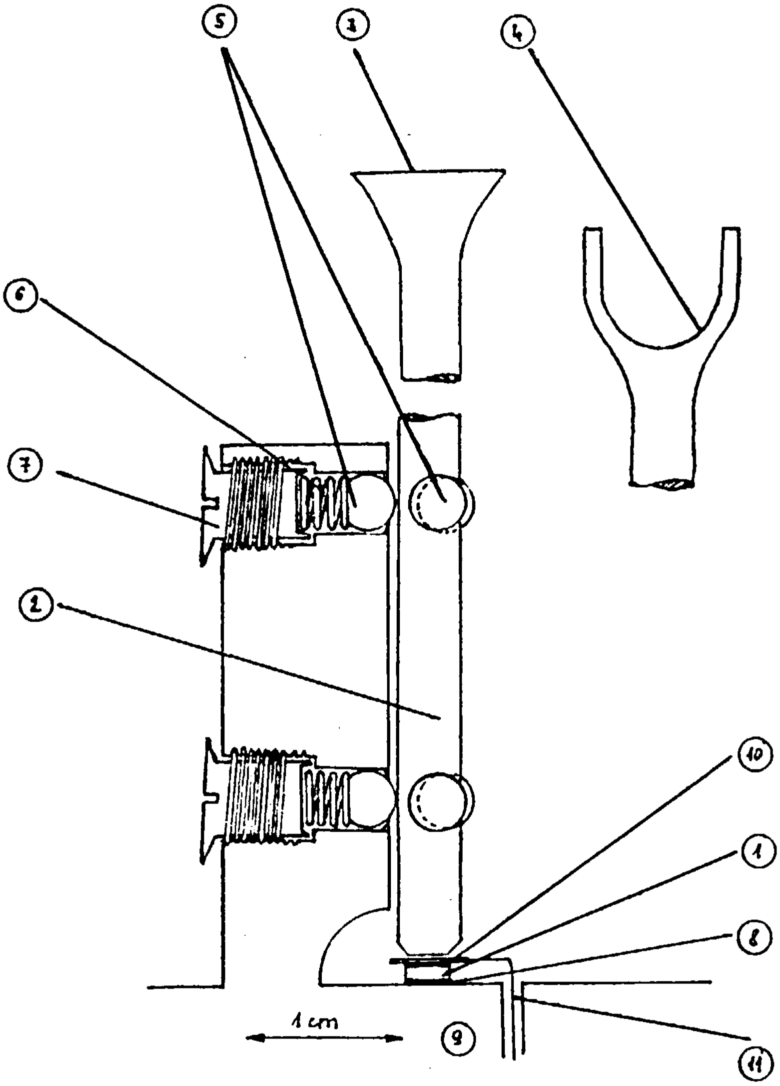


FIGURE 32B

effects of heats and external forces; time-dependent deformation should be studied also. In a case of no time-dependent effect, we have an equilibrium deformation that is elastic deformation, while in a case of time dependency we deal with a nonequilibrium situation that is viscoelasticity. Figures 33 and 34 show practical solutions for these measurements.[177,178] The instruments may be characterized usually that they have variable measuring heads, so both in loaded and unloaded state volume, linear dilation and other type measurements can be carried out, with alternating mechanical stress. Yalof and Hedvig[179] described a multipurpose equipment suitable to carry out DTA, thermoelectrical and thermomechanical (dynamic torsional, cyclic compressional, and creep included) measurements. Figure 35 shows for comparison an expansional and compressional curve together with DSC.

Paulik and Paulik[180] designed an adapter for simultaneous dilation measurements to derivatograph, working in quasi-isothermic, -isobaric condition, too. Dynamic

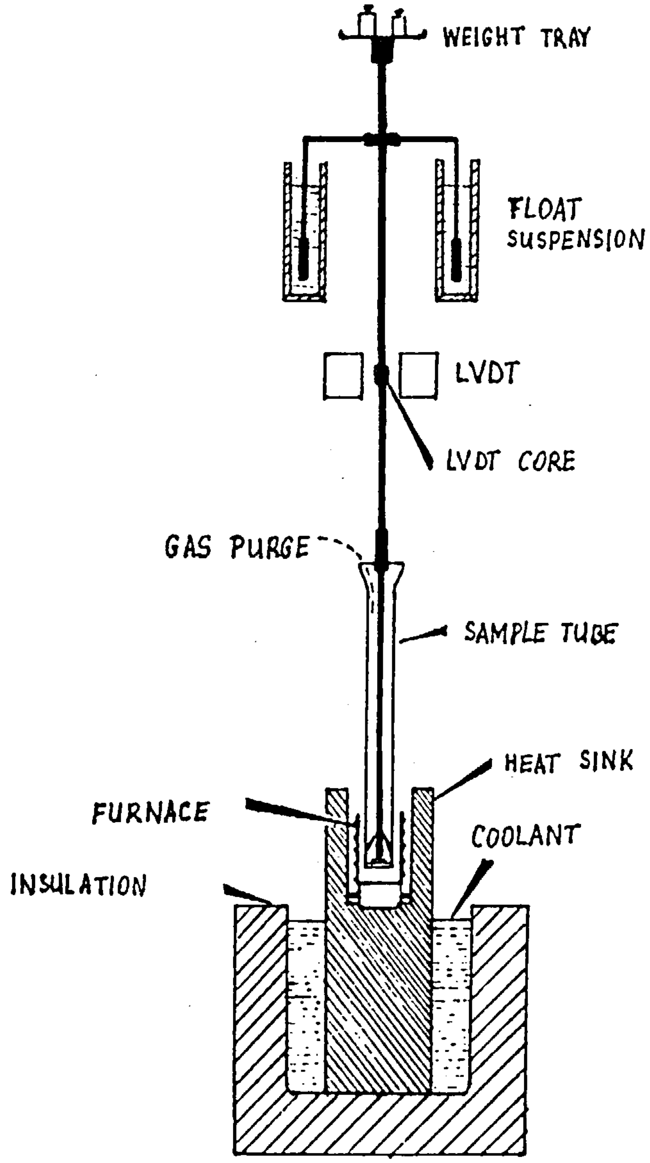


FIGURE 33. General view of a thermomechanical analyzer. (From Instrument News, Perkin-Elmer Corp., 19(4), 8, 1969. With permission.)

thermomechanometry is a somewhat different method. For the dynamic load there are some oscillation forces to be used. This measurement records the energy absorption or dissipation of a material as it responds to periodic or variable force field. E^x complex tensile modules may be obtained from tensile flexure measurement. $E^x = E' - iE''$ where E' is the tensile modulus, E'' is the loss modulus and $E''/E' = \tan\delta$ is the loss tangent or damping response. From torsional measurement we may obtain the corresponding shear moduli G^x, G', G'' and $\delta = G''/G'$ as a function of temperature.

This is a nondestructive technique suitable to study polymers, particularly those which are sensitive to crystallization or crosslinking. Vibration frequency is used either in the

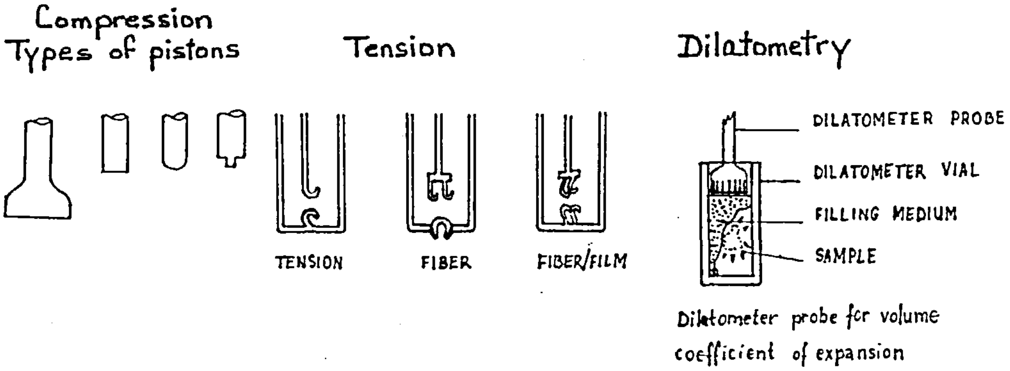


FIGURE 34. Various changeable accessories for TMA. (From Product Bulletin, Du Pont Co. With permission.)

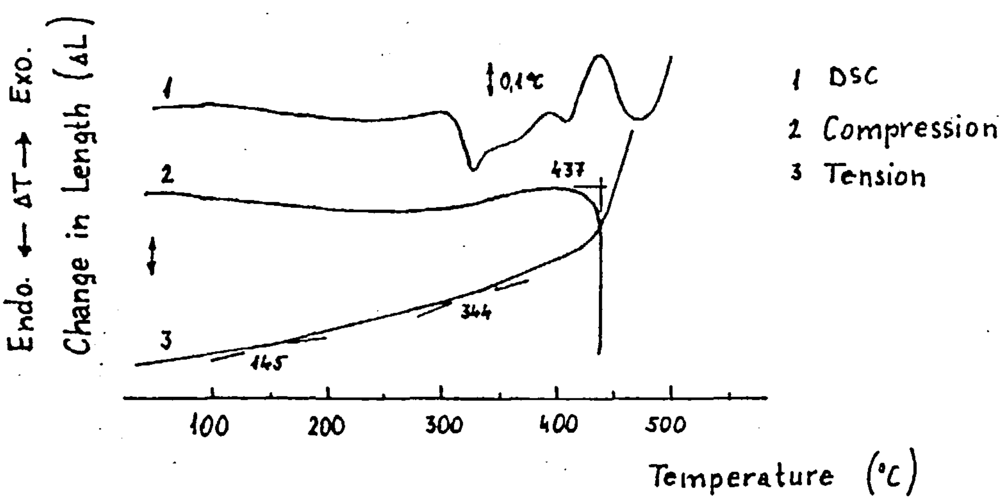


FIGURE 35. DSC, TMA measuring (tension, compression) on Lead Oxide Silica Glass. DSC sample size: 12.2 mg; DSC atmosphere: Air; DSC heating rate: 20°C/min; TMA heating rates — Compression: 5°C/min; Expansion: 10°C/min. (From Product Bulletin, Du Pont Co. With permission.)

range 0.01 to 10 cps or 10 to 1000 cps. In the latter case, Young's modulus and the damping factor may be calculated.

A novel approach in dynamic method is the torsional braid analysis (TBA).[181,182] A very small sample is used as the torsional pendulum freely oscillates in the temperature range of about 200 to 900 K. The sample is supported on an inert multifilamented substrate (the braid). Solid, melted, and glassy states may be investigated this way. The excitation taking place by torsional frequency, the conversion of mechanical oscillation into an electric analogous signal is carried out by a transducer. The transducer operates on the basis of electro-optical principle. Since measurement takes several days and more than 1000 dampened sine waves are generated, data collection, reduction, and processing requires a computer which also controls the operation of equipment. The method determines the relative rigidity and the mechanical damping index as a function of temperature. Each peak in the thermal spectrum obtained corresponds to various properties of the polymer.

The TBA is a complex, expensive, and time-consuming technique for polymer investigations. It is unlikely that this will be used widely in the near future.

E. Thermal Electrometry

This is a thermoanalytical method to study electrical properties of materials. Both AC and DC measurements could be applied to produce an electric field, and either gross macroscopic properties (e.g., phase transition) or changes on the molecular level may be studied as a function of temperature. Conductivity, dielectric constant, and polarization properties are most frequently measured. For example, during polymorphic transformation the transient conductivity may increase. Here we have a peak-type signal, while in the case of phase transition, because of the substantial steady change in structural order, the signal is stepwise. The change in low-frequency AC conductivity with temperature can yield information on the activation energy for carrier mobility, on the formation energy of point defect, and on the relation between structure and conduction mechanism. On the other hand, changes of the dielectric constant (ϵ') of a molecule in a high-frequency field (i.e., dielectrometry) may arise from changes in orientational freedom of its component molecules or groups of molecules brought about by a chemical reaction or phase transition. The variation of ϵ' with frequency can also be studied to give information on the magnitude of dispersion brought about by polarization by various mechanisms. Peaks in the dielectric loss factor (ϵ'') or loss tangent ($\tan \delta = \epsilon''/\epsilon'$) as a function of temperature or frequency can lead to the study of dielectric relaxation mechanisms which correlates with the defected model of the sample.

From the point of structural data, low-temperature measurements are particularly important. Rajeshwar et al.[183] call attention to the inherent polarization effect in cases of compounds with significant ionic interaction, which makes the interpretation of data obtained rather difficult. They also mention experimental difficulties from the point of the nature of dynamic thermal analysis. According to the authors, it is difficult to realize a continuous recording for most of the cases since bridge arrangements are used and they are operated manually in a stepwise manner. The frequency sweeps for bridge circuits are usually hindered. These statements are overestimating the problems and pioneering activity of authors[184] as well. Let us mention that the authors of this review published results in 1973 on continuous conductivity measurements,[185] and there are also other papers[186-189] dealing with the same subject. According to Chiu,[189] ETA operated in either DC or AC mode offers the following fields of application:

1. Measuring the electrical parameters, together with the respective thermal coefficients to characterize the sample
2. Study of physical transitions
3. Contribution to structure elucidation, primarily for solids
4. Investigation of polymer degradation
5. Study of moisture, impurity, etc., effects
6. With the additional parameter of frequency, the electric technique provides more insight into the segmental motions of molecules and relaxation phenomena.

We present a few examples, as follows. In Gray's book the thermoelectrical techniques for investigating liquid crystals is reviewed.[190] Meisel et al.[191] found and qualitatively interpreted a conductivity memory effect in thermoelectric behavior of smectic mesomorphic fatty acid salts. In this case the low-frequency conductivity of the mesomorph phase is influenced by the cooling rate applied during transition from isotrope to mesomorph state. This finding occurred mainly in the case of Thallium (I) salts and varied with cell geometry, with the occasionally applied shear force, and with the dimension of fatty acid molecules. The result is shown in Figure 36. It should be noted that combined DTA-ETA technique is suitable for investigating complicated polymorph and phase transitions. Klingbiel et al.[192] described dielectric and conductivity anisotropy as a function of temperature. The signal shapes highly depend on molecular structure.[193]

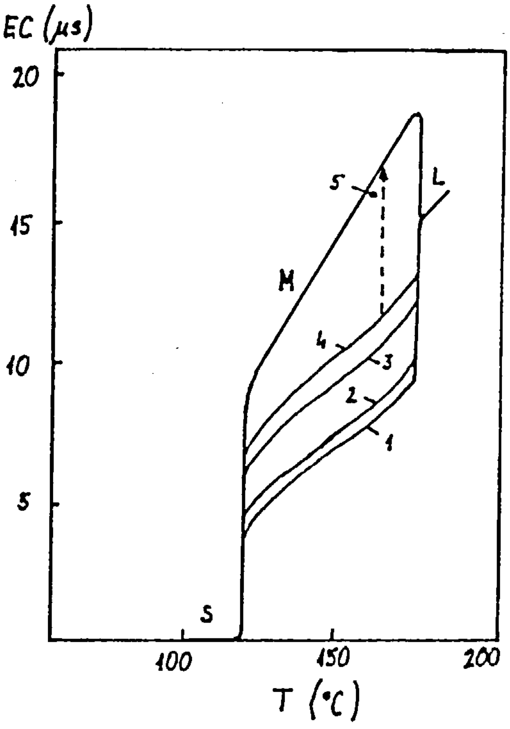


FIGURE 36. Thermoelectrical conductivity of thallium miristate with different cooling rates (indicated) applied at transition from i. liquid into mesomorphic phase. 1 = 0.5, 2 = 1, 3 = 5,4 = 8°K/min, 5 = effect of sheer force; S = solid; M = mesomorphic; L = i. liquid phase. (From Halmos, Z., Meisel, T., and Seybold, K., *Proc. ICTA Budapest*, Vol. 2, 1974, 429. With permission.)

This method is widely used in polymer investigation. The users refer to their equipment as a dielectric spectroscope. Storage and dissipation of alignment energy may be measured, due to the surrounding dipoles electric field, which are termed capacity and dissipation, over a range of frequency up to 100 kHz.[179]

Thermoelectric measurement of metals and semiconductors contributed substantially to revealing their fine structure. Because of the many aspects of this area, we could not discuss it in the present review.

It should be emphasized that evaluation of results is not always easy. The measured values are influenced by many subsidiary circumstances. Significant uncertainties may arise from impurities, solvent, moisture, changes in electrode surface, surface phenomena, non-reproducible contacts, gas evolution, etc. Despite all this, in several cases valuable information, inaccessible by other methods, may be obtained by thermoelectric measurements.

F. Thermooptometry

Methods of thermal analysis used for measuring the optical characteristics of a sample as functions of the temperature belong in this group. In general three properties, the transmittance, reflection, and thermally initiated light emission (luminescence, or in the presence of oxygen, chemiluminescence) are measured.

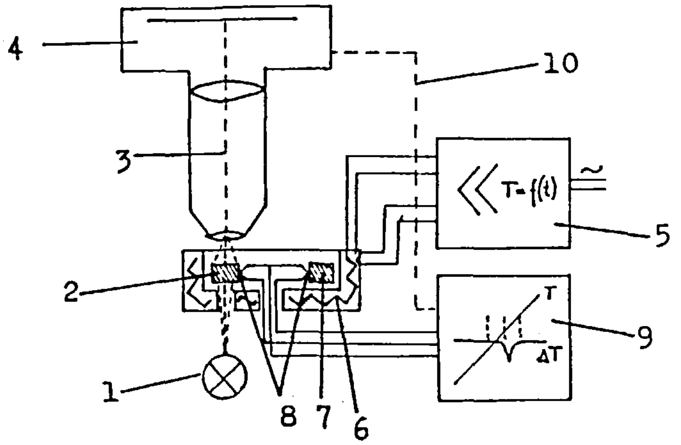


FIGURE 37. Schematic view of a hot stage microscope combined with DTA. (1) light source, (2) sample, (3) microscope, (4) camera, (5) temperature controller, (6) heater, (7) reference, (8) thermocouples, (9) recorder, (10) event marker. (From Schultze, D., *Thermochim Acta,* 29, 233 (1979). With permission.)

Thermomicroscopy, which is also considered a thermooptical method, is a visual observation of the thermal behavior of a sample under the microscope. In designing the technique of measurement of thermooptical phenomena in the preliminary estimation of the information expected, it should be considered that the wavelength of the light can also be used as a dependent variable in addition to the measured property which is temperature dependent.

The thermomicroscope has long been used as an efficient laboratory tool. An improvement of the technique was brought about by the simultaneous use of a DTA apparatus, and by the construction of high-temperature, hot-stage variations. The field of application became wider with the use of polarized light and interference filters. The use of microscopes with polarized light enabled the phases of compounds with liquid crystal structure to be investigated.[190] This way wonderful colors, motions, and shapes can be observed and studied, and observation can be completed by photographic or cinematographic recording. In Figure 37 a thermomicroscope is shown which can be operated simultaneously with a DTA device. Construction problems may arise due to the fact that microscopes for higher temperature ($\geqslant$800 K) have to withstand a high thermal load. Therefore, a special arrangement has to be chosen in which the distance between the microscope and heating block is optimal.

A survey of high-temperature microscopy has been presented by Heide[195] with special regard to the investigation of solid-phase reactions, in which the optical properties of solids and the possibilities of their measurement by a microscope have been dealt with.

Refractive index and its anisotropy are properties which are most often measured as functions of the temperature. If some structural characteristics are intended to be elucidated this way, the dispersion (the dependence on wavelength) is also to be investigated. A measurement technique and data-processing procedure has been described by Karawacki and Gustafsson[196] for measuring refractive indexes of inorganic melts at high temperatures. The birefringence phenomena of smectic mesophases have been studied by, among others, Pelzl and Sackmann,[197] with the aim of characterizing the molecular structure and phases.

A different but important thermooptical technique is the investigation of the reflection of solid samples. The total reflected radiation from a mat surface, R_T, consists in general of two components:a regular reflectance component (called surface or mirror reflection) and a diffuse reflection component R_∞. R_T is due to the reflection at the surface of single crystallites; R_∞ is produced from the radiation penetrating into the interior of the sample and turning back to the surface after some extent of scattering. The theory, instrumentation, and application problems of reflection spectroscopy have been summarized by Wendlandt.[198] In our opinion the method provides useful information about changes taking place at solid surfaces if the reflection properties of the sample are studied as functions of both the temperature and the wavelength.

Heat-initiated emission brought about by continuous radiation can be studied by the method of thermoluminescence, and by thermochemiluminescence. In the course of the measurement the so-called glow curve can be recorded (i.e., the plot of the intensity of the emitted light against temperature). This could be used to investigate trap energies existing in solids. The detailed relations of the traps and luminescent centers is still under discussion, but it is clear that electrons may be excited to traps by any ionizing radiation. Thermoluminescence is therefore a function of both the radiation environment and the thermal history of a substance.[199] The use of a strictly linear temperature program is essential as irregularities may result in spurious peaks on the glow curve.

The method was used for studying geological samples and polymers, in some cases coupled with simultaneous DTA. The technique has been used by Nambi et al.[200] for investigating lunar and meteorite samples. Although the method might provide special information and is relatively simple, it is mainly used in solid-state physics. The interpretation of the phenomena needs further theoretical investigations.

Other thermooptical methods, such as the study of infrared spectra and others as functions of the temperature, will not be treated here as they may be considered special cases of the basic techniques.

G. Thermomagnetometry

If a substance with magnetic properties is placed into a magnetic field, attracting and repulsing forces may arise which can be measured by means of a balance as they are manifested as an apparent mass change. The magnetic susceptibility of a sample may also depend on the temperature. The method in which the susceptibility is measured as a function of the temperature is called thermomagnetometry. The temperature dependence of magnetic susceptibilities of various types of materials is shown in Figure 38.

Different magnetisms arise from different atomic and crystal structures in the material, and consequently the magnitude and temperature dependence of various magnetic susceptibilities also differ. It is to be noted that magnetic properties of semiconductors and refractories show a more complex temperature dependence. The measurement is based on the Faraday principle. Accordingly, if a sample with small mass is placed into a uniform magnetic field with a gradient dH/dz in the direction of the force moment, the force on the sample is given as

$$F = \int_{H_0}^{H} \chi\, m H \frac{dH}{dz} \qquad (36)$$

where m is the mass of sample, χ is the specific magnetic susceptibility, and H is the magnetic field strength. In general the absolute values of χ need not be known, if only the changes are to be studied. In practice, most often the ferro-to-paramagnetic transition is investigated, i.e., the Curie point is determined. The phenomenon is the base of the best temperature calibration process in thermogravimetry (Figure 39).[201]

An interesting measurement has been described by Simmons and Wendlandt[202] (Figure 40). The thermal decomposition of the complex $Co(NH_3)_6Cl_3$ was studied by

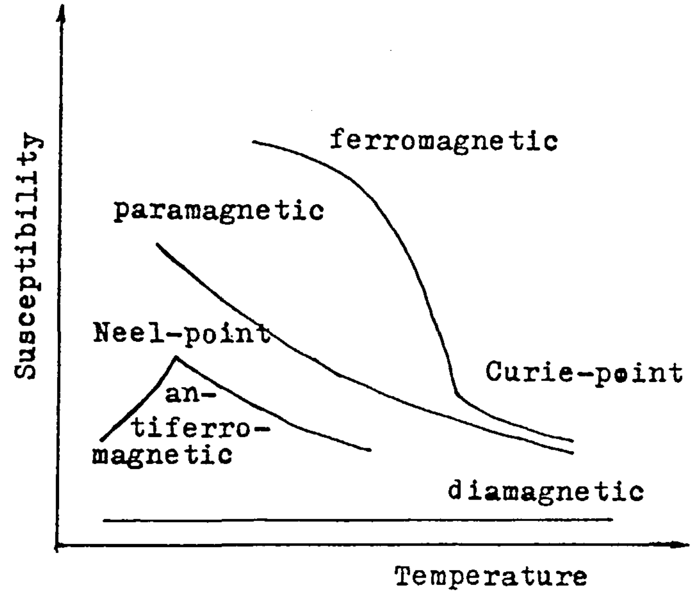


FIGURE 38. Dependence of different type magnetific susceptibilitics on temperature.

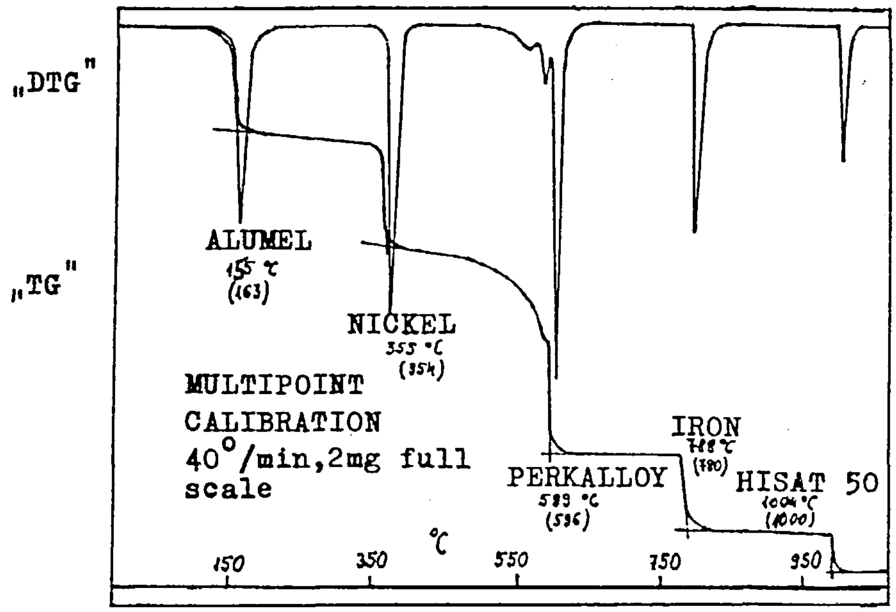


FIGURE 39. Typical multi-point calibration run of five ferromagnetic standards. Recommended as temperature standard for TG. Temperatures in brackets are true transition temperatures. (From Norem, S. D., O'Neil, M. S. O., and Gray, A. P., *Thermochim. Acta*, 1, 29, 1970. With permission.)

TG, in a temporarily applied magnetic field, enabling the transformation of the paramagnetic Co(III) to form diamagnetic Co(II) to be detected during the decomposition.

The magnitude of the signal depends on the sensitivity of the balance, the strength of

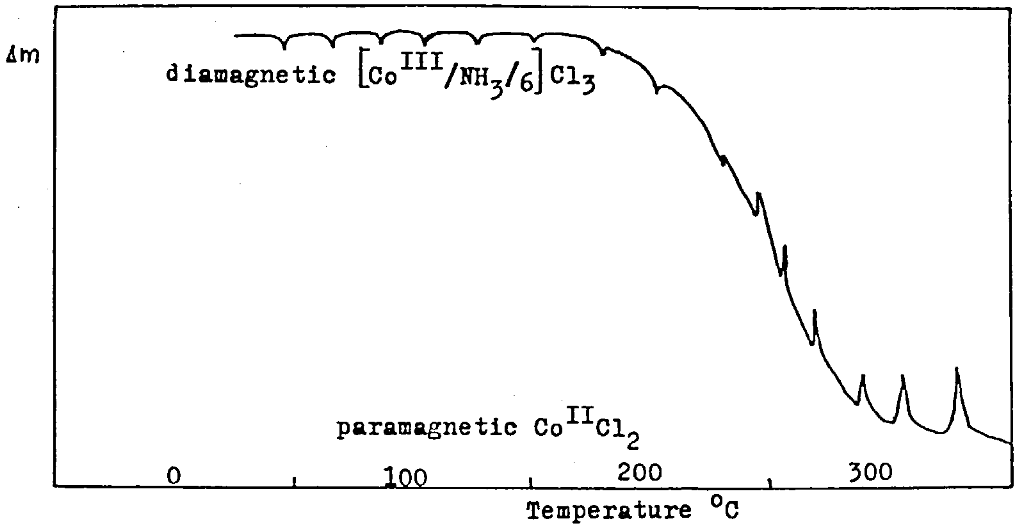


FIGURE 40. Combined TG and thermomagnetic measurement of decomposition of Co(III) $(NH_3)_6$ Cl_3. (From Simmons, E. L. and Wendlandt, W. W., *Anal. Chim. Acta*, 35, 461, 1966. With permission.)

the applied magnetic field, and the nature of the magnetism. Accordingly, the measurement has to be designed in advance. Magnetic transitions as secondary changes can also be studied by the DTA-DSC method, giving rise to peaks or causing peak displacement.

Thermomagnetometry has a relatively narrow range of application but it provides valuable information on a special property.

VII. CONCLUSION

The future expected trends of development and application can be summarized as follows, based on intuition and the present state of the field:

1. With respect to instrument development, modular systems are expected to spread further, and more complete instrument families are likely to appear on the market. Efforts will also be made to increase sensitivity, to enable sub-milligram samples to be studied, and to introduce fast measuring techniques. Computers will be of general use in data acquisition, conditioning, processing, and storage. In special cases, on-line computerized data processing and possibly control can be expected. Special solutions of C-P units with microprocessors may also be expected. In the opinion of the authors, new techniques based on new principles are not likely to develop, but improvements in multiple techniques and new instruments are to be expected.
2. With respect to the theory, a development may be brought about in the interpretation of the phenomena by the adaption of the concepts of irreversible thermodynamics and the use of its mathematical apparatus. This may lead to a more exact theoretical treatment. It is rather difficult to predict the future of thermokinetics. No appreciable development can be expected if the present views and evaluation methods remain unchanged. It might help if the effects of external factors influencing the rate of reactions could be eliminated by a suitable experiment and instrument design, if the rate of a given reaction could be studied and determined

separately. The results provided by the different methods of thermal analysis will promote the elucidation of the fine structure of solids. It seems probable that the proportion of papers of descriptive nature also will decrease in the field of thermal analysis.

3. Regarding applications, the methods of thermal analysis will find use in the investigation of the thermal behavior of new compounds in cases where it provides valuable theoretical and practical information. We believe that, increasingly, it will become a standard method of material control. A method becomes really useful if it also serves practical purposes. This is highly probable in the case of thermal method of analysis; it will be used as a routine method in quality control as a process control method in various technologies. Its role as a tool of theoretical research will also increase.
4. Last but not least, thermal analysis has become part of the curriculum at universities. If graduating chemists are familiar with these methods, a further development of the field is to be expected.

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