

RECENT TRENDS IN THERMAL ANALYSIS

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ABSTRACT

After a brief survey of events of the past fifteen years, the author outlines four areas which currently call for attention, namely nomenclature, quality of literature, the need for trained personnel and an expansion of thermal analysis into quality control and other fields outside the research and analytical laboratories.

The application of low temperature DTA techniques to carbon tetrachloride, cyclohexanol and glycerides is discussed. The potentialities of DTA-mass spectrometry are outlined and the application of one experimental arrangement to a study of polyvinylalcohol is described. The possible use of DTA or DSC in purity determinations of organic compounds is outlined.

INTRODUCTION

To be concerned with recent trends in thermal analysis, one is involved not only with an examination of the facts and figures of the last decade or so, but also with the workers in the field. I therefore wish to commence by paying tribute to two outstanding and well-known thermal analysts, who have died recently, each of whom has made a distinctive contribution to thermal analysis and from whose work some of the trends, which will achieve greater importance in the future, have found their inspiration.

The first of these, Robert LeGrand Stone, holder of the Second Mettler Award in Thermal Analysis, died on 10 October 1969. Although relatively few publications are credited to him, his influence over the past decade and longer has been considerable in two aspects, namely the technique of DTA and its instrumentation. R. L. Stone had a clear understanding of the effect of atmosphere on decompositions and pioneered the technique of the dynamic atmosphere¹⁻⁴. *Figure 1* shows schematically an early Stone equipment in which it is possible for the atmosphere to flow directly through the sample. This gives intimate contact between solid and gas, to ensure complete reaction, and it also means that where volatiles are evolved from the solid they are swept out from the site of the reaction immediately to reduce the possibility of any recombination reactions. Such work opened the way towards meaningful DTA studies on catalyst materials⁵. In the West the name of the R. L. Stone Co. (now part of Tracor Inc.) is associated with highly sophisticated instrumentation for DTA and latterly for TG, which incorporated facilities for close atmosphere control which his own studies had shown to be of such value. Amongst other features which were noteworthy was that of thermocouple design⁶. R. L. Stone's work on thermocouple ring design and on the use of small samples has led to much

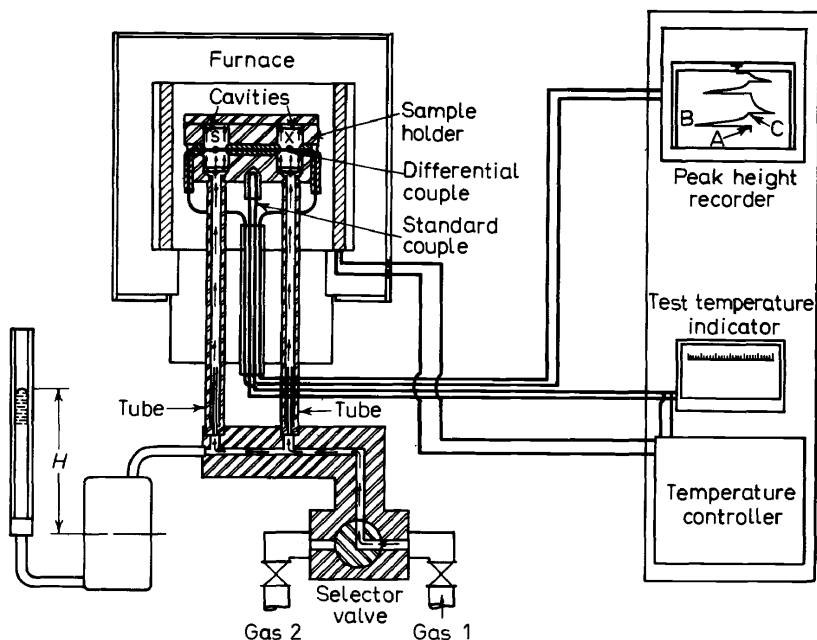


Figure 1. Schematic illustration of the Stone DTA apparatus.

commercial instrumentation adopting similar arrangements with consequent advantages for DTA operators.

The second of these, Laszlo Erdey, died on 21 February 1970. There is no doubt that this very Conference, with one section devoted to thermal analysis, was inspired by his work and that of his colleagues. In 1954 and 1955 some significant Hungarian patents⁷⁻⁹ appeared. The first two of these covered derivative thermogravimetry whilst the latter covers derivatography (in which the techniques of TG, DTG and DTA were brought together and applied simultaneously to a single sample). From that period on a steady stream of publications has appeared under the authorship of the Hungarian School; these cover many fields of chemistry and indicate the tremendous depth of thermal analysis as a technique. A more recent review¹⁰ highlights the thinking which led to the development of this simultaneous instrument. 'DTA gave, in general, high resolution peaks, occurring at well-defined temperatures, but it is, however, more tedious and less accurate to determine the quantitative composition of a sample from the DTA curve. With TG the situation is reversed as regards the accuracy. The resolution of the method is very low, and therefore it is very difficult to identify the components by means of the TG curve. For the purpose of quantitative analysis, however, TG is the most suitable of all the thermal methods of analysis. . . The numerical values of the measured weight changes express the stoichiometric relationships of the reactions, and therefore exact calculations can be made. . . Hence it seemed that if the DTA and TG methods were used simultaneously, they could well complement each other. . . The methods of thermal analysis

were used singly by thermoanalysts up to the late 1950s, and with few exceptions simultaneous thermoanalytical studies were not carried out.' This combination of techniques, as in the derivatograph, was considered unfashionable, but with the clearer understanding of the dynamic nature of TA investigations, of the influence of such factors as atmosphere, and of the increasing sensitivity of commercial equipment leading to the use of smaller sample sizes, many manufacturers have since introduced simultaneous equipments some ten years after the pioneering work of Erdey and his collaborators.

Then

The last fifteen years can be labelled as a period of growth, and it is instructive just to pause to consider the tremendous changes which have occurred in the TA scene in that time.

(i) *Publications*—By 1960 only relatively few books on any aspect of TA had been published^{11–15}, whereas in the following ten years some 25 or more books have been published¹⁶. A survey of literature¹⁷, commenced in 1962, then listed some 700 to 800 papers on the subject appearing in a year, whereas now the rate is around some 2500 to 3000 papers a year.

1969 and 1970 have seen the launching of two journals which are concerned primarily with thermal investigations^{18, 19}.

(ii) *International and national associations*—1962 and 1963 were years in which, in the U.K., short courses and symposia on thermal analysis became very popular. On two of these courses I found myself as one of the lecturers, along with, amongst others, Dr R. C. Mackenzie of the Macaulay Institute for Soil Research, Aberdeen. Certain discussions took place in which it was suggested that it would be valuable to hold an international conference. This led to the holding in 1965 of the First International Conference of Thermal Analysis in Aberdeen, Scotland²⁰ and to the formation of the International Confederation for Thermal Analysis, (ICTA). The Council of ICTA at that time set up three specialist committees, namely Nomenclature, Publications and Standardization. All three have already covered a great deal of ground. For example, the Nomenclature Committee has already reported to the Second Conference²¹ and its recommendations are being adopted by many bodies. Specialist groups working in different countries have been adopting the terminology for use in their own language. Parallel to the establishment of ICTA has been the inauguration of national groups in many countries; to mention a few: U.S.A. and Canada (N.A.T.A.S., the North American Thermal Analysis Society), Italy, Japan, U.K. (T.A.G., the Thermal Analysis Group of the Society for Analytical Chemistry), Russia.

(iii) *Manufacturers*—At the time of preparation of Smothers and Chiang's book¹⁵ there were relatively few manufacturers of thermoanalytical equipment, so that these authors spent a great deal of space in describing particular DTA equipment in different laboratories, whereas Mackenzie's recent book lists some 32 manufacturers concerned with DTA equipment²² and some 22 manufacturers concerned with TG equipment and five with simultaneous TG and DTA equipment²³. Thus, save for specialized requirements, e.g. for extremely high temperature or pressure, or for corrosive atmosphere work,

it is now conventional practice for workers in the field to purchase commercially available material. Relatively few papers are now published on instrumental aspects of TA. Equally significant have been the fundamental design changes over the last period, whereas at the commencement most instruments were large, cumbersome to operate and often free-standing, modern designs, incorporating a considerable number of electronic components are compact, relatively light in weight and perhaps most significantly much easier and more reliable to operate.

(iv) *Diversification of application*—Early applications of TG and DTA were primarily in three main areas, namely metallurgy, mineralogy and analytical chemistry. In 1961 C. Duval could write in his preface to the second edition of his book²⁴: ‘Up to the present it has been analytical chemistry which has profited from the recent progress of thermogravimetry, and this is the reason the word analysis has been retained in the title, but the reader will discover that this edition deals also with kinetic studies, investigations of catalysis, reactions in the solid state, and studies of the behaviour of standard materials for titrant solutions, and also of various substances which are not employed in analysis.’ A number of manufacturers publish applications sheets and a recent list included the following: polymers, pharmaceuticals, cements, catalysts, glass, medical and biological applications, fats, metallurgical applications²⁵, which serves to illustrate the tremendous diversity of applications which have been studied usefully by thermo-analytical methods.

Now

Such marked growth is not accomplished without growing pains and problems and there are four areas which I want to highlight:

(i) *Quality of Thermal Analysis literature*—There are two aspects on publication of papers and books to which I would like to refer. The first of these is that there is a lack of good introductory texts in this field. In spite of the considerable number of books published, only two or three can be classed as introductory texts^{26, 27}. The second comment refers to the standard of published papers. I believe that the two journals in this field^{18, 19} have a very important role to play in maintaining a high standard so that TA is not debased in any way.

(ii) *Need for trained personnel*—In many places now more is being done to introduce students and industrial chemists to the possibilities of thermo-analytical techniques. In the U.K., for example, two Easter Schools, one in 1965 and one in 1970, have been organized by the Thermal Analysis Group of the Society for Analytical Chemistry, and a number of short courses and graduate courses do include TA as a subject. Nevertheless much ground here needs to be covered to make chemists and others aware of the field.

(iii) *Is Thermal Analysis only for research*—Whilst it is true that papers have appeared which cover an extremely broad field of applications for TA, it is true that, in general, TA has not, except in a few isolated cases, become adopted as a worthwhile technique outside the research or analytical laboratory. There are, however, numerous diagnostic and quality control areas to which it can be applied, e.g. to the study of catalyst materials and performance²⁵ and to the blending of fats and oils²⁵. It is hoped that scientists and

manufacturers will take time and trouble to outline the potential applications to quality and process control laboratories.

(iv) *Sensible nomenclature*—The Nomenclature Committee of ICTA has made certain recommendations²¹ and further suggestions are in the process of being drafted. In the main the Committee has sought to adopt the best available practice, but the literature is still full of some unfortunate usages. For example, the terms thermogravimetric curve or TG curve and derivative thermogravimetric curve or DTG curve are to be preferred to the following all of which have appeared in the literature from time to time: thermogravimetric analysis curve, thermolysis curve, thermoweighing curve, thermogravigram, thermoponderogram, thermogram, differential thermogravimetric curve, differential thermogram, derivative thermogram and polytherm.

SOME SIGNIFICANT AREAS

From the preceding broad sweep I propose now to consider three areas which are likely to achieve considerable importance in the next decade. It seems unlikely that this period will show the marked growth that has characterized the previous fifteen years, but nevertheless there will be consolidation and perhaps growth of a less spectacular nature.

(i) *Low temperature applications*

Low temperature is here defined as temperature below ambient, i.e. from liquid nitrogen (or other suitable coolant) to around $+20^{\circ}\text{C}$. Thus the experiments require some form of cooling to be introduced of necessity. TG work below ambient does not seem to have been attempted save in the study of the freeze drying of foods, but DTA has been widely applied. It seems that the first workers in the field were Taylor and Klug²⁸. These workers studied molecular rotations in copper sulphate pentahydrate. Their apparatus is shown in *Figure 2*. The specimen holder was cooled by solid

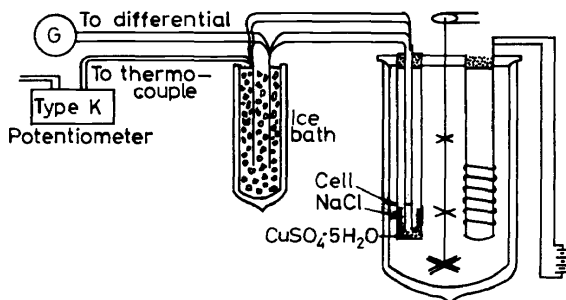


Figure 2. Apparatus for sub-ambient DTA by Taylor and Klug²⁸.

carbon dioxide. Some 25 to 30 runs were made at different heating rates. Sample size was around 1.5 g and sodium chloride was used as a reference material. The paper did not, however, reproduce any curves below 10°C since they found no reportable peaks below that temperature. *Figure 3* shows a typical curve obtained on their apparatus. Another early paper, by Jensen and Beever²⁹, dealt with low temperature transformations in

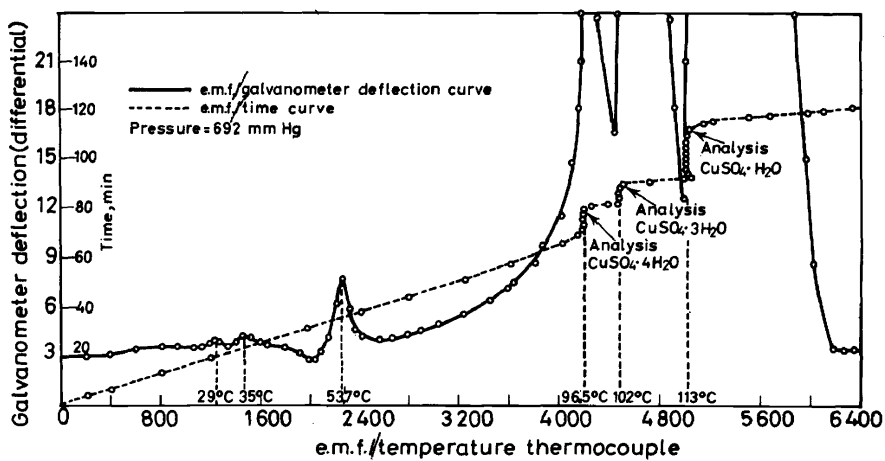


Figure 3. DTA curve for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ obtained by Taylor and Klug²⁸.

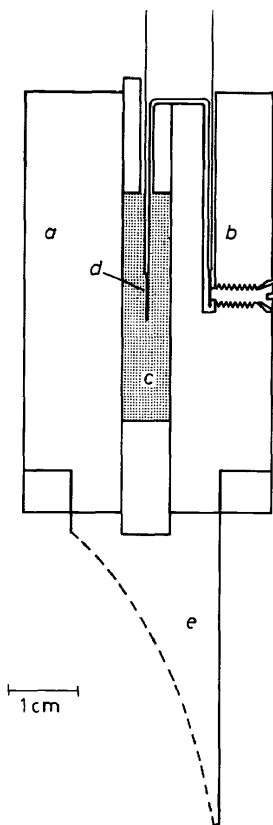


Figure 4. Apparatus for sub-ambient DTA by Jensen and Beevers²⁹. (a) copper block; (b) reference copper-constantan thermocouple; (c) sample; (d) sample copper-constantan thermocouple; (e) copper foil nib so shaped that lowering system by an electric motor into a Dewar vessel containing liquid air gave a linear temperature/time curve.

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inorganic materials. Their apparatus is shown in *Figure 4* and their results for hexammino nickel(II) nitrate $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$, are shown in *Figure 5*. They detected an endotherm at -28.6°C . They were unable to reproduce the work of Taylor and Klug on copper sulphate pentahydrate.

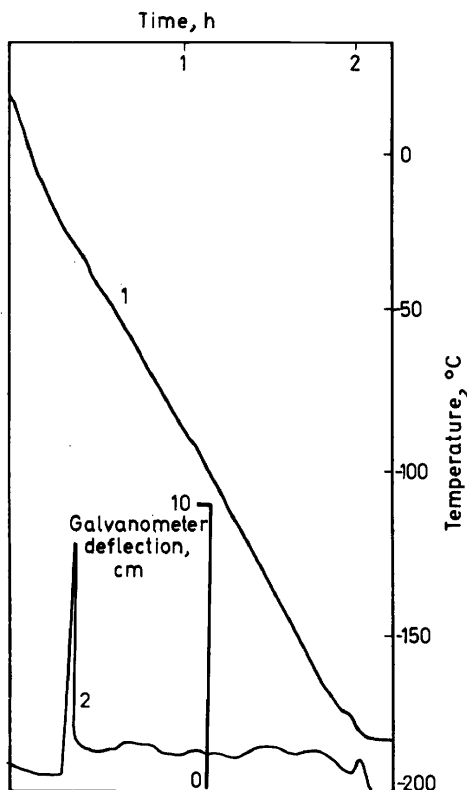


Figure 5. Temperature/time (1) and DTA (2) curves for $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ using apparatus shown in *Figure 4*.

Subsequent literature on low temperature DTA appears to be sparse, and the only review to date is that of Bohon³⁰. Applications and work are now going on in the study of first and second order transitions of simple compounds. There is heavy usage in industrial laboratories in the study of the glass transition temperatures and crystalline behaviour of polymers and elastomers. Low temperature DTA has been applied successfully to the study of the softening points of oils and fats. There are a few reports of work of biological interest whilst it seems likely that both atomic energy and space research projects will have important outlets for the technique. Much of the published work has been carried out on specially constructed instruments, and it is only comparatively recently that manufacturers have introduced equipment suitable for sub-ambient use. Three examples will be quoted of low temperature investigations.

(a) *Carbon tetrachloride*—Carbon tetrachloride melts at -22.88°C and is reputed to have a crystalline inversion from a low temperature (rhombohedral) form to a face-centred cubic form at -47.7°C . Japanese workers³¹ have used DTA to show that the crystallization behaviour is significantly dependent upon cooling rate. Bohon³⁰ has further investigated this phenomenon. The curves of *Figure 6* were obtained with carbon tetrachloride

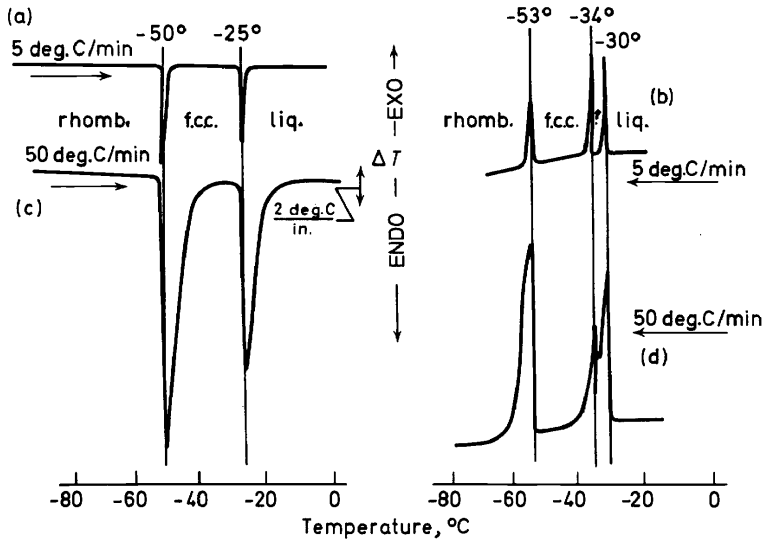


Figure 6. DTA curves for carbon tetrachloride in helium atmosphere using a modified Du Pont 900 DTA cell. Sample suspended on silicon carbide in a 4 mm tube.

suspended on silicon carbide in a modified Du Pont 900 apparatus. The heating curves (run at 5 deg.C/min and at 50 deg.C/min) show a single crystalline transition at -50°C and a melting endotherm at -25°C . On the cooling cycle there are, in addition to the -30°C freezing exotherm, two first-order transitions, one at -34°C and one at -53°C . This behaviour suggests that a metastable stage forms first on freezing, which converts to the cubic form and that this transforms to the face-centred cubic form at -53°C . *Figure 7* shows similar curves run on a Perkin-Elmer DSC-1B with sealed cups. The carbon tetrachloride was again suspended in silicon carbide. Whilst the heating curves were essentially identical, the cooling curves show a higher resolution and indicate a very complex crystalline behaviour. There are clearly defined transitions at -40° , -54° , -56° and -58°C . When no silicon carbide is present the cooling curves (*Figure 8*) are very similar to those shown on *Figure 7*, perhaps with some improvement of resolution. However, the heating curves now show a multiplicity of transitions. *Figure 8(i)* was obtained after the encapsulated sample had been quench cooled. These results indicate that the crystalline behaviour of carbon tetrachloride is somewhat more complicated than first reported³².

(b) *Cyclohexanol*—Cyclohexanol has also been studied in some considerable detail^{30,33}. *Figures 9* and *10* indicate the extreme complexity of

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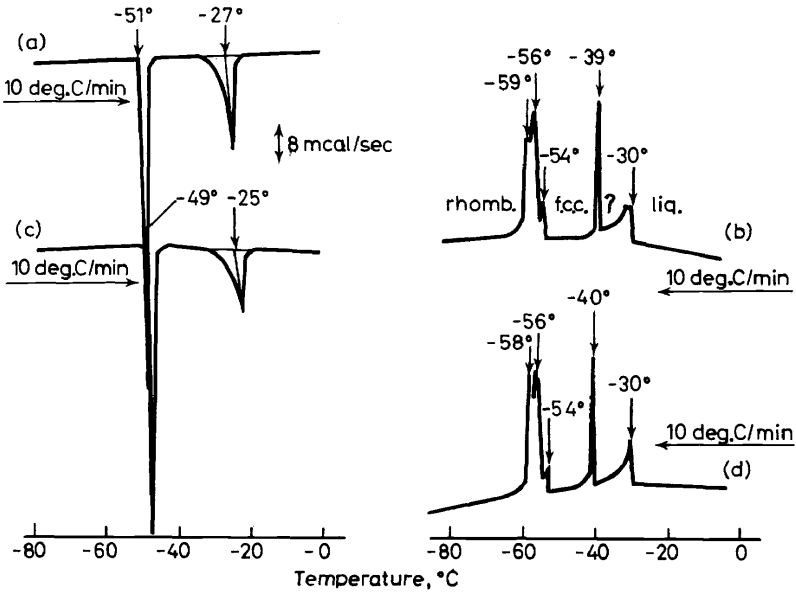


Figure 7. DTA curves for carbon tetrachloride in helium atmosphere using the Perkin-Elmer DSC-1B. Sample suspended on silicon carbide in a sealed cup.

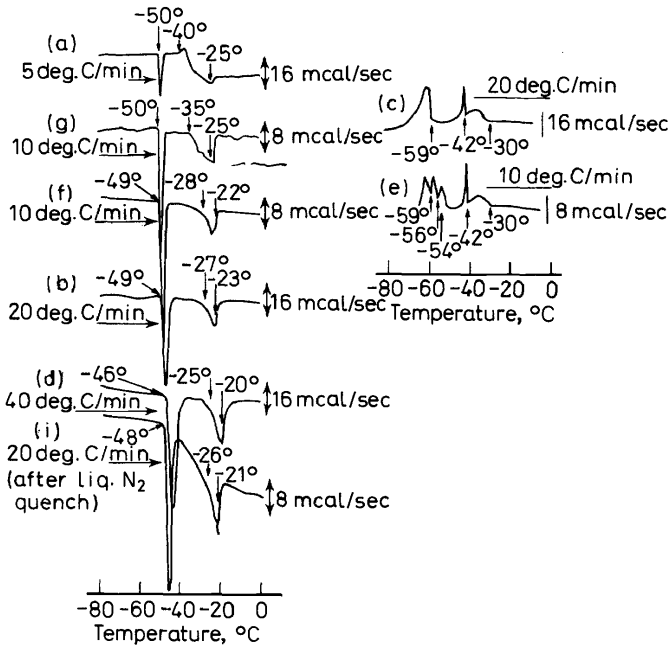


Figure 8. DTA curves for carbon tetrachloride in helium atmosphere using a Perkin-Elmer DSC-1B. Samples in a sealed cup.

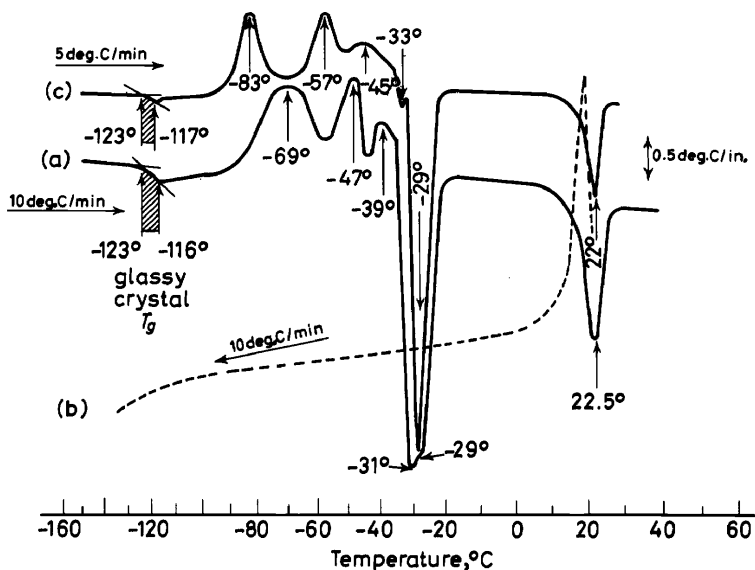


Figure 9. DTA curves for cyclohexanol in helium atmosphere using a modified Du Pont DTA cell. Samples placed in 4 mm tube without silicon carbide.

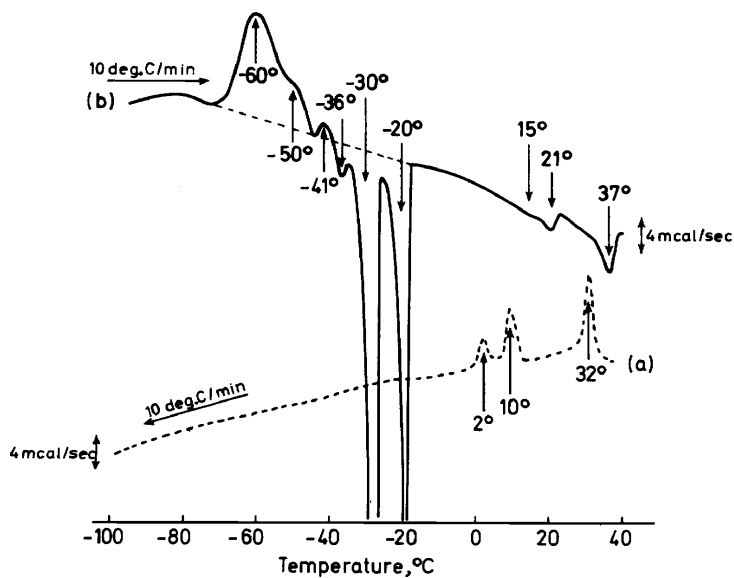


Figure 10. DTA curves for cyclohexanol in helium atmosphere using a Perkin-Elmer DSC-1B. Sealed cup.

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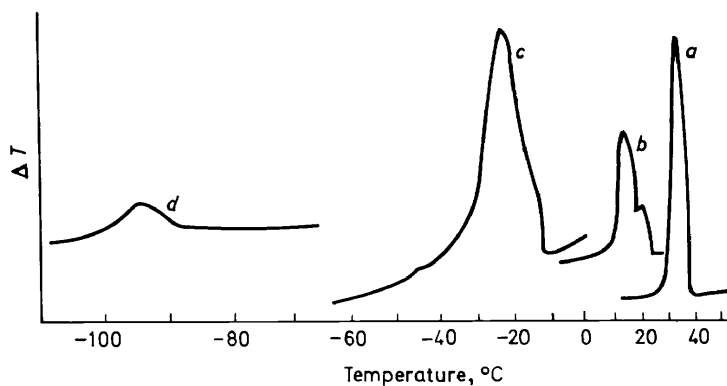


Figure 11. DTA cooling curves of synthetic glycerides: (a) myristodipalmitin; (b) oleodipalmitin; (c) palmitodicolein; (d) trilinolein.

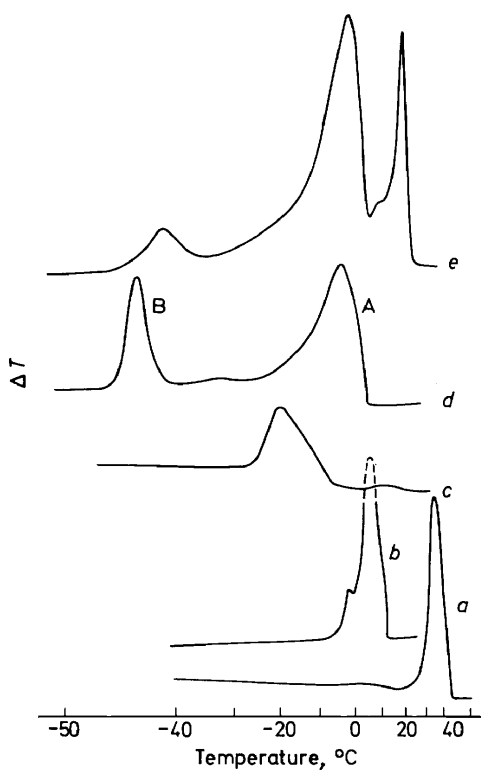


Figure 12. DTA cooling curves of palm oil and its fractions from thin layer chromatographic separation: (a) 000 glycerides; (b) 100 glycerides; (c) 110 glycerides; (d) peak (A) 210 and 200 glycerides, peak (B) 111 glycerides; (e) whole oil.

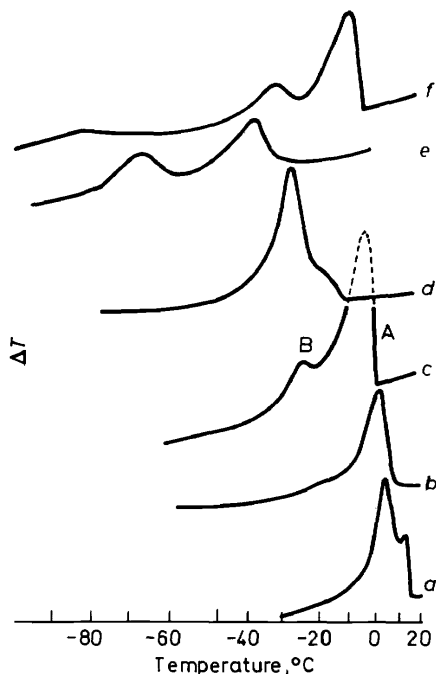


Figure 13. DTA cooling curves of cotton seed oil and its fractions from thin layer chromatographic separation: (a) 000 glycerides; (b) 110 and 200 glycerides; (c) peak (A) 210 glycerides; peak (B) 111 glycerides; (d) 211 and 200 glycerides; (e) highly unsaturated glycerides; (f) whole oil.

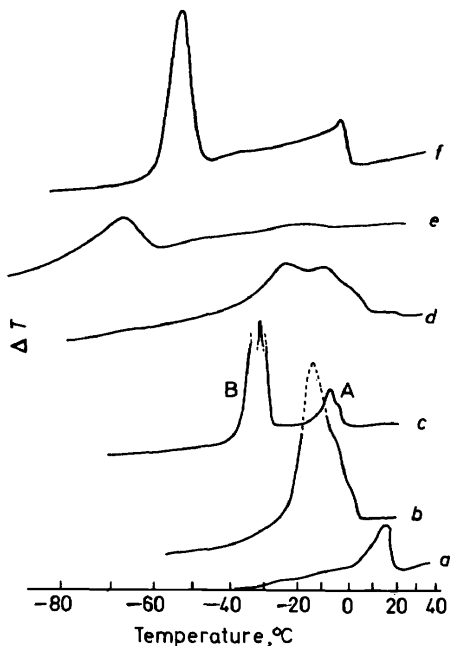


Figure 14. DTA cooling curves of groundnut oil and its fractions from thin layer chromatographic separation: (a) 100 glycerides; (b) 110 glycerides; (c) peak (A) 200 glycerides, peak (B) 111 glycerides; (d) 210 glycerides; (e) highly unsaturated glycerides; (f) whole oil.

the transitions. The cooling curve with the Du Pont apparatus did not reveal any transition whereas the DSC-1B cooling curve shows at least two phase transitions below the freezing point. The heating curves, however, show a bewildering set of exotherms and endotherms. Using the Du Pont apparatus it also proved possible to detect a glass transition at -123°C .

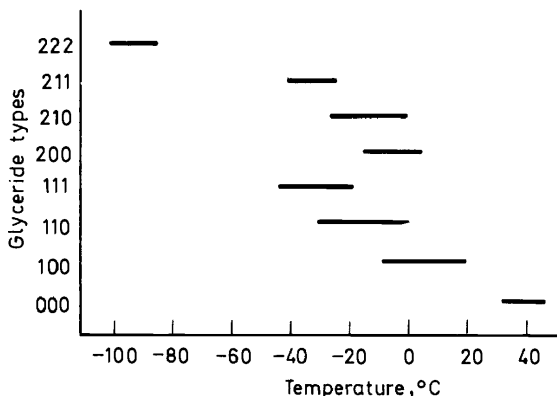


Figure 15. Crystallizing ranges of glyceride types.

(c) *Glycerides*—Berger and Akehurst³⁴ have used cooling curves to study synthetic glycerides, and fractions of defined glyceride composition from palm oil, cotton seed oil and soya bean oil. By using cooling curves complicated effects due to polymorphism are not obtained and the interpretation is somewhat simpler. The DTA cooling curves of four synthetic glycerides of various degrees of unsaturation are shown in Figure 11. Peak *a*, myristodipalmitin, a fully saturated glyceride, gives a peak at about 33°C whereas the unsaturated trilinolein gives a single peak at about -95°C . The other two glycerides, which are partially saturated give peaks at intermediate temperatures. Examination of the cooling curves of palm oil and its fractions from thin layer chromatography, cotton seed oil and its fractions, and groundnut oil and its fractions (Figures 12, 13 and 14) suggest that it is possible to define crystallizing ranges for the various glyceride types (Figure 15). Of particular interest is the marked effect of introducing one saturated acid into a bi-unsaturated glyceride. The temperature of crystallization is raised by some 20 degC . Figure 16 shows curves for a commercial hardened palm oil (m.pt $49^{\circ}\text{--}51^{\circ}\text{C}$) in mixtures with soya bean oil in various proportions. From these DTA curves the area under peak (A) is directly related to the proportion of hardened oil, whereas the area under peak (C) is proportional to the amount of soya bean oil. These results suggest that the technique offers a rapid 'finger print' method for routine control purposes and that quantitative estimation of certain mixtures of fats can be obtained.

(ii) *Simultaneous DTA-mass spectrometry*

The DTA curve gives information as to when and at what temperatures processes occur and may be used to determine the quantitative parameters describing the reaction e.g. ΔH or its kinetics under the conditions of the experiment, but no information is provided *per se* as to what the evolved

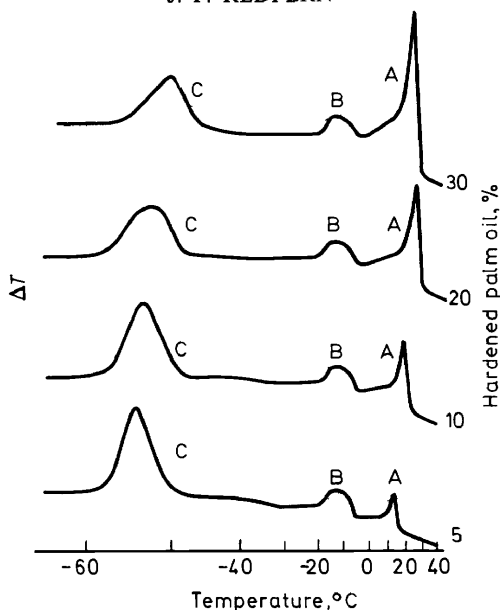


Figure 16. DTA cooling curves of mixtures of soya bean oil and hardened palm oil (melting point 49° – 51° C).

volatiles are from any reaction involving decomposition. The mass spectrometer is ideally suited to the identification of the evolved volatiles. I want to outline briefly some initial results obtained using a simple mass spectrometer³⁵. A block diagram is shown in Figure 17. The DTA equipment is a Stanton 671 DTA (Figure 18) which operates over the temperature range -150° to $+500^{\circ}$ C and the mass spectrometer is a GEC-AEI MS10. This is a 50mm radius 180° deflection mass spectrometer fitted with an electrostatic 1850 gauss permanent magnet or an electromagnetic scanning instrument.

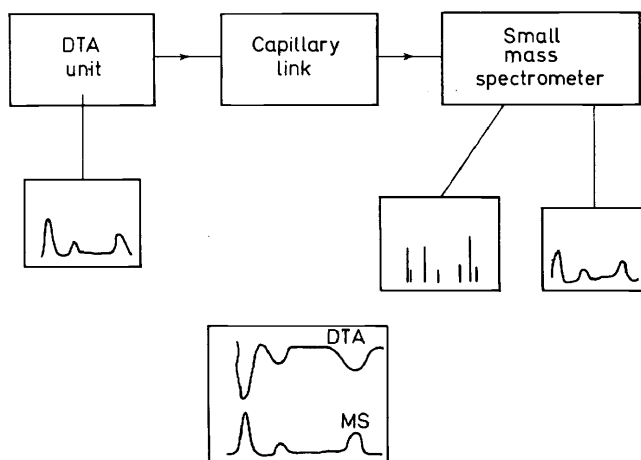


Figure 17. Block diagram of a DTA-mass spectrometry system.

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The MS10 covers the mass range up to 200, with a slow scan speed of $13\frac{1}{2}$ minutes or a narrow scan facility. Thus it is possible to scan one particular mass, e.g. m/e 18, throughout a DTA experiment or to scan a particular range, e.g. m/e 45 to m/e 12, to show the build-up of one particular ion and the disappearance of another. Three types of interface have been used. The first is a continuous inlet system with bypass. This system employs a heated stainless steel capillary which samples from directly above the sample cup.

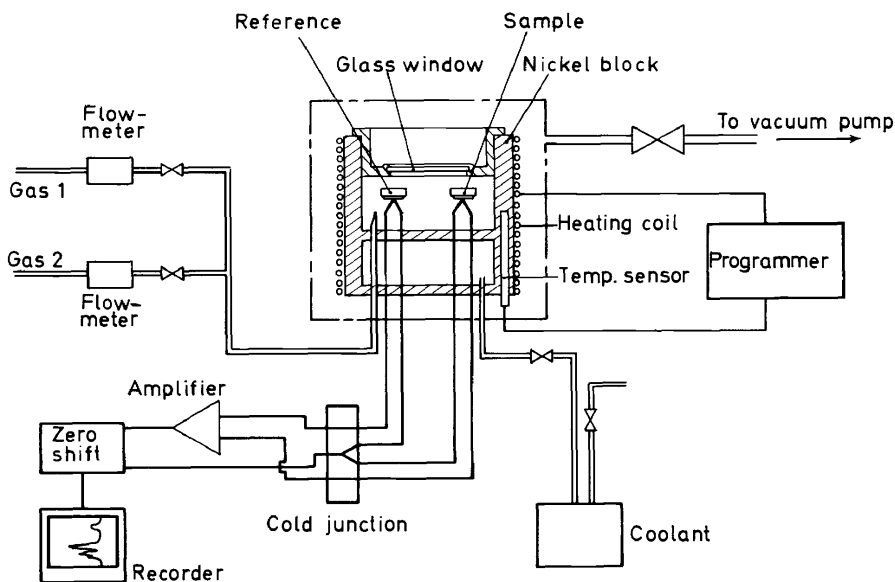


Figure 18. Schematic of Stanton DTA equipment.

The major portion of the evolved volatiles is pumped away. With this inlet system DTA experiments could be carried out at atmospheric pressure using air, a controlled atmosphere or an inert gas such as helium. The second type of interface is the drift tube which is identical to the previous system except that a Hoke valve is fitted between the mass spectrometer and the capillary which isolates the MS10 whilst the DTA apparatus is down to air. The DTA chamber was pumped to around 0.1 torr and the MS10 operated at 5×10^{-6} torr. This system has improved sensitivity and has proved valuable in examining organic systems under vacuum. The third interface technique employs a thin silicone rubber membrane; organic molecules readily dissolve in the membrane and are passed through it with a time constant of one to two seconds, whereas a carrier gas such as helium has a low permeability. This interface gives a factor of ten increase in sensitivity over the first system and is applicable where DTA runs are carried out in a flowing gas atmosphere. One example is given from the present studies.

(a) *Polyvinyl alcohol*—Figure 19 shows polyvinyl alcohol run in air with the mass range 12–45 scanned. Figure 20 is a similar run but this time

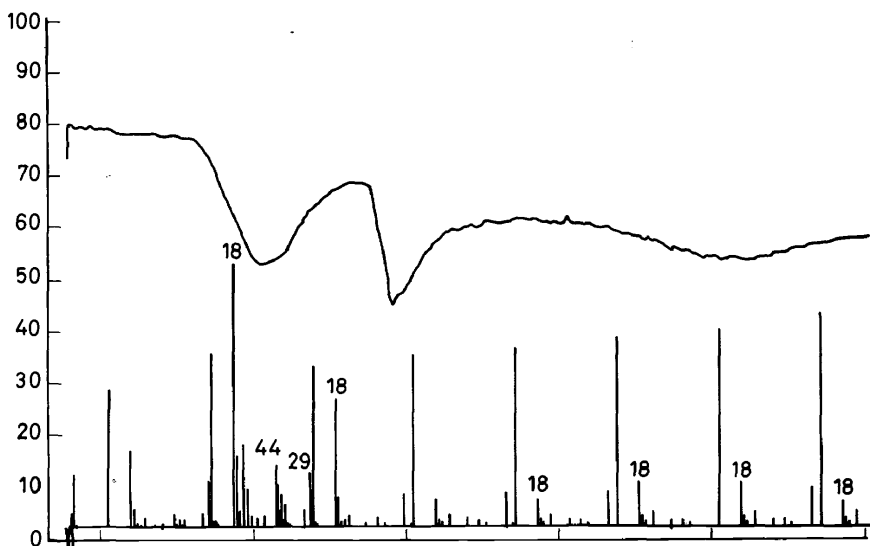


Figure 19. DTA-mass spectrometric curves of polyvinylalcohol sample run in air.

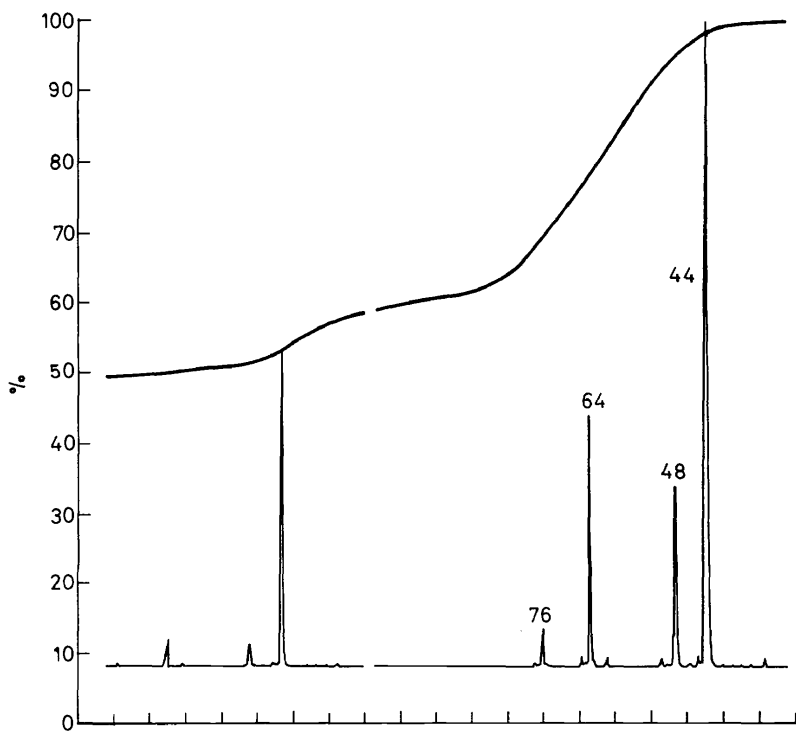


Figure 20. DTA-mass spectrometric curves of polyvinylalcohol sample run in vacuum.

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carried out in vacuum. The sample has been acid cured and the mass spectrum shows some evidence of m/e values of 48 (SO), 64 (SO_2) and 76 (CS_2). Figure 21 is a composite picture built up from a succession of runs in which stainless steel capillary which samples from directly above the sample cup.

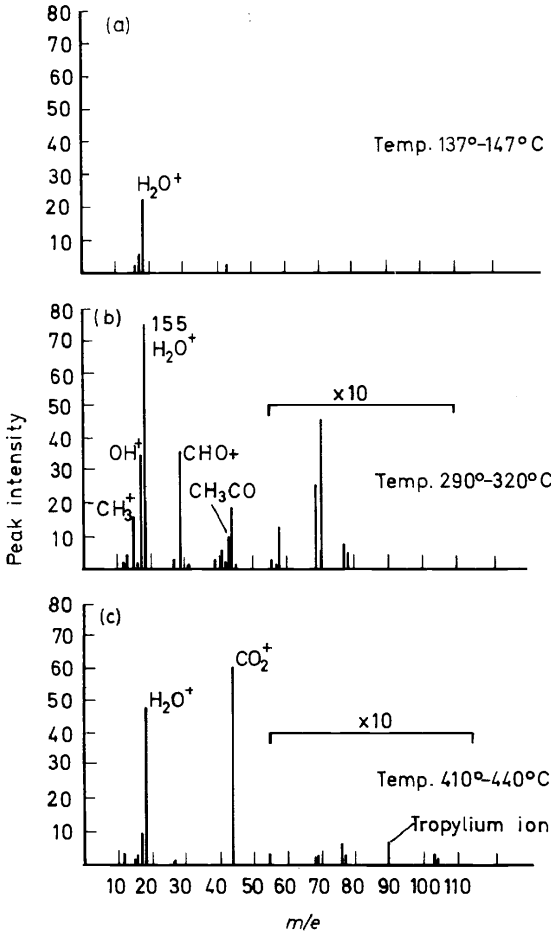
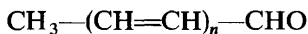


Figure 21. Composite figure showing decomposition pattern for polyvinylalcohol over three temperature ranges.

results it may be concluded: (a) that the first DTA endotherm is due to water, (b) that the second DTA endotherm is a decomposition into simple organic products, predominantly aldehydes (acetaldehyde and crotonaldehyde are the most likely), (c) above 350°C oxidation occurs and the chief products are water and carbon dioxide with a few low intensity higher

molecular weight ions (e.g. alkyl benzenes). With the helium membrane separator molecular ions m/e 70, 96, 122 and 148 were identified as



where $n = 1-4$.

(iii) *Quantitative aspects of thermal analysis*

Much has been published on the quantitative aspects of TG and DTA, in particular the last decade has seen a great deal of attention placed on the use of TG to determine kinetic parameters, see e.g. Coats and Redfern³⁶. More recently attention has turned to the question of determining impurities in organic materials by DTA or DSC³⁷⁻³⁹. This has been made possible by the increased sensitivity of equipment.

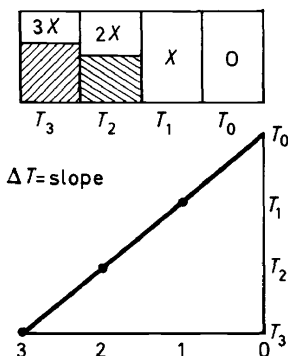


Figure 22. Determination of purity by DTA or DSC liquid-soluble, solid-insoluble impurities. Mol % impurity = $100(\Delta H_f/RT_0^2)\Delta T$ where ΔH_f denotes heat of fusion, R is the gas constant, T_0 = m.pt zero impurity, and ΔT = m.pt depression.

The level of impurity can be calculated using DSC or DTA data and applying this to the Van't Hoff equation, or equations derived therefrom. For example, the expression derived by Plato and Glasgow³⁹ is

$$\text{Mol \% impurity} = 100 \times (\Delta H_f/RT_0^2) \times \Delta T$$

where ΔH_f is the heat of fusion per mole, R is the gas constant, T_0 is the m.pt of the pure sample and ΔT is the m.pt depression. The area under the DTA or DSC curve gives ΔH_f . T_0 and ΔT can be determined from the DTA or DSC curve (see Figure 22). If it is considered that the impurity is liquid-soluble, solid-insoluble then it may be argued: the right-hand box represents a sample with zero concentration of impurity and a m.pt of T_0 . The next box shows a real sample with X concentration of impurity and a m.pt of T_1 , i.e. $T_0 - T_1 = \Delta T$. For a half melted sample all the impurity is in the liquid phase and its concentration will be $2X$, and, since concentration and m.pt depression are linearly related, $T_0 - T_2$ (T_2 is m.pt when concentration is $2X$) = $2\Delta T$. Similarly for a sample one third melted the concentration of impurity in the liquid phase will be $3X$ and $T_0 - T_3 = 3\Delta T$. When the increase in impurity concentration is plotted versus the corresponding temperature a straight line should result with a slope of ΔT and the zero intercept will be T_0 .

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Treatment of actual data is shown in *Figure 23*. For very pure samples (over 99.99 mol %) the plot is linear but where less pure compounds are involved curvature is observed. An arbitrary correction to linearize results and to correct for premelting is applied. This technique has been applied to some 95 different organic compounds.

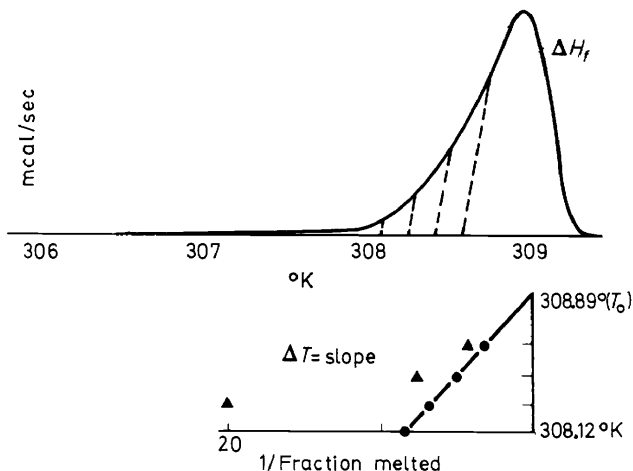


Figure 23. Calculation of purity from DSC curve; 99.55 mol % methyl 4-(2,4-dichlorophenoxy) butyrate. DSC curve: the parallel dashed lines represent the superimposition of the low temperature slope of the indium peak to correct for thermal lag inherent in the system.

Temp. K	Area sum	1/F	Area sum 15% corr.	1/F
308.119	52	55.2	483	6.84
308.256	146	19.7	577	5.72
308.422	371	7.74	802	4.12
308.590	781	3.68	1212	2.72
	2871		3302	

Lower curve: ▲ uncorrected; ● corrected.

Mol % impurity = $100(\Delta H_f/RT_0^2)\Delta T = 100 \times \{7600/2(308.9)^2\} \times 0.11 = 0.45$ mol % impurity.

CONCLUSIONS

In conclusion it is pertinent to pose the question, 'What is the purpose of using thermoanalytical techniques?' To me the answer is clear; it is no longer an esoteric research tool but it is a technique for material and process evaluation. Thus the trends which are likely to develop in the next decade will largely be governed by the requirements of material and process evaluation. Superimposed on this is likely to be the general trend towards increased instrumentation and the need for instrumentation to be reliable and have a relatively low down time, as well as the trend towards more efficient retrieval of information. It is to be hoped that all workers in the field will see the tremendous challenge of their role.

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REFERENCES

- ¹ U.S. Pat. No. 2947163 (1960).
- ² R. L. Stone, *J. Am. Ceram. Soc.* **35**, 76 and 90 (1952).
- ³ R. L. Stone, *J. Am. Ceram. Soc.* **37**, 46 (1954).
- ⁴ R. L. Stone, *Analyt. Chem.* **32**, 1582 (1960).
- ⁵ R. L. Stone and H. F. Rase, *Analyt. Chem.* **29**, 1273 (1957).
- ⁶ U.S. Pat. No. 3298220 (1967).
- ⁷ Hung. Pat. No. 144548 (1954).
- ⁸ Hung. Pat. No. 143332 (1955).
- ⁹ Hung. Pat. No. 145369 (1955).
- ¹⁰ F. Paulik, J. Paulik and L. Erdey, *Talanta*, **13**, 1405 (1966).
- ¹¹ L. G. Berg, A. V. Nikolaev and E. Ya. Rode, *Termografiya*. Izd. Akad. Nauk, SSSR: Moscow and Leningrad (1944).
- ¹² H. Lehmann, 'Die differential Thermoanalyse', *Tonindustriezeitung*, Beiheft 1 (1954).
- ¹³ R. C. Mackenzie (ed), *The Differential Thermal Investigation of Clays*, Mineralogical Society: London (1957).
- ¹⁴ C. Duval, *Inorganic Thermogravimetric Analysis*, 1st ed. Elsevier: Amsterdam, London and New York (1953).
- ¹⁵ W. J. Smothers and Y. Chiang, *Differential Thermal Analysis. Theory and Practice*. Chemical Publishing Co.: New York (1958).
- ¹⁶ H. G. McAdie, private communication.
- ¹⁷ J. P. Redfern (ed). *Thermal Analysis Review*. Stanton Redcroft Ltd: London (1962). Now published six times a year.
- ¹⁸ *J. Thermal Analysis*. Published by Akademiai Kiado: Budapest, and Heyden and Son Ltd.: London (1969).
- ¹⁹ *Thermochimica Acta*. Published by Elsevier: Amsterdam (1970).
- ²⁰ J. P. Redfern (ed). *Thermal Analysis '65*. Macmillan: London (1965).
- ²¹ R. C. Mackenzie, *Talanta*, **16**, 1227 (1969).
- ²² R. C. Mackenzie and B. D. Mitchell in *Differential Thermal Analysis. Vol. I*. R. C. Mackenzie (ed). Academic Press: London and New York (1970).
- ²³ J. P. Redfern in *Differential Thermal Analysis, Vol. I*. R. C. Mackenzie (ed). Academic Press: London and New York (1970).
- ²⁴ C. Duval, *Inorganic Thermogravimetric Analysis*, 2nd ed. Elsevier: Amsterdam (1963).
- ²⁵ Technical Applications Sheets published by Stanton Redcroft Ltd, London.
- ²⁶ M. Harmelin. *La Thermo-Analyse*. Presses Universitaires de France: Paris (1968).
- ²⁷ C. J. Keattch, *An Introduction to Thermogravimetry*, Heyden & Son Ltd: London (1969).
- ²⁸ T. I. Taylor and H. P. Klug, *J. Chem. Phys.* **4**, 601 (1936).
- ²⁹ A. T. Jensen and C. A. Beevers, *Trans. Faraday Soc.* **39**, 1478 (1938).
- ³⁰ R. L. Bohon in *Proceedings of the Third Toronto Symposium on Thermal Analysis*. H. G. McAdie (ed). 33 (1969).
- ³¹ K. Kotake, N. Nakamura and H. Chihara, *Bull. Chem. Soc. Japan*, **40**, 1018 (1967).
- ³² American Institute of Physics *Handbook*, 2nd ed. Section 4j. McGraw-Hill: New York (1963).
- ³³ K. Adachi, H. Suga and S. Seki, *Bull. Chem. Soc. Japan*, **41**, 1073 (1968).
- ³⁴ K. G. Berger and E. E. Akehurst, *J. Food Technol.* **1**, 237 (1966).
- ³⁵ J. P. Redfern, B. L. Treherne, M. L. Aspinall and W. A. Wolstenholme, *Proceedings of the A.S.T.M. Conference on Mass Spectrometry*. Dallas, Texas. 158 (1969).
- ³⁶ A. W. Coats and J. P. Redfern, *Analyst*, **88**, 906 (1963).

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- ³⁷ N. J. Deangelis and G. J. Papariello, *J. Pharm. Sci.* **57**, 1868 (1968).
- ³⁸ C. Plato and A. R. Glasgow, *Analyt. Chem.* **41**, 330 (1969).
- ³⁹ G. J. Davis and R. S. Porter, *J. Thermal Analysis*, **1**, 449 (1969).